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CLAYS, FROM THE OCEANS TO SPACE

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CRYSTAL STRUCTURE OF DEFECTIVE LAMELLAR MINERALS AND THEIR X-RAY IDENTIFICATION: ENVIRONMENTAL IMPLICATIONS

Bruno Lanson (1)*, Eric Ferrage (2)

(1) ISTerre, CNRS - Univ. Grenoble-Alpes, Grenoble, France - Bruno.lanson@univ-grenoble-alpes.fr, (2) IC2MP, CNRS - Univ. Poitiers, Poitiers, France

Layered minerals and materials are ubiquitous and characterized by the frequent occurrence of stacking defects that are key to their reactivity. These defects range from local defects such as isomorphous substitutions, layer vacancies, or atomic displacements, to random or well-defined stacking faults induced by non-periodic layer rotations, translations or twinning, and to mixed layering resulting from the coexistence within a given crystal of layers having different structure, thickness, or interlayer displacement. The occurrence of stacking faults in lamellar structures is favoured by the energetic similarity of the different stacking modes, owing to the weak interactions between adjacent layers. In addition, layered materials and minerals often exhibit minute crystal sizes that may be considered as an additional type of defect because of the induced disruption of the three-dimensional crystal periodicity.

To determine, control, or predict mineral / material reactivity a detailed structural characterization of layered structures, including structure defects, is thus essential, and X-ray diffraction (XRD) has been the preferred method of investigation for this purpose. However, as a result of their non-periodicity or their reduced periodicity, the diffraction maxima recorded from these compounds do not strictly obey Bragg's law, thus hampering the use of conventional diffraction approaches. Profiles and intensities of diffraction maxima are affected by the nature, content, and distribution of structure defects, however, thus allowing the determination of these parameters with diffraction techniques and specific algorithms have been developed.

From the results of a few examples, this presentation will outline how our understanding of defective structures and mixed layers has improved over the last decade or so and describe some of the new perspectives opened by this improvement, with special emphasis on the induced reactivity.

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SOIL CARBON SEQUESTRATION: A NEW PARADIGM FOR ENVIRONMENTAL APPLICATION OF CLAY MINERALS

Balwant Singh

School of Life and Environmental Sciences, University of Sydney, Sydney, NSW 2006, Australia

The useful properties of clays and/or clay minerals have been known since pre-historic times. Clays are naturally occurring materials composed primarily of fine-grained minerals usually less than 2 to 4 μm whereas clay minerals refer to phyllosilicate minerals and other minerals which impart plasticity to clay and which harden upon drying or firing [1].

Clay minerals possess several unique properties, such as fine particle size, large specific surface area and permanent and variable surface charge, which makes them ideal for various environmental applications. Additionally, clay minerals are widely available, occur in vast amounts and are relatively inexpensive. The environmental applications of clay minerals are extensive and wide ranging, e.g. industrial processes, agriculture, construction and environmental protection. In the last few decades the relevance of clay minerals in soil carbon storage has been recognised. Mineral associated carbon accounts for up to 91% of the total soil carbon and thus plays an important role in the cycling and storage of carbon in soils [2]. Soil is the largest terrestrial carbon pool containing more than twice the carbon of the atmosphere [3]. Hence, small increases in the flux of soil carbon may result in greater atmospheric CO_2 concentrations and associated global warming. This talk will explore the processes and mechanisms of organic carbon and mineral associations in soils in relation to carbon sequestration in soils. The factors that affect the mineral-carbon associations in soils will be discussed using laboratory and field examples.

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NEXT GENERATION OF ADVANCED MATERIALS DERIVED FROM CLAY MINERALS

Eduardo Ruiz-Hitzky

Instituto de Ciencia de Materiales de Madrid, CSIC, c/ Sor Juana Inés de la Cruz 3, 28049 Madrid, Spain
eduardo@icmm.csic.es

Since many centuries ago, humans have largely used day-to-day clay-based materials as clays represent an abundant, wide-spread, cheap, eco-friendly and versatile resource in Earth. Building materials, pottery, pencils and tablets for writing, and a huge variety of decorative products, are examples of world-wide traditional clay-based objects. Nowadays, at the High-Tec Era and at the Information Age, clays still play a significant role in current life addressed to the development of the so-called *advanced materials* based on these minerals. As it is well known, in the current global economy, most of the materials advancements are directly derived from a knowledge-based society. Particularly, research on clay minerals represents a paradigmatic field where Natural Sciences such as Geology, Physics, Chemistry and Biology, and Applied Sciences such as Materials Science and Engineering meet. Taking into account these features it arise the following key question: how can we create new clay-based advanced materials? To answer that question, it should be considered that as occurs with other type of low-dimensional inorganic colloidal particles, advanced materials derived from clay minerals could be developed under the Nanoscience and Nanotechnology concepts, in particular on the basis of the Nanoarchitectonics discipline [1]. In this way, novel approaches are being applying using this natural resource in a rational and ecological way to prepare nanostructured materials deserving diverse type of applications from energy production and storage to pharmaceutical and biomedicine fields. Recent contributions from our Group at the Materials Science Institute of Madrid (CSIC) related to diverse clay-based nanostructured materials will be introduced in this lecture and discussed on light of their promising future usages. For instance, smectites and sepiolite clay minerals deserve as starting building units that can be assembled to diverse metal and metal-oxide nanoparticles (NPs) for the design and preparation of highly-efficient adsorbents and catalysts, provided in some cases of superparamagnetic behavior giving rise to multifunctional materials useful for its easy recovery upon use. This type of nanoarchitectures can be applied in the elimination of pollutants such as organic dyes, radionuclides, pesticides and drugs in wastewater [2-5]. Furthermore, the assembly of carbon-nanoparticles, such as graphene and carbon nanotubes, to clay minerals can be achieved either by their direct combination under sonomechanical treatments or by the *in situ* generation of the carbon material from sucrose and other biomass sources. The resulting supported carbon materials exhibit good electrical conductivity and there is not necessary the removal of the silicate substrate for diverse applications, including clean energy production and storage, sensor devices as well as fillers of polymers for the development of conducting polymer-clay minerals nanocomposites [6,7]. Finally, by means of clay-organic interactions it can be prepared as well diverse biohybrids and bionanocomposites provided of specific and predetermined behaviors of interest in the removal of pollutants, controlled drug delivery, sensing agents for selective ion-recognition, immobilization and carrier of virus particles for improved adjuvant of vaccines [8], or as non-viral transfection vectors of nucleic acids [9].

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CLIMATE SIGNIFICANCE OF CLAY VARIABILITY IN SEDIMENTS

FAGEL NATHALIE

AGEs - **A**rgiles, **G**éochimie et **E**nvironnement **s**édimentaires, Département de Géologie, Université de Liège, Quartier Agora,
14 Allée du 6 Août, Sart-Tilman 4000 Liège, Belgium
nathalie.fagel@ulg.ac.be

Paleoclimate reconstructions are derived from the interpretation of temporal series of various sedimentary proxies (e.g., fauna, flora, mineralogy, chemistry, isotopic composition). Among these, marine or lacustrine sedimentary clays can be powerful tools (Fig. 1) for continental climatic reconstructions [1]. However, paleoclimate interpretation of clay mineral data requires to fulfil two main assumptions:

1) clays must be detrital in origin, representing primary (inherited clays) or secondary products of continental weathering and pedogenesis (transformed or neoformed clays);

2) they must not be significantly altered by diagenesis.

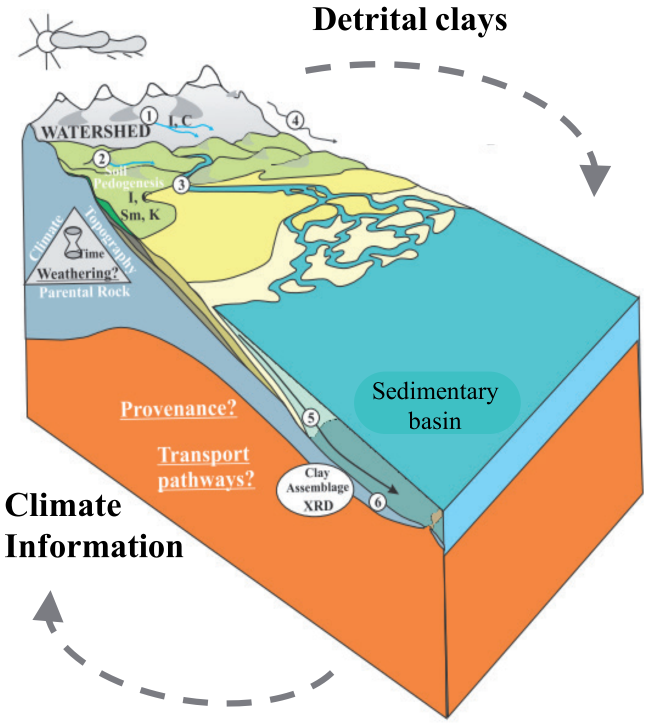

Fig. 1. *The clay tool box* (modified from Fagel 2007). The diagram presents the evolution of the detrital clay minerals through the sedimentary cycle, from their formation in continental watersheds (steps 1-2) to their transport (steps 3-4) and settling in sedimentary basins (steps 5-6). In the sediments, the evolution of the detrital clay assemblages over depth/time reflects the changes of the weathering conditions in the adjacent watershed, allowing to infer past climate information.
1. Physical weathering = primary or inherited clays. 2. Chemical weathering = secondary, transformed or neoformed, clays.
3. Transport by river.
4. Transport by wind.
5. Current redistribution.
6. Sedimentary settling through water column.

In most cases the geochemical signature of the clays allows to decipher between detrital clay minerals delivered by continental heritage or authigenic clays formed by chemical precipitation from a saturated solution (e.g., hydrothermalism [2]). Likely diagenesis influence may be evidence by the progressive evolution of clay mineral assemblages over burial depth, leading to a simple mineral assemblage mainly illite and/or chlorite [3]. Deciphering climate significance in detrital sedimentary clays first requires to identify both the source areas and the principal transport agents. For this purpose the mineralogical and geochemical (trace elements and radiogenic isotopes) composition of the sedimentary clays may be compared with the average composition of the adjacent surroundings to identify the main continental source areas and therefore, but indirectly, the transport agent [4,5].

From the sixties, down-core variations in marine clay mineral assemblages have been interpreted in terms of changes in the climate conditions prevailing in the continental source areas and have been widely used to reconstruct paleoclimates [3,6]. The clay proxy was set from the latitudinal, climate-driven, clay minerals distribution trends observed in deep-sea floor sediments [7]. Over the last decades climate significance of qualitative and (semi-)quantitative evolution of clay assemblages has been emphasized in many studies of marine sediments. For instance the alternations of two contrasted clay mineral assemblages, expressed by clay mineral ratio, have been used to trace seasonal direction changes of transport agent related to monsoon circulation in Arabian Sea [8], Central Indian Basin [9] like in South China Sea [10]. In the Arabian Sea basin, fluctuations in clay assemblages reflect the periodic inversion of atmospheric circulation related to monsoon: different clay species are conveyed either by the summer monsoon from the deserts of Somalia or by the winter monsoon from the Indus Plain. The spectral analysis of clayey parameters indicates orbital-like periodicities, confirming the climate control of the clay sedimentation. Over glacial/interglacial cycles, the clay variability usually reflects changes in oceanic circulation [11-12]. This assumption is supported by the similitude between clay assemblages in surface sediments and water mass distribution, as evidenced in North [5], Subtropical [13], and South Atlantic [14] and in the southeast Indian oceans [15].

In lakes, a few studies, in particular on Lake Baikal, have also emphasized that clay mineral variability record, as sedimentary diatom abundance, glacial/interglacial cycles [16-18]. The climate significance of clay assemblages is attested by a bimodal clay-data distribution in agreement with different clay sources and/or formation processes between glacial and interglacial periods. The climate interpretation of clay assemblages was mainly based on the evolution of the smectite/illite ratio [19-20] and/or of smectite abundance [17]. Those clay parameters were used as proxies for hydrolysing conditions [21] in the lake watershed assuming that all smectites result from soil pedogenesis processes in the catchment.

In the talk, the *clay tool box*-based discussions will be presented for different sedimentary settings. The aim is to emphasize that sedimentary clay assemblages may record climate variability at different timescales and represent therefore an interesting proxy for paleoclimate reconstructions.

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THE NATURE OF ILLITIC SUBSTITUTION IN WHITE MICAS

Fernando Nieto (1), Isabel Abad (2)*

(1) Departamento de Mineralogía y Petrología and IACT (CSIC-UGR), Facultad de Ciencias, Universidad de Granada, Avda. Fuentenueva s/n, 18002 Granada, Spain, (2) Departamento de Geología and CEACTierra, Unidad Asociada IACT (CSIC-UGR), Universidad de Jaén, Campus Las Lagunillas s/n, 23071 Jaén, Spain
*miabad@ujaen.es

Illitic substitution is a significant component in low-temperature micas where it is common to find K-mica crystals with small but significant deficits in interlayer charge. According to the IMA, the term illite should be used to designate interlayer-cation-deficient (<0.85 a.f.u.) micas as a name of a series consisting of a coupled substitution of ($SiAl_{-1}$) in the tetrahedral site and of (vacancy K_{-1}) in the interlayer site (Rieder *et al.,* 1998).

When mica formulae are calculated, the most common method is on the basis of $O_{10}(OH)_2$ a.p.f.u., which, in practice, is equivalent to 22 negative charges, due to the lack of information about water content. The calculated factor for the normalization depends, therefore, on the assumption of a given Fe^{2+}/Fe^{3+} ratio and is inevitably affected by the lack of data about some positive cations. As H_3O^+ and NH^+_4 cannot be routinely determined, the overall calculated positive charge is smaller than the real one and the rest of the cations are artificially overestimated, producing octahedral sums >2. However, when the excess water is assumed to fill the interlayer sites in the form of H_3O^+, the octahedral sheet is very close to 2. The partially refined Rietveld model of illite published by Nieto et al. (2010) showed in particular, that the attempts to introduce octahedral cations in excess of 2 were fruitless and a water loss in the region of 263 ºC exactly corresponded to the theoretical content in H_3O^+, justifying the excess water measured by Hower and Mowatt (1966). Computational studies have shown that the hydronium cations in aqueous solutions are likely to be intercalated in the interlayer space of illite, exchanging for K cations and IR vibration spectra frequencies revealed that the hydronium cations and water molecules interact strongly with basal O atoms through H bonds forming a silanol-type complex Si-O-H (Escamilla-Roa et al., 2016). On the basis of these previous results, which consider that the real nature of the illitic substitution is ($K_{-1}\ H_3O^+$) and/or ($K_{-1}\ O_{-1}\ OH^-$) the conclusion is that the appropriate normalization may necessitate fixing of the sum of tetrahedral and octahedral (iv+vi) cations to six.

We have renormalized to 6 (iv+vi) cations the compilation by Abad et al. (2006) of high-quality in-situ analyses of coexistent illites and muscovites from clastic materials of various diagenetic and very low-grade metamorphic sequences generated in different geodynamic settings. From bivariate diagrams relating respectively Si/interlayer sum, Si/Fe+Mg and Al/Fe+Mg, we have obtained the following conclusions:

No correlation exists between Si and interlayer sum ($R^2 = 0.16$), that is, the interlayer deficit is not compensated by an increase in Si. The correlation coefficient was only slightly better for the formulae normalized, according to the traditional criterion, to $O_{10}(OH)_2$ a.p.f.u, due to the artifactual increase of Si motivated by a charge deficit, which was produced, in turn, by the lack of information about other cations as H_3O^+ and NH_4^+. In the Si/Fe+Mg diagram the most of the data fall upward the line representing the theoretical phengitic substitution. Therefore, a significant part of Fe must be present as Fe^{3+}. The diagram Al/Fe+Mg shows the best correlation ($R^2 = 0.68$) due to the combined effect of the phengitic (Si, Al_{-1}; Fe+Mg, Al_{-1}) and ferriceladonitic substitutions ($Al_{-1}\ Fe^{3+}$).

In conclusion, even accepting a possible small di-trioctahedral substitution, higher error is introduced in charge-based normalization criteria (due to numerous source of errors) than in the proposed criterion based on (iv+vi) cations = 6.

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DISPERSION POTENTIAL AND BIOLOGICAL AND CHEMICAL STABILIZATION OF BENTONITE, SEPIOLITE, AND KAOLIN CLAYEY SOILS

Hakime Abbaslou (1)*, Soheila Sadat Hashemi (2), Hojat Hadifard (3)

(1) Assistant professor in Civil Engineering Department, Sirjan University of Technology. Sirjan, Iran, (2) Assistant professor in Soil Sciences Department, Malayer University. Malayer, Iran, (3) MSc. student in Hydraulic structures, Civil Engineering Department, Sirjan University of Technology, Sirjan, Iran

Clay Soil is often used in construction of hydraulic structures particularly core of earthen dams, cutoff walls, grouting curtains, covering channels due to its swelling properties, low permeability and abundance in the nature. One of the most important issues that should be considered in the civil engineering projects is dispersivity of clay soils. Dispersive soils, as a problematic soil for different applications, are prevalent over wide areas of the world, especially in arid and semi-arid regions. Dispersive soils are comprised from clays particles contain high content of sodium ion in their adsorptive ions that can be easily washed by the waters with low salt contents [1]. Amongst the most obvious of the factors affecting the dispersion and migration of clays are particularly their spatial arrangement in relation to the fabric, their micro-aggregate structure, morphology, surface area, porosity and particle size distribution. It may be noted, however, that generally the clay minerals of most interest with regard to fines migration have formed during diagenesis [2]. Bentonite, kaolin, and fibrous (sepiolite) clay soils are among the most important and useful industrial materials. Therefore, three clay soils of bentonite, kaolin and sepiolite were chosen to investigate dispersivity potential by adding 4 percent dispersive materials (Sodium hexamethaphosphate) and performing shear strength, crumb, double hydrometer, pinhole tests and chemical experiments. Results showed Sodium Adsorption Ration changed in order of kaolin>sepiolite>bentonite. Stabilization practices using chemical and biological methods were done after soil divergence. $CaCl_2$, $CaSO_4$, $AlCl_3$, $Al_2(SO_4)_3$ were used for chemical stabilization and also *Bacillus sphaericus* and *Bacillus pasteurii* with two optical densities (1 and 2) were used as biological stabilizers. Bases on chemical properties, stabilization potential was in the order of kaolinite>sepolite>bentonite. As a consequence, the role of *Bacillus pasteurii* on soil strength parameters was outstanding rather than *Bacillus sphaericus*. The role of calcium and aluminium cations were prominent in improving mechanical and dispersivity properties, respectively. Changes in soil characteristics during chemical treatment are likely due to the cation exchange Na^+ with divalent cations like Ca^{2+} and trivalent cations like Al^{3+}, reduction in the thickness of diffused double layer, and the subsequent reduction in the repulsive forces of the clay particles [3]. In a general conclusion, the biological stabilization treatments will be proposed as an efficient and eco-friendly choice for soil amelioration in regard with engineering, chemical and physical properties to reach sustainable development objectives. Sarmast et al. [4] used bacterial species (*Sporosarcina pasteurii* and *Sporosarcina ureae*), for cementation of sand grains and infilling of pore spaces by CaCO3. Micromorphological observations showed a high degree of calcite crystals' bridging, coating on sand particles and as well infilling of pore spaces. *S. pasteurii* is thus recommended for being used in stabilization of sand dunes; due to its significant effects on CaCO3 deposition and as well on sand grain cementation.

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PLASTIC CONCRETE CUT-OFF WALLS IN EARTH DAMS: A PERSPECTIVE OF ARID ENVIRONMENT CLAY MINERAL RESOURCES

Hakime Abbaslou*, Amir Tavana Amlashi, Ali Reza Ghanizadeh

Civil Engineering Department, Sirjan University of Technology. Sirjan, Iran

Plastic concrete consists of aggregates, cement, water and clay, mixed at a high water cement ratio, to produce a ductile material [1]. It is used for creating an impermeable barrier (cut-off wall) for containment of contaminated sites or seepage control in highly permeable dam foundations. The effects of clay type and clay dosage on compressive strength, tensile strength and water penetration depth of plastic concrete were investigated. To fulfillment the desired objectives, bentonite and sepiolite were selected in different perecent and cement factors. Also, different concentrations of cadmium adsorption by clays were assessed to address the best clay adsorption capacity. The results indicate that the clay type, clay dosage and water to binder ratio have great influence on the mechanical properties of plastic concrete. There is a tendency of decrease in the compressive strength, splitting tensile strength of plastic concrete with the increase of water to binder ratio and clay dosage. To improve the resistance to deformation of cut-off walls constructed with plastic concrete, the low cement factor (200 kg cm-3 compared to 280 kg cm-3) and 40 percent clay dosage can be selected to decrease the elastic modulus of plastic concrete in the practical design and applications of plastic concrete on condition that the plastic concrete has enough compressive strength and tensile strength. In addition to these findings, plastic concretes exhibit significant time-dependent behaviour similar to that observed for clays, and the variation of mechanical properties of concrete made with sepiolite is comparable to concrete made with bentonite which can be recommended under the condition of available sepiolite material and seepage water with high contamination. Based on the results that have been obtained from experiments on plastic concrete samples which have various mixing plans, certain diagrams have been presented to obtain an ideal mixing plan for plastic concretes which result in determining a key relationship to be able to estimate an appropriate mixing of cut offs to control leakage under the dam. While under current situation, using these relationships to estimate the appropriate mixing for plastic concrete in order to control leakage under the dam is almost with amount of errors.

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THERMOCHRONOLOGY OF FAULT ACTIVITY FROM CLAY MINERALS (EXAMPLE OF PIC DE PORT VIEUX THRUST, PYRENEES, SPAIN)

Ahmed Abd Elmola (1), Martine D. Buatier (1)*, Delphine Charpentier (1), Patrick Monié (2)

(1) UMR 6249 Chrono-environnement, Université Bourgogne Franche-Comté(UBFC), Besançon, France, (2) Géosciences Montpellier, UMR 5243, Université de Montpellier, France

Pic-de-Port-Vieux thrust is a second-order thrust related to the major Gavarnie thrust in the Axial Zone of the Pyrenees. The footwall consists of Upper Cretaceous dolomitic limestone that has progressively transformed into mylonitic limestones near the fault contact, while the hanging-wall consists of lower Triassic red pelites and sandstones. The core zone of the fault hanging wall is composed of intensely foliated green pelites of 0.6 meter and the damage zone presents numerous fractures affecting several meters of red pelites. A transect in the hanging-wall was investigated to determine the clay mineralogical changes induced by deformation and attributed to the fault activity and to date the fault activity using synkinematic newly formed clay minerals.

Mica and chlorite are the two major phyllosilicates in the studied pelites (red and green pelites) identified by XRD analyses. Diagnostic reflections for mica polytypes indicate that muscovite 2M1 is the major polytype with a relatively small amount of 1M. The Kübler index suggests high anchizone metamorphic conditions. These data are confirmed by temperature estimations using chlorite thermometry, i.e. the temperature of synkinematic chlorite (filling tectonic veins) is about 280-300 °C.

Five fractions (<0.5; 0.5-2; 2-16; 16-50 µm; bulk) from two samples (one in the core zone and another from the damage zone) were dated using the $^{40}Ar/^{39}Ar$ step-heating method. Each fraction was encapsulated in a quartz tube prior to irradiation. The ^{39}Ar recoil was measured before the step heating experiment. The age of the finest fraction derived using total gas age is 37.39 ± 0.24 Ma, whereas the coarser fraction produces a staircase shaped spectrum that reaches a maximum age of 305.80 ± 1.47 Ma.

All clay fractions of the core zone samples have younger ages compared to the samples from the damage zone. This can be explained by recrystallization of younger mica in the sample strongly affected by deformation. SEM images confirm the occurrence of higher deformation microtextures in the core zone compared to the damage zone. Indeed, quartz pressure solution but also synkinematic mica recrystallization are observed.

Fault activity age estimation by correction methods developed by [1] and [2] will be discussed combining $^{40}Ar/^{39}Ar$ results with microstructures and clay characterization in the Pic the Port Vieux Thrust fault.

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DEFORMATION CONDITIONS REGISTRATED BY PHYLLOSILICATES IN A THRUST FAULT (PIC DE PORT VIEUX FAULT, PYRENEES)

Ahmed Abd Elmola (1), Delphine Charpentier (1)*, Martine Buatier (1), Pierre Lanari (2), Vincent Trincal (3), Patrick Monié (4)

(1) UMR Chrono-Environnement, Université de Bourgogne Franche-Comté, Besançon, 25030, France, (2) Institute of Geological Sciences, University of Bern, Bern, CH-3012, Switzerland, (3) Centre de recherche de l'école des Mines de Douai, Douai, 59508, France, (4) Géosciences Montpellier, Université de Montpellier, Montpellier, 34095, France

During the evolution of sedimentary basins, the composition, crystal structure and texture of clay minerals can change in response to burial diagenesis, tectonics activities, and interactions with fluids. Consequently clay minerals can be used to deduce the deformations mechanisms and the P-T-X conditions of tectonic events. The Pic de Port Vieux is a second-order thrust related to the major Gavarnie thrust in the Axial Zone of the Pyrenees. It juxtaposes Triassic pelites of the hanging wall and Cretaceous limestone of the footwall. It was chosen to investigate the conditions of the deformation propagation in this area.

In order to determine the mineralogical and geochemical changes in the fault zone and to deduce the conditions of the fault activity, sampling was conducted along a transect in the thrust fault hanging wall pelites. The core fault zone is estimated to about 1meter thick. It is intensively foliated and characterized by the development of quartz-chlorite veins. It shows a green colour, whereas the damage zone is composed of several meters of red pelites. The difference in colour is related to hematite, only present in the damage zone. Pelite are mainly composed of quartz, calcite and clay minerals (chlorite and mica) ± hematite.

Clay minerals of the damage zone are mainly inherited mica and chlorite. In the core zone, newly formed chlorite is aboundant and preferencially located in veins. It is more Fe-rich compared to chlorite from the red pelites. The well-defined foliation in the core zone is overlined by preferentially oriented mica grains which have homogeneous compositions, with less Na and relatively more Fe than mica from the red pelite.

Newly formed clay minerals (chlorite and mica) in the fault core zone are synkinematic to the fault activity. They are both related to deformation processes and fluid rock interactions. Therefore, we used Kübler index measurement and chlorite thermometry to estimate the maximum temperature that occured during the fault activity: synkinematic clay minerals registrated temperature of 270°±50 °C for the damage zone and 285°±50 °C for the core zone.

Numerical modeling were then performed to determine the favorable conditions for the mineralogical transformations between red and green pelites. A serie of calculation at various redox and temperature conditions have been carried out using the geochemical modelling code PhreeqC. It suggests that the main critical parameter favoring hematite dissolution and chlorite précipation is the redox condition. Hematite dissolved under reducing conditions. Besides, the iron release by hematite dissolution can be used for iron-rich chlorite precipitation and mica transformation into more iron-rich mica instead of magnetite only if the conditions are very reducing.

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VARIATION IN PHYSICO-MECHANICAL PROPERTIES AND ENVIRONMENTAL IMPACT OF FIRED CLAY BRICKS INCORPORATING WITH MOSAIC SLUDGE INDUSTRY

Aeslina Abdul Kadir*, Ahmad Shayuti Abdul Rahim, Noor Amira Sarani

Department of Water and Environmental Engineering, Faculty of Civil and Environmental Engineering, Universiti Tun Hussein Onn Malaysia, 86400 Batu Pahat, Johor, Malaysia
*aeslina@uthm.edu.my

Fired clay brick is one of the most common masonry units used as building material. Due to the demand recently, different types of waste materials have been investigated to be incorporated into bricks. The incorporation of these waste materials in fired clay bricks usually has positive effects on the properties such as lightweight bricks with improved shrinkage, porosity, and strength. The main objective of this study is to focus on the properties and environmental impact of the mosaic sludge incorporated into fired clay bricks. The characteristics of raw materials were obtained by using the X-Ray Fluorescence Spectrometer. The results have shown that chemical composition of clay soil and mosaic sludge was high with silicon dioxide and aluminium oxide. Both of the raw materials showed the same chemical composition, therefore sludge are suitable to replace clay in brick manufacturing. Two types of mosaic sludge namely bodymill sludge and polishing sludge incorporation was recommended up to 30% as the results obtained higher compressive strength with 25 N/mm^2 and low initial rate of suction under the limit of 5 g/mm^2. The leachability tests such as Toxicity Characteristic Leaching Procedure, Synthetic Precipitation Leaching Procedure and Static Leachate Procedure were conducted to determine the leachability of heavy metals and all the results are complied with the United State Environment Protection Agency and Environment Protection Agency Victoria. As for the indoor air quality, fired clay bricks containing bodymill sludge and polishing sludge demonstrated good indoor air quality based on the Industry Codes of Practice on Indoor Air Quality standards. Therefore, the incorporation of bodymill sludge and polishing sludge can be an alternative low cost material that produces adequate brick quality whilst providing environmental friendly disposal method.

Keywords: fired clay brick, mosaic sludge, physical and mechanical properties, leachability, indoor air quality.

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PROPERTIES AND ENVIRONMENTAL IMPACT OF INCORPORATING CIGARETTE BUTTS WASTE INTO FIRED CLAY BRICK

Aeslina Abdul Kadir (1)*, Noor Amira Sarani (1), Abbas Mohajerani (2)

(1) Department of Water and Environmental Engineering, Faculty of Civil and Environmental Engineering, Universiti Tun Hussein Onn Malaysia, 86400 Batu Pahat, Johor, Malaysia, (2) School of Civil, Environmental and Chemical Engineering, RMIT University, Melbourne Australia
*aeslina@uthm.edu.my

Comprehensive environmental studies on the incorporation of waste into building materials are still very limited by few researchers. Most attention has been directed to the physical and mechanical properties, yet leaching of heavy metals and indoor air quality impact are still insufficient. Therefore, this study is focusing on the environmental impact of using cigarette butt waste into fired clay bricks by providing comparative evaluation on leachability and indoor air quality, as well as physical and mechanical properties. Bricks were manufactured with different percentages of cigarette butts (0%, 2.5% and 5.0%) and fired at 1050 °C. Heating rates were applied during firing processes with 1 °C/min, 3 °C/min and 5 °C/min respectively. The results suggested brick with 2.5% cigarette butt and fired at 1 °C/min heating rates are adequate to achieve optimum properties. The physical and mechanical properties have achieved maximum compressive strength with 19.9 MPa and density becomes lightweight by 16% to 21% compared to conventional bricks. Increasing percentages of cigarette butts resulted in low thermal conductivity (improved from 24% to 46%), due to increasing porosity and low density. Leachability results may vary with different percentages of cigarette butts, however low heavy metals leached from all manufactured brick. The laboratory testing for Indoor Air Quality revealed that cigarette butt brick omits low concentration of gas emission and complied with Industry Code of Practice on Indoor Air Quality. As the conclusion, cigarette butt can be potentially utilized into fired clay brick to produce low-cost lightweight brick and constituting an ecological way to manage this waste by producing less environmental pollution.

Keywords: fired clay brick, cigarette butt, physical and mechanical properties, leachability, indoor air quality.

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EFFECT OF NANO-TUBE IMOGOLITE ON RBL 2H3 CELLS

Nurul Hiedayati (1), Zaenal Abidin (2), Alyya Shidiqqa (1), Erfira (1), Kazutaka Maeyama (3)

(1) Lab. of Pharmacology, Fac. of Medical of Health Sciences, Islamic State University Jakarta Indonesia, (2) Department of Chemistry, Fac. of Math & Natural Sciences, Bogor Agricultural University Indonesia, (3) Fac. of Medicine, Ehime University Japan

This study is a preliminary study of imogolite's application on drug delivery system. Here several imogolite synthetic with different in length and natural imogolite has been used. We investigated the possible effects of imogolite on RBL 2H3 cells by measuring histamine release. The results show after incubation for 48 hours RBL 2H3 cells with natural imogolite, synthetic imogolite A (short type), synthetic imogolite B (long type) and control group histamine content are, 4.5pg, 5.4pg, 4.9pg, and 4.5pg respectively. To investigate RBL 2H3 cells 's function, we incubate RBL 2H3 with imogolite overnight and stimulate histamine release by challenge with DNP-BSA. The result from control group, DNP-BSA, natural imogolite, imogolite A, imogolite B are 3%, 59%, 58%, 60% and 59%, respectively. Both results show there is no significant different between the control group and imogolite group.

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IMOGOLITE AS INDONESIAN HERBAL DELIVERY MATERIAL

Zaenal Abidin (1), Aisyah (1), Impron (2), Nugraha EdySuyatma (3), Nurul Hiedayati (4), Naoto Matsue (5)

(1) Department of Chemistry, Fac. of Math & Natural Sciences, Bogor Agricultural University Indonesia, (2) Department of Geophysics and Meteorology, Fac. of Math & Natural Sciences, Bogor Agricultural University Indonesia, (3) Department of Food Science, Fac. of Agricultural Tech, Bogor Agricultural University Indonesia, (4) Lab. of Pharmacology, Fac. of Medical of Health Sciences, Islamic State University Jakarta Indonesia, (5) Fac. of Agriculture, Ehime University Japan

Imogolite is fibrous acid-dispersible clay, gelatin-like form when it is in high pH solution and it becomes thin film under dried condition. Imogolite has a nano-tubular chemical structure within side diameter of 1.0 nm and outside diameter of 2.0 nm with a well-defined fibrous electron-diffraction pattern indicating that the tubes are uni-dimensional crystals. These tubes may be several thousand-nanometers in length. It has high surface area through which gases can be easily adsorbed both inside and outside the particle. Because of its large surface area, imogolite has capability to adsorb large amount of water and alcohol molecules as hydrogel form. The quality of gelatin-like solution from imogolite depend on its length of tubular (Abidin, unpublised data). Tubular imogolite has capability to protect degradation of methylene blue molecules from heat and UV-radiation (Abidin et al., 2008). This evidence of sheltering effect of imogolite suggests that the bundle of tubular become important part of imogolite, not only as adsorption sites but also as protection site. Antioxidant materials such as catechin and ascorbic acid can be loaded into imogolite easily. Transparent gel of antioxidant-imogolite complex has capability to scavenging 1,1-Diphenyl-2-pircrylhydrazil (DPPH) radical (Abidin et al., 2008).

Results of our previous research clearly indicated that imogolite has a potency for sunscreen and supporting herbal medicine compound due to its unique characteristics. In this research, we used colloidal of synthetic imogolite. The aim of this study was to develop application of imogolite as herbal delivery material that has a function as an antibacterial agent. Here we selected *tabat barito* (*Ficus deltoidea*) leaf extract based on its antibacterial activityas “herbal medicine model”. The leaf extract was obtained from maceration using ethanol 96% and 30%. Nanocomposite film of imogolite/*tabat barito*was formed by mixing *tabat barito* leaf extract and imogolite. The antibacterial capability of the composite were tested on *Staphylococcus aureus* and *Escherichia coli*.

The freeze-dried particles extract of tabat barito samples were difficult to redissolved in absolute ethanol solvent. It could be said that chemical compounds contain in the particles extract samples interacted each others to form a stong aggregation during drying process. By changing in the solvent which has high polarity such as dimethyl sulfoxide, the dried particles extract samples were easily dissolved. However, change in the degree of polarity of solution has affected the stability of extract solution, as shown by floculation formation on the extract solution after adding water or ethanol solvent. However, adding imogolite solution into the particles extract solution did not cause floculation formation. The two components are stable and can disperse homogenously. Also, thin film was formed when mixing of imogolite/*tabat barito*was driend in glass slide. These results shown that imogolite can create anemulsifier-like form between extract particles and the solvent. The colloidal imogolite can accomodate particles extract by strong interaction in the intertubular space of imogolite. Antibacterial activity of the imogolite/*tabat barito*nano composite film against *Staphylococcus aureus* bacteria was better than that of *Escherichia coli*. However, the antibacterial activity of the film was lower as compared to the blank.

Keywords: antibacterial activity, imogolite, maceration, tabat barito, nano thin film.

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A NEW DEVICE FOR SWELLING/SHRINKING TESTS ON BENTONITES

Renata Adamcova (1)*, Magdalena Dziakova (1), Tom Schanz (2)

(1) Comenius University in Bratislava, Faculty of Natural Sciences, Bratislava, Slovakia, (2) Ruhr-University Bochum, Department of Civil and Environmental Engineering, Bochum, Germany

A lot of research was done on bentonites for the engineered barrier systems (EBS) of deep geological repositories of radioactive waste (RW) in last decades. One of the most important questions is the swelling potential of applied bentonites. This controlls the closing of spaces between bentonite blocks, bentonite and the host rock, as well as the self-healing of any unexpected cracks in the EBS. When no more free spaces are left and further volume increase is impossible, bentonite starts producing swelling pressure that depends on the bentonite dry density. These were the two main questions of the related research about the bentonite saturation by underground water in the past: a) the relative swelling index [%] expressing the linear or volume increase during free swelling, b) the swelling pressure [MPa] at constant volume. Just a small number of shrinkage tests were done on the saturated bentonite considering either the volume reduction or the shrinkage limit w_s [%]. But, what happens to the swelling pressure during shrinking that could be the result of the heat coming from the container with RW? How will the saturated bentonite behave if the confining pressure decreases due to any unexpected reasons? How will the swelling pressure change if strain is increasing? What will be the swelling pressure if the bentonite sample is saturated on one side and dried on the other side (resembling the water input from the host rock mass and drying near the hot container)? What is the difference of swelling by saturation with water or with water vapour?

These and other questions can be answered by applying a unique device constructed for measuring swelling pressures up to 20 MPa expected in saturated high-density bentonite blocks. It is a special oedometer, a prototype constructed in cooperation of Sondermaschinenbau Schudy and Ruhr-University Bochum in Germany and Comenius University in Slovakia. The normal stress is applied by a special loading segment with controlled air pressure from a compressor. It allows tests where both, volume and load, can be either constant or variable. The pressure in the test chamber is measured by a pressure cell contacting the piston. The measured data are collected automatically by a datalogger, frequency of measurements is programmed by a PC. Standard consolidation tests are possible, as well, but the main purpose is the measuremnt of stress and strain during swelling. Saturation can be done from the bottom to the sample top or from both sides to accelerate the saturation. A simple byrette is used for saturation with water under constant hydraulic gradient. If saturation with water vapour is desired, oedometer can be attached to a flask with a concentrated solution producing defined saturated vapour pressure. The same compressor drives the vapour through the filter plate under much lower pressure than is used for the sample loading. Depending on used solution, either saturation or desaturation, i. e. drying will happen. Cyclic loading/unloading, as well as cyclic saturation/desaturation are possible without taking the sample out from the chamber. Samples can be pressed from the bentonite powder directly into the test ring very precisely in a special device. The sample diameter is 50 mm, the hight is either 10 mm or 20 mm. The equipment is a very new acquisition. Bentonite BKT from Slovakia considered for EBS is the first material tested in different ways in this oedometer from February 2017. First experience with the equipment operation and the received results will be presented at the 16th ICC in Granada in order to promote the useful tool to other researchers.

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HALLOYSITE-ALLOPHANE AND GOETHITE-FERRIHYDRITE PRECIPITATION AT KARSTIFIED CONTACT OF SANDS AND CALCARENITES IN VECHMAAL (BELGIUM)

Adriaens Rieko (1)*, Ronchi Benedicta (2), Mertens Gilles (3), Hollanders Sofie (1), Elsen Jan (1), Dusar Michiel (4), Vandenberghe Noel (1)

(1) University of Leuven, Leuven, Belgium, (2) ISSeP, Liège, Belgium, (3) Qmineral Analysis & Consulting, Heverlee, Belgium, (4) Royal Belgian Institute of Natural Sciences, Brussels, Belgium

In Belgium, numerous karstified sand-carbonate contacts are known for their association with halloysite precipitation. In the Hinnisdael caves of Vechmaal, eastern of Belgium, a similar geological setting is observed in dolines of karstified calcarenite of the Cretaceous Maastricht Formation filled with glauconiferous sand of the Oligocene St. Huibrechts-Hern Formation. At the sand-calcarenite interface, a discontinuous lithological succession occurs of white clay and oxidized rust, which occur almost perfectly segregated and have a thickness varying from 1cm to 25cm. These lithologies are authigenic precipitations of high mineralogical purity consisting of only halloysite-allophane and goethite-ferrihydrite respectively. The halloysite was found in-situ to occur as the hydrated 10 Å structure which already started to dehydrate after sampling in normal air-dry conditions (20 °C, ±335% relative humidity). After 24 hours of air-drying, the halloysite structure completely altered to the dehydrated 7 Å structure.

The Al, Si and Fe necessary for this precipitation were derived from the short-range distance dissolution of glauconite and other silicate minerals present in the overlying sand unit. The mobilization of these ions was realized by the progressive oxidation of pyrite to jarosite leading to a significant acidification of the percolating water. It is furthermore observed that seemingly small variations in local conditions in the Curfs quarry of Valkenburg, the Netherlands, result in alunite, gibbsite, halloysite, allophane precipitation instead of jarosite, halloysite-allophane and goethite-ferrihydrite.

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MINERALOGICAL STUDY OF THE POZZOLANIC PROPERTIES OF CALCINED CLAYS

Hollanders Sofie (1), Cizer Ozlem (2), Adriaens Rieko (1)*, Elsen Jan (1)

(1) Division Geology, Department of Earth and Environmental Sciences, University of Leuven, Celestijnenlaan 200E, 3001 Heverlee, Belgium, (2) Building Materials and Building Technology Section, Department of Civil Engineering, University of Leuven, Kasteelpark Arenberg 40, 3001 Heverlee, Belgium
*rieko.adriaens@kuleuven.be

Portland cement-based materials, like concrete, are nowadays the most important construction material. The expansion of the cement industry might be a cause for concern, since the production process is very energy-intensive and because of the large amounts of carbon dioxide that are emitted, it’s extremely large-scale production implies that it is responsible for 5 - 8% of the anthropogenic CO2 emissions. The addition of supplementary cementitious materials (SCMs) is considered to be one of the most effective ways of reducing the environmental impact of the cement industry. SCMs, also known as pozzolans, chemically react at ambient temperature with calcium hydroxide in the presence of water to form compounds that possess cementitious properties. Commonly used SCMs like blast furnace slag from steel production and fly ash from coal combustion face complete utilization and future trends in steel and electricity production may reduce their availability. Therefore, there is an urgent need for alternative SCM sources. One of the most promising alternative ones are calcined clays. However, calcined clays are hardly used as SCM due to the complexity of clay minerals and the ignorance of the underlying reaction mechanism and reaction products. Hence this study investigates the potential use of calcined clays from a mineralogical point of view by linking the characteristics of the untreated clays to the pozzolanic activity of the calcined clays and to the reaction products of the cement-calcined clay reaction.

The key starting point of this study consists of a detailed chemical, mineralogical and physical characterization of both the raw and calcined material. To increase the reactivity of natural clays, the raw clay is calcined in a fixed-bed electrical furnace at temperatures ranging between 500 °C and 900 °C. The characterization of the raw and calcined clays includes the determination of the mineralogical (XRD) and chemical (ICP-OES) composition, physical characteristics like grain size (laser diffraction) and specific surface area (BET) and spectroscopic characteristics (FTIR & NMR). After heat treatment, their pozzolanic activity is evaluated with the Chapelle test and with thermal analysis (TGA) on mortars after 3, 7 and 28 days. The combined results of this study indicate that the mineralogical composition of the starting material is one of the primary factors controlling the pozzolanic reactivity of the calcined clay. Especially two mineralogical features are critical namely:

1) The type of the dominant clay mineral, with its characteristic thermal behaviour, for pure clays the reactivity can be summarized as follows: Kaolinite >> Ca montmorillonite > Na montmorillonite > illite > hectorite.

2) The amount of the clay mineral and presence of impurities. The presence of non-clay minerals can have an effect on the pozzolanic reactivity. Inert materials like quartz, feldspar and muscovite have no direct influence on the reactivity, but feldspar and muscovite enhance the sintering phenomenon upon calcination resulting in a coarser grain size and consequently a decrease of the reactivity. Moreover, several reactivity tests on artificial mixtures with a variable impurity content demonstrated that the quantity of the inert material can be linearly correlated to the pozzolanic reactivity. Additionally the presence of up to 30% of calcite appears to increase the pozzolanic potential of the clay, especially at early ages of the hydration reaction.

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SIZE DEPENDANT MINERALOGY OF YPRESIAN AND RUPELIAN CLAYS IN BELGIUM

Adriaens Rieko (1)*, Van Baelen Herve (2), Vandenberghe Noel (1), Wouters Laurent (2)

(1) University of Leuven, Leuven, Belgium, (2) ONDRAF/NIRAS, Brussels, Belgium

In the past, the mineral composition of the poorly-indurated Rupelian Boom Clay and the Ypresian Ieper Group clays in Belgium has been determined qualitatively and quantitatively by X-ray diffractometry (Zeelmaekers et al., 2015) by using a classical approach of mineralogical characterization at two levels: the bulk level and the concentrated clay fraction <2 µm. At the bulk level, clay minerals are quantified in groups using full pattern fitting software based on the Mineral Intensity Factor approach (Środoń et al., 2001). For example, in the Boom clay and Ieper Group clay, the group "2:1 Clays" involves the clay species dioctahedral smectite, Illite, interstratified illite/smectite and muscovite. Quantification of the individual clay species in the <2 µm fraction is performed by clay modeling on oriented clay slides using the multispecimen approach (Sakharov et al., 1999). Hereby, one integrated mineralogical composition is calculated by subdividing the clay groups quantified in the bulk, into the different components and in the relative abundances as quantified in the <2 µm.

This approach is based on the presumption that the clay minerals quantified in the <2 µm fraction are representative for the entire sample, which evidently is not guaranteed for all clay minerals, and certainly not for muscovite. Therefore, a research strategy was set up to investigate the validity of this approach by characterizing the mineralogy of 4 Boom clay and 9 Ieper Group clay samples in 6 different size fractions: <0.2 µm; 0.2-2 µm; 2-5 µm; 5-15 µm; 15-38 µm and >38 µm. The different size fractions are isolated by timed and multiple centrifugation steps after a thorough chemical pretreatment and sonification to remove aggregate-forming substances such as carbonate cements, organic matter and coatings of free oxides (modified after Jackson, 1969). Of each size fraction, random oriented powders (modified after Środoń et al., 2001) and oriented clay slides were measured with X-ray diffraction and quantified. Each size fraction was quantified to species levels. Muscovite was quantified separately as it occurs as 2M1-polytype whereas illite only occurs as disordered illite ("1Md").

Results indicate that over the 6 different size classes the mineralogical composition evidently changes from a clay mineral dominated mineralogy in the finest size fractions to a quartz dominated mineralogy in coarser size fractions. Smectite and interstratified illite/smectite however occur in significant quantities in the 2-5 µm fraction and even as traces in the 5-15 µm size fraction which is most likely due to insufficient disaggregation during preparation or the incomplete size separation procedure. For the Ieper Group clays, zeolites of the clinoptilolite-heulandite group occur only in size fractions >5 µm whereas opal-CT only occurs in finest size fractions <5 µm. Whereas the plagioclase type in the Ieper Group clays is generally considered as albitic, a more anorthite/andesine type of the plagioclase was found in the 5-15 µm fraction. These minerals suggest a, at least partial, volcanic origin for the Ieper Group clay, although the clay was probably transported over short distances before deposition. The most remarkable result is however that the mineralogical composition of each size fraction seems to be extremely stable when comparing different samples of the same clay formation. This was observed for both Ieper Group clay and Boom clay, although the mineralogy within the same size classes is different in both clay formation. Slight differences, but again systematic, were observed between the most clayey and the most silty lithologies. This means that the total mineralogy of such clay samples is nearly entirely determined by their grain-size distribution. The mineralogy reflects a very stable provenance and indicates that the bulk mineralogical differences between different samples of the same clay formation are probably entirely related to differences in grain-size distribution and therefore sedimentological and depositional conditions.

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ASSESSING THE POTENTIAL OF UŞAK CLAY AS A CERAMIC RAW MATERIAL BY COMPARING WITH UKRAINIAN CLAY

Tural Agayev*, Ceren Küçükuysal

Muğla Sıtkı Koçman University, Engineering Faculty, Geological Engineering Department, Muğla, 48000, Turkey
*tural_aqayev@yahoo.com

For thousands of years, clay has been an indispensable natural material for ceramics. Its industry in the last century rapidly grows in all over the world which reveals the need to seek a new ceramic raw materials. This is the case for Uşak, western Turkey as well. The well-known kaolinite deposits in Uşak had been widely explored and used, so the investigation of the new resource from the same area is indeed an essential subject of the present study. It aims to characterize Uşak clay (Usc) material mineralogically, physico-chemically and technologically by comparing with a well-known reference ceramic raw material, Ukrainian clay (Ukc).

For this study, various analyses were carried out, they were X-ray Diffraction (XRD), Scanning Electron Microscope (SEM), Fourier Transform Infrared (FTIR), X-Ray Flourescence (XRF), Differential Thermal and Thermogravimetric (DTA -TG), atterberg limits, particle size distribution and specific technological tests like bending and compressive strength, total linear shrinkage, color, water absorption and unit volume mass at temperatures between 800 -1430 °C. Bulk mineralogical composition of Ukc was defined as dominantly kaolinite and quartz rich while Usc was dominantly composed of quartz and illite with a little amount of kaolinite and dolomite. The particle size distribution of Ukc showed 54% clay (<4 µm), 32% silt (4-63 µm), 14% sand (> 63 µm) size fractions, whereas that of Usc presented 25% clay (<4 µm), 58% silt (4-63 µm), 18% sand (>63 µm). Additionally, Ukc is found to be more plastic than Usc. However, water absorption of Usc was recorded as 14,75% while Ukc was 24,27% at 1100 °C. The bending strength values of Usc measured in a wide range of 1 MPa to 19,4 MPa also showed better characteristics than Ukc with a narrow values of 0,3-3,4 MPa. Due to the abundance of kaolinite (80,2%) and very small amount of Fe_2O_3 (0,3%), Ukc is categorized as whiter in color than Usc.

Comparison between the two materials presently studied and the selected commercial raw materials for ceramics reveal that Ukc is more compatible for raw materials of tile, brick, white stoneware, earthenware and tableware, while Usc is a potential raw material only for brick and tile production and might be used as plasticty lowering additives for the common ceramics.

Keywords: Ceramic, technological properties, industrial application, physico-chemical properties, firing characters.

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RHEOLOGICAL AND FILTRATION PROPERTIES OF CLAY-POLYMER SYSTEMS: IMPACT OF POLYMER STRUCTURE

Hafiz Mudaser Ahmad (1), Muhammad Shahzad Kamal (2), Mamdouh A. Al-Harthi (1)

(1) Department of Chemical Engineering, King Fahd University of Petroleum and Minerals, 31261 Dhahran, Saudi Arabia,
(2) Center for Integrative Petroleum Research (CIPR), King Fahd University of Petroleum & Minerals, 31261 Dhahran, Saudi Arabia

Bentonite clay is the basic constituent of drilling fluid formulations but the use of only bentonite clay suspensions causes' shale instability and thermal induce flocculation at deep well conditions. In water based drilling fluid formulations, polymers are employed to customize rheological and filtration properties. Polymer encapsulates the shale with a thin layer and prevents the migration of water into the formations. The objective of this work was to study the rheological and filtration properties of bentonite-polymer suspensions in the deionized water and salt water at different temperatures. The polymers evaluated were partially hydrolysed polyacrylamide (HPAM) and copolymer of acrylamido tertiary butyl sulfonate and acrylamide (ATBS-AM). The steady shear rheological data was fitted to Herschel-Bulkley model to compute rheological parameters like yield stress and flow behaviour index. The incorporation of polymers in bentonite suspensions showed the substantial improvement in rheological properties such as yield stress, steady shear viscosity and gel strength. The presence of electrolyte in clay-polymer suspensions showed the decreases in rheological properties. At elevated temperature, the rheological properties such as yield stress and gel strength of bentonite-HPAM suspension showed better properties as compared to the bentonite-copolymer and bentonite suspensions in the deionized water and electrolyte solution. This increase in rheological properties at elevated temperature was attributed to the hydrophobic interactions among bentonite and HPAM. The API filtration experiments of bentonite-polymer suspensions were performed at 25 °C. The minimum filtrate loss was observed for bentonite-HPAM suspension. The overall results exhibited the good properties of bentonite-HPAM suspension in electrolyte solution and at elevated temperature.

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SYNTHESIS AND CHARACTERIZATION OF HOLLOW NANOSHERE LAYERED DOUBLE HYDROXIDE AS DRUG CARRER

Sumio Aisawa*, Honoka Takemura, Sang Jing, Hidetoshi Hirahara

Faculty of Science and Engineering, Iwate University, Morioka 020-8551, Japan
*aisawa@iwate-u.ac.jp

Layered double hydroxide (LDH) consists of a positively charged metal hydroxide layer and charge-balancing interlayer anions and these interlayer anions are generally exchangeable. LDH has a biocompatibility, anion exchangeability property and the intercalation of various biomolecules into the LDH interlayer. Carbon nanosphere (CNS) is one of carbon nanomaterials and constituted of a carbon framework and a hydrophilic surface. CNS can be synthesized by the hydrothermal reaction of saccharides solution. Hollow materials are well-known as a light weight and high dispersible material in solution, and they exhibits properties different than solids. In this study, we investigated the synthesis of hollow nanosphere LDH using CNS as a template and the intercalation of anticancer drug, 5-fluorouracil (5-FU) into LDH by the reconstruction method. In order to promote the cellular uptake of 5-FU, the cytotoxisity assay of the 5-FU/LDH nanosphere has also been stuied for applications of a drug carrer.

CNS was prepared by hydrothermal treatment of D-glucose solution at 200 °C for 3 hours. A hybrid of CNS and the LDH (CNS-LDH) was obtained by co-precipitation method, which $Mg(NO_3)_2$-$Al(NO_3)_3$-methanol and NaOh-methanol solutions were added to the CNS dispersed methanol solution. Then, CNS was removed by calcinations at 600 °C for 3 hours and the hollow nanosphere LDH oxide (hollow LDH-ox) was obtained. Finally, a hollow 5-FU/LDH was synthesized by reconstruction of the hollow LDH-ox in 5-FU solution with polyethylene glycol (PEG). Characterization of the solid products was evaluated using methods such as XRD, SEM, TEM and dynamic light scattering (DLS). Cytotoxicity assay of the hollow 5-FU/LDH for HeLa cell (human, cervix) was carried out using WST-8 assay.

The DLS measurement showed the average particle size of the CNS was 150 nm. The SEM images of CNS-LDH showed they are spherical particles, and the TEM images of the hollow LDH-ox implied that the LDH shell formed a small sphere after calcination of the CNS-LDH. The XRD patterns of the hollow 5-FU/LDH demonstrated that 5-FU was intercalated for the LDH. The d-values of hollow 5-FU/LDH were 0.98 and 0.78 nm. These d-values depended on the amount of 5-FU intercalated indicating that the intercalated 5-FU was vertically or horizontally oriented in the LDH interlayer space. The FT-IR spectra of hollow 5-FU/LDH showed that the assingned adsorption peaks of 5-FU which were 1221 cm^{-1} for C-F, 1687 cm^{-1} for C=O and 1590 cm^{-1} for C=N. The XPS spectra of hollow 5-FU/LDH suggested that the binding energy assigns to F1s at 688 eV shift to 685 eV, meaning that the electrostatic force acts between the negative intercalated 5-FU and the positive LDH basal layer. The TEM images of hollow 5-FU/LDH show the powdery products maintained the spherical and hollow shape of the CNS-LDH. In addition, the cytotoxicity of hollow 5-FU/LDH in HeLa cells was greater than that of 5-FU. These results indicate the increase of delivery efficiency and increase of cellular uptake for 5-FU.

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ON THE ORGANOCLAY INTERACTION IN INVERSE EMULSION DRILLING FLUID SYSTEM

Rezki Akkal (1)*, Mohamed Khodja (2)*, Nathalie Cohaut (3)

(1) Ecole Nationale Polytechnique, 10 Rue des Frères OUDEK El Harrach 16200 Alger, Algérie, (2) SONATRACH/ Direction Centrale Recherche et Développement, Avenue 1 Novembre 35000 Boumerdes Algérie, (3) Centre de Recherche sur la Matière Divisée, 1b rue de la Ferollerie, CNRS-Université, Orléans 45071, France
*rezkidzmin@yahoo.fr

The organoclays are used in the complex formulations of Oil-Based Mud (OBM) drilling fluids whose stability during time depends closely on the size and the state of dispersion of anisotropic organophilic clay particles in the continuous phase. These clays control the rheological and filtration properties of the Oil-Based drilling fluids dispersions. The properties of fluids are mainly governed by the interactions between the three major component water, oil and organophilic clay.

In this work we have modified hydrophilic clays in the laboratory referred to as, Sodic Wyoming and Laponite naturally sodic. We have also used three types of organophilic commercial clays, namelyVG69, Bentone 38 and Geltone. The hydrophilic clays were prepared on the basis of aqueous dispersion. The surfactant used was benzyl chloride dimethyl ammonium stearyl monohydrate $C_{27}H_{50}ClN$. The thickness of the interlayer space of hydrophilic clays was investigated with X Ray Diffraction (XRD) on raw clays, on raw clays dispersed in water and in mixtures of clay-suspension of surfactant, after centrifugation. The role of the modified clays as well as the interlayer thickness was investigated with small Angle X-ray Scattering (SAXS) under shear to study the relationship between the viscosity of Oil-Based inverse emulsions, the structure and the orientation of the organophilic clays dispersed in the organic phase. The results of X Ray diffraction showed that the $d_{(001)}$spacing ranged from 18.6 Å at 1CEC to 45.5 Å for 4 CEC of the clay. Except for Laponite, all other oragnoclays presented an excess of surfactant, which was probably hosted in the porosity of aggregates of particles or was fixed to the surface or on the edges of smectite particles. The SAXS technique showed that the dispersion of the sheets is the most marked. The clay smodified in the laboratory (Wyoming and Laponite) have large interlayer spacing and lower densities compared to their commercial counterparts (VG69, Geltone and Bentone) which displayed smaller interlayer spacings and relatively high densities. This indicates strong intercalation of the organic matter in the interlayer space of the clays modified in the laboratory. The magnitude of the interlayer distances for the commercial clays indicates that they were only partially modified.

Keywords: Oil-Based Mud, Organoclay, SAXS, Emulsion.

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ZnO/SEPIOLITE HETEROSTRUCTURED MATERIALS FOR PHOTOCATALYTIC DEGRADATION OF EMERGING POLLUTANTS IN WASTEWATER

Marwa Akkari (1,2)*, Pilar Aranda (1), Carolina Belver (3), Jorge Bedia (3), Abdessalem Ben Haj Amara (2), Eduardo Ruiz-Hitzky (1)

(1) Instituto de Ciencia de Materiales de Madrid, CSIC, 28049 Madrid, Spain, (2) University of Carthage, 7021 Zarzouna, Tunisia, (3) Autonomous University of Madrid, 28049 Madrid, Spain
*akkari.maroi@gmail.com

The development of porous nanoarchitectures materials based on clays minerals is a topic of growing interest, being typically addressed to catalysis and adsorption applications [1,2]. Among clay minerals, sepiolite fibrous clay provides larger external surface area as well as the presence of external silanol groups in comparison to typical layered silicates (e.g., smectites), which favours the immobilization of diverse nanoparticles (NP). In this communication it will be introduced several porous ZnO-sepiolite nanostructured materials prepared using sepiolite or organosepiolite as intermediate to control the assembly and aggregation of the metal-oxide nanoparticles. On the one side, ZnO-sepiolite nanoarchitectures were prepared following a process based on the assembly of previously synthesized ZnO NP to sepiolite modified with hexadecyltrimethylammonium ions, both dispersed in 2-propanol medium, to produce an intermediate that after a thermal treatment consolidates the final ZnO/clay nanoarchitecture [3]. On the other side, the ZnO NP were incorporated to a sepiolite previously modified with SiO_2 NP produced following a sol-gel methodology reported elsewhere [4]. In this case, it is intended to have a support of ZnO NP with a larger accessible surface area and also appropriate chemical reactivity of the clay surface. Finally, a novel heterostructure has been prepared using directly the sepiolite as substrate on which magnetite NP were *in situ* growth [5] and then ZnO NP were assembled as in the previously described materials. All types of samples have been characterized by diverse characterization techniques (XRD, FTIR, specific surface area and porosity determinations, TEM, FE-SEM-EDX, SQUID, etc.) and their activity in the photocatalytic degradation of emerging pollutants in water was tested. In this way, solutions of paracetamol, antypirine and ibuprofen drugs were exposed to a lamp that simulates solar light and the variation of their concentration with time of exposure was followed by HPLC. For instance, it has been observed that the ZnO/sepiolite heterostructure exhibits better photoactivity than ZnO/SiO_2-sepiolite and ZnO/Fe_3O_4-sepiolite materials for the degradation of ibuprofen. However, the last material has an important advantage as it presents superparamagnetic afforded by the magnetite NP and it can be easily recovered from the reaction media by applying an external magnetic field, which makes very easy the reusability of the photocatalyst in consecutive cycles of treatment.

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INTEGRATIVE EXPERIMENTAL STUDY OF CLAY-FLUID INTERACTIONS TO ENHANCE THE DURABILITY OF SHALE STABILIZATION

Mohammed Al-Arfaj (1), Ibnelwaleed Hussein (2)*, Md. Amanullah (1), Abdullah Sultan (3)

(1) EXPEC Advanced Research Center, Saudi Aramco, Dhahran, 31311, Saudi Arabia, (2) Gas Processing Center, Qatar University, P.O. Box 2713, Doha, Qatar, (3) Petroleum Engineering Department, King Fahd *University of Petroleum & Minerals, Dhahran, 31261, Saudi Arabia,*
*ihussein@qu.edu.qa, mohammad.arfaj.1@aramco.com

The use of water-based drilling fluids to drill shale formations can cause wellbore stability problems as a result of the reaction of water with clay minerals. When it comes in contact with water, clay starts to react, swell and/or disperse leading to shale disintegration and sloughing. Different types of clays give rise to different types of problems. For example, when it is exposed to water, a shale sample with a high percentage of smectite swells while another shale sample with a high percentage of kaolinite disintegrates and disperses. Consequently, tight hole might develop and/or higher solids loading in the wellbore might be experienced and, hence, the chance to get stuck pipe increases and the hole cleaning efficiency of drilling fluid decreases significantly. Moreover, shale inhibitors/stabilizers need to provide the required stabilization for a period of time long enough to drill the shale section, reach the planned casing point and run the casing string. If the stablization effect breaks down earlier and, for any reason such as encountering a loss circulation zone, a decision was made to switch from inhibitive drilling fluid to fresh water, the shale formation starts to react with water again and causes problems.

Four samples of a Silurian shale formation collected from different locations and depths were characterized in a previous study [1]. This paper describes the experimental work conducted on the same four shale samples to assess clay-fluid interactions and the durability of shale stabilization. After conducting mineralogical analysis using X-ray diffraction, shale inhibition tests including dispersion, inhibition durability and swelling tests were carried out using de-ionized water, 5% potassium chloride brine and 5% Polyamines solution. Also, moisture content was measured and adsorption isotherms were established. From adsorption isotherms results, the adsorptive potential for every shale and clay sample was determined and the samples were ranked based on this parameter. The work has been extended to cover different pure clay samples: sodium montmorillonite, illite and illite smectite mixed layer.

Dispersion results showed that shale recovery percentages varied from 30.8% for shale sample dominated by kaolinite to 98.65% for those with low kaolinite content. For the high kaolinite sample, the recovery percentage jumped from 30.8% to 59% with potassium chloride and eventually to 85.5% when the polyamine solution was used. Inhibition durability testing revealed the superior performance of the polyamines compared to potassium chloride in stabilizing the shale over extended periods of time. While potassium chloride recovered only 12% of the kaolinite-dominated sample after 18 hours of re-exposing the shale sample to fresh water, polyamine results showed 84% of shale recovery after 12 days. When the samples were tested in the swell meter, results showed higher swelling percentage values for those samples with higher smectite content followed by illite while two samples showed no potential swelling as they have low clay content of less than 15%. Moreover, swelling percentages showed strong correlation with moisture content of the four shale samples along with the pure clay samples. The date points were correlated with a linear trend line whose coefficient of determination is equal to 0.99.

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TIXOTROPIC EVALUATION OF DISPERSIONS OF NEW OCCURRENCES OF BRAZILIAN BENTONITIC CLAYS FOR ORGANIC BASED DRILLING FLUIDS

Isabelle Albuquerque Da Silva (1)*, Ivna Daniele Souza Pereira (1), Francisco Kegenaldo Alves De Sousa (2), Romualdo Rodrigues Menezes (1), Gelmires De Araújo Neves (1), Heber Carlos Ferreira (1)

(1) Academic Unit of Materials Engineering, Federal University of Campina Grande - UFCG, Bodocongó, Campina Grande - PB, 58109-970, Brazil, (2) Academic Unit of Production Engineering, Federal University of Campina Grande - UFCG, Bodocongó, Campina Grande - PB, 58109-970, Brazil
*isabelle_albuquerquecg@hotmail.com

The state of Paraíba in Brazil is one of the largest national producers of these clays, with its production concentrated in the city of Boa Vista, whose reserves have great diversity [1]. New deposits were found in the state, a fact that may represent an interesting technological alternative to the future shortage in the city of Boa Vista, Paraíba, Brazil, bentonitic clays, expansion of mineral production in the region and consolidation of the state as the largest producer in the country. A study [2] about the modification of the new reservoirs of the state of Paraíba, Brazil, with non-ionic surfactants for use in organic base drilling fluids, analyzing the properties [3] and swelling [4] of dispersions in different organic media. After this study, it was also necessary to evaluate the thixotropic properties of the dispersions previously studied, in order to observe the relationship with the rheological properties, thus obtaining a larger and more complete study. Therefore, this work proposes the thixotropic evaluation of the dispersions of new occurrences of Brazilian bentonitic clays for organic base drilling fluids. The organophilization process was evaluated by the results of X-ray diffraction (XRD) and thermal analysis (DTA and TG), where in the latter the contents of non-ionic tensoativos incorporated were quantified; The rheological properties were evaluated by the swelling and apparent viscosity of the dispersions in different organic media, observed in detail by [2], who related the influence of the non-ionic surfactants on the rheology of the dispersions obtained. For this work, the thixotropic properties were studied by the obtained flow curves. The previous study [2] showed with its results that the organophilic clays with the non-ionic surfactants presented potential of use as mineral viscosifier in organic base drilling fluids, using diesel. In the present study, the results of flow curves of the organophilic clays showed pseudoplastic behavior and the presence of hysteresis, indicating the presence of thixotropy, also having a relation between the thixotropy and the apparent viscosity of the obtained dispersions. These results complement the previous study, thus confirming the suitability of dispersions to organic base drilling fluids.

Keywords: Bentonitic clays, organophilic clays, thixotropy, drilling fluids.

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ZEIN-SEPIOLITE SUPERPARAMAGNETIC BIONANOCOMPOSITE FOAMS

Ana C.S. Alcântara (1,2), Yorexis Gonzalez-Alfaro (1,3), Margarita Darder (1),
Pilar Aranda (1)*, Eduardo Ruiz-Hitzky (1)

(1) Instituto de Ciencia de Materiales de Madrid, CSIC, 28049 Madrid, Spain, (2) Universidade Federal do Maranhão, 65080-805, São Luís, Brazil, (3) Centro de Estudios Avanzados de Cuba (CEAC), CITMA, 17100 La Habana, Cuba
*pilar.aranda@csic.es

Bionanocomposites are a versatile type of materials that may offer both remarkable structural and multifunctional properties [1]. Interestingly, they can be conformed by different types of processing, giving rise for instance to films and foams of interest for a wide variety of applications, such as bioplastics, gas separation membranes, adsorbents, scaffolds for tissue engineering, packaging or building insulation. In this context, bionanocomposites foams can be prepared by diverse strategies including gas foaming, particulate leaching or freeze-drying [2], being this last one the mostly applied method as hydrophilic polysaccharides or proteins are the largest employed biopolymers and water is used as their main solvent [1,2]. The presence of inorganic solids, for instance clay minerals, as fillers in the biopolymer matrix could help the foaming process, affording nucleation sites that may control the cell density and also contributing to enhance mechanical and physical properties [2,3]. Despite this, the high hydrophilicity of most of the commonly used biopolymers limits the bionanocomposite foam stability in aqueous media, hampering their use in certain applications that involve its immersion in aqueous media, e.g., removal of pollutants in water. To overcome this drawback it is possible to stabilize the foam using cross-linking agents or less hydrophilic polymers. For instance, in the case of hydrophobic biopolymers such as zein, the main storage protein of corn, polymeric foams have been prepared using supercritical CO_2 or a previously modified zein with hydrophilic compounds [4,5].

Recently, our group has reported a methodology that plays with the different solubility of zein components in presence of ethanol and water to produce zein-montmorillonite nanocomposites [6]. This communication will show how this convenient property of zein can be also applied to produce bionanocomposite foams by assembly of sepiolite to zein following a process that implies the subsequent immersion of mixtures of both components in anhydrous ethanol and water, followed by a final step of freeze-drying. Bionanocomposite foams can be also prepared using a sepiolite that incorporates magnetite nanoparticles (NP) from a ferrofluid, previously prepared by a methodology that have proved to produce very stable superparamagnetic multifunctional materials [7]. As occurs in other biohybrids involving zein assembled to sepiolite and palygorskite fibrous clays [8], the presence of this protein affords hydrophobicity and stability in water to the resulting bionanocomposite foams. Moreover, the existence of strong affinity between zein and the sepiolite-based fillers results in foams that show good mechanical properties and, in certain cases, additional superparamagnetic properties, when they incorporate the magnetite-based filler. The resulting bionanocomposite foams have been tested as adsorbents of 4-chloro-2-methylphenoxyacetic acid (MCPA), here selected as model herbicide, to prove their potential usefulness in environmental remediation. Furthermore, as the zein-sepiolite superparamagnetic bionanocomposite foams could be easily recovered from the aqueous media by applying an external magnetic field (magnet) this type of adsorbent could be easily applied in open water areas.

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QUATERNARY PALAEOENVIRONMENTS PRESERVED IN CLAYS AND CLAY-ORGANIC-COMPLEXES: EVIDENCE FROM THE SEA OF AZOV REGION

Andrey Alekseev (1)*, Pavel.Kalinin (1), Tatiana Alekseeva (1), Veronika Alekseeva (2)

(1) Institute of Physicochemical and Biological Problems in Soil Science, Russian Academy of Sciences, Pushchino, 142290 Russia, (2) Faculty of Geography, Moscow State University, 119992, Moscow, Russia
*alekseev@issp.serpukhov.su

Succession of Quaternary palaeoenvironments over the past 0.7 million years reveal a complex of Loess-palaeosol exposures along Taganrog Bay, Sea of Azov, in southern Russia. At the key section of Chambur- Kosa, four palaeosol complexes were identified. The earliest Vorona palaeosol complex in the section correlated with the late Muchkap Interglacial. The soil type corresponds to modern subtropical Mediterranean region soils. The later Middle Pleistocene Inzhavino palaeosols transitional between kastenozems and chernozems developed during the Likhvin Interglacial. Palaeosol complex of Kamenka Interglacial is typified by Luvic Chernozemic soils, possibly formed under prairie conditions. Finally, the Mezinpalaesol developed during Mikulino Integlacial (Late Pleistocene) is represented by chernozems similar to the modern (Holocene) steppe soils of the region. The sequence indicates that moisture supply and temperatures during successive interglacials shifted progressively towards increasingly cooler, somewhat drier climates, influencing soil formation. The palaeosols record, by changes in physical, mineralogical and/or chemical properties, not only the soil forming climate prior to burial (and effective fossilisation) of the soil profile but also changes in soil evolution, vegetation, and environment.

The aim of this study was to estimate the weathering status of the Pleistocene paleosols loess sections using, clay mineral assemblages, geochemical indicators (coefficients based on ratios of different element concentrations), iron oxide magnetic mineralogy and clay-organic complexes. A variety of climatic proxies wereused to estimate the relative intensity of the Quaternary climatic change: magnetic susceptibility of the loess and paleosol: weathering index PWI, CIA, Rb/Sr ratio, stable isotope study, clay mineralogy, etc. Clay minerals indicate evidence of temporal and spatial differences during cold periods when loess wasdeposited, and warm stages when paleosols formed. Illite and chlorite are the dominant clay minerals in loess. Illite is not easily weathered by warm and wet conditions, whereas chlorite is very susceptible to weathering. I/C ratios, therefore, display changes in chlorite weathering intensity in glacial-interglacial sequences that result from differences in climate. The I/C ratios provide a tool to evaluate past climate. I/C ratio values above about 3.0 is characteristic of paleosols and indicate chlorite weathering and thus an intensive weathering stage. The weathering and destruction of chlorite is significant under a humid condition (an annual precipitation exceeding about 450 mm).

Clay fractions of palaesols generally hold the highest content of soil organic matter (SOM), clay minerals protect efficiently SOM from decomposition. The clay fractions of loess and palaesols were analysed by solid-state ^{13}C NMR spectroscopy. The clay-organic-complexes pronounced shifts of SOM quality in palaeosols. Amounts of C-species according to $_{13}$C NMR spectra demonstrate the changes in structure of organic matter versus climate of soil formation. Carbon isotope compositions (δ^{13}C) of organic matter in clay fractions of loess-palaeosols suggest changes of the paleovegetation, C3 or C4 type of plant, which dominated in specific periods and climatic conditions over time in steppe environment.

Geochemical and mineralogical data of clays and clay-organic-complexes from loess-palaesol are useful indicators of past environments and climate. Comparisons between clay mineralogy and other paleoclimatic records (oxide magnetic mineralogy, geochemical indicators) evaluate the efficacy of mineralogy as a palaeoclimatic tool.

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THE MISSISSIPPIAN PALAEOSOL SEQUENCE FROM THE SOUTHERN PART OF MOSCOW SEDIMENTARY BASIN: MINERALOGY, GEOCHEMISTRY, PALAEOENVIRONMENTS

Tatiana Alekseeva*, Andrey Alekseev, Pavel Kalinin

Institute Physical Chemical and Biological Problems of Soil Science RAS, Pushchino, 142290, Russia
*alekseeva@issp.serpukhov.su

The chronosequence of five Visean (Aleksinian-Venevian interval) palaeosols on the territory of Moscow calcareous sedimentary basin (Bronzi quarry, Kaluga region) was studied in detail. All palaeosols are polycyclic and consist of (1) a lower unit (substrate) consisting of limestone which was altered to different degrees by weathering/pedogenesis, which is overlain by (2) a terrigeneous topclay which represents an individual palaeosol developed prior to subsequent marine flooding. Some topclays are capped by coal. High-amplitude sea-level fluctuations at the Mikhailovian-Venevian boundary followed by prolonged subaerial exposure of limestone resulted in the development of the deep karst capped by a pronounced paleosol and then by several palustrine beds. This laterally extensive terrestrial complex with local name “Kholm unconformity” is the important stratigraphical unit for the territory [1]. Carbonates within the sequence are presented by calcite with $\delta^{13}C$ isotopic composition in the broad range: $-4.63‰ < \delta^{13}C < +4.38‰$; thus at least some of them have pedogenic/biogenic origin. Topclays are weakly calcareous playa deposits rich in clay . Besides Si and Al, they are enriched in Fe, Mg, Ti, Ga and some other elements. The close TiO_2/Al_2O_3 values which charaterize all five levels testify for the constant souce of parent material. The mineralogical composition of palaeosols is similar. The substrates consist of calcite. The topclays are almost monomineralic and smectite dominated (low charge beidellite and montmorillonite). Palaeosols of Aleksinian-Mikhailovian interval additionally contain kaolinite, goethite (α-FeOOH) and lepidocrocite (γ-FeOOH). Electron microscopy study of topclays shows that Fe-oxides are closely associated with plant material (substitude roots, fill root channels). Presence of lepidocrocite was supported by XRD and thermomagnetic study. The occurrence of this mineral is a reliable indicator of hydromorphous character of several palaeosols. Calculated (CIA-K) geochemical index varied from 1 to 78 (largest for topclays). Palaeosols of the Aleksinian-Mikhailovian interval demostrate the larger values of this index which together with the smectite-kaolinite-goethite/lepidicrocite association suggest deeper weathering of this interval. Two Venevian palaeosols contain no kaolinite or goethite and have smaller (CIA-K) values. Climate, terrigeneous input, relief, duration of exposure, atmospheric CO_2, and diagenesis could affect the mineralogy. Clay fractions separated from topclays contain different amount of bound organic carbon (2-19%). Its ^{13}C NMR study showed that the most preserved is carbon of aromatic functional groups. Calculated mean annual precipitation (MAP) shows that the Visean climate on the given territory had cyclic character. The most humid conditions (>1000 mm/y) existed during Mikhailovian time. Authigenic smectites and lepidocrocite testify for the seasonal type of climate. Later, starting from Venevian, MAP decreased to $\leq$750 mm/y, then to 300-400 mm/y at the end of Mississippian and into the Pennsylvanian. As a result, wet subtropical swampy palaeosols under predominantly arborescent lepidodendron vegetation were replaced by semi-arid palaeosols [1].

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EFFECT OF HEAVY METALS ON HERBICIDE MESOTRIONE FATE IN FOUR CONTRASTING SOILS

Tatiana Alekseeva (1)*, Pascale Besse-Hoggan (2), David Pinsky (1), Anastasia Maltseva (1), Claude Forano (2), Ilya Rusin (1), Pavel Kalinin (1)

(1) Institute Physical Chemical and Biological Problems of Soil Science RAS, Pushchino, 142290, Russia, (2) Institut de Chimie de Clermont-Ferrand (ICCF), CNRS, UMR 6296, Université Clermont Auvergne, 63178 Aubière Cedex, France
*alekseeva@issp.serpukhov.su

Mesotrione {2-(4-methylsulfonyl-2-nitrobenzoyl)-1,3-cyclohenanedione}, a member of the triketone family, is a recent selective herbicide used in maize culture. The aim of the present research was to determine the effects of heavy metals (HMs) - Cu, Pb and Zn - on mesotrione adsorption and retention in soils. Four soils with markedly different geneses and contrasting properties were chosen and investigated in detail: Chernozem, Luvisol, Red Soil and Vertisol. The selected soils represented a range of soil parameters that could affect the behaviour of HMs and the weakly acidic herbicide mesotrione (pKa = 3.12). The soil characteristics taken into consideration were: pH, cation exchange capacity (CEC), carbonate content, granulometry, chemical composition (XRF), bulk and clay mineralogy (XRD), Fe-oxalate and Fe-dithionite-citrate-bicarbonate extractable, organic carbon (OC) content and its characteristics (humic acids/fulvic acids, input of C-containing functional groups based on solid state ^{13}C NMR data).

Mesotrione adsorption experiments with soils polluted with HMs (2 g/kg on a dry weight basis) and HM-free (bulk soils and their clay fractions) were carried out using the batch equilibration technique. The adsorption experiments were carried out at the room temperature and we used 1:3 solid:solution ratio with mesotrione solution concentrations ranging from 10 - 1000 µM and a contact time of 24 h. The pesticide concentrations in equilibrium solution were quantified by HPLC. For one step mesotrione desorption experiments, supernatants obtained after 24 h adsorption were completely replaced by distilled water and the tubes were shaken for the next 24 h.

HM polluted soils were prepared based on isotherms of HM - nitrate adsorption. These experiments were also carried out using the batch equilibration technique. All isotherms obtained of HM adsorption were of L-type and were well described by the Langmuir equation. Reliable positive correlations were obtained between Langmuir parameters and soil properties- content of clay and silt, pH, CEC, content of carbonate and OC in alkyls. Five steps of HM desorption experiments showed their large (≤10% from adsorbed) retention which depended on HM cation as well as soil properties. Data obtained evidence different mechanisms of HM stabilization in the studied soils.

Isotherms of mesotrione adsorption by HM-free soils were linear and were well described by the Freundlich equation. As a rule, adsorption parameters abtained for clay fractions are larger. Mesotrione is relatively weakly adsorbed by all soils and 40-76% was released after the first desorption step. Mesotriobne retention by clay fractions is larger (35-59% release). A statistical treatment of the data obtained shows that adsorption parameters are positively correlated with contents of free Fe-oxides and OC in alkyls and are negatively correlated with pH and total OC content. Consequently, competition for the adsorption sites between mesotrione and HM is not expected. Conversely, investigation of mesotrione adsorption on HM-polluted soils showed that the presence of adsorbed HMs increased the affinity of mesotrione towards soils. When Zn^{2+} and Pb^{2+} were present, the linear character of the adsorption isotherms persisted. Whereas the presence of Cu^{2+} considerably modified and increased the adsorption depending on soil, first of all with acid pH (Red Soil and Luvisol). In these cases, mesotrione adsorption became almost irreversible (<4% of mesotrione desorbed). The formation of Cu^{2+} - mesotrione complexes could explain the observed phenomenon [1]. Thus, the presence of HMs in soils will reduce most probably the bioavailability of mesotrione and influence the kinetics and possibly the pathways of its biodegradation.

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SEDIMENTOLOGY AND PALEOGEOGRAPHY OF RED FORMATION OF DOGGER DEPOSITS IN OUANINA BASIN, HIGHT ATLAS, MOROCCO

Ahmed Algouti*, Fatiha Hadach, Abdellah Algouti

Cadi Ayyad University, Faculty of Sciences Semlalia, Laboratory Geosciences, Geotourism, Natural Hazards and Remote Sensing"2GRNT", Geology Department. BP 2390, 40000, Marrakech, Morocco
*ahmedalgouti@gmail.com

The diffractometric analyzes performed on the Dogger clay samples of the Wanina basin, in the basins of Aït Ourir of the High Atlas of Marrakech gave the following results:

The illite: it is present in all the cross-section, often in very large quantity. Its abundance suggests an active erosion of the internal zone. It would probably come from the deterioration surface of pre-existing fibrous minerals. His association with kaolinite in most Dogger seems to indicate a fluvial contribution of the piedmont area.

The chlorite: it's in low quantity (5-25%), but it is constant. This could suggest an erosion of areas emerged to accentuated relief. It would come as well of the ante-Jurassic series rich in chlorite. But the multiple factors that influence its crystalline Network, a partial genesis by transformation of the smectite.

The kaolinite: is a mineral of meteoric alteration in the regions with alternation of two seasons, warm and humid. It is a mineral characteristic of the superficial alterations in a leached acid environment. It is the existence of such environment in the warm and humid climate area which justifies the abundance of kaolinite in their pedological profiles. The phenomena of diagenetic neo-formation of kaolinite are caused by the circulation of the diluted solutions. The simple diagnostic of kaolinite to X-rays without the review at the scanning electron microscope for example, doesn't allow a precise determination of its own nature. However, the percentage of the kaolinite is relatively low and it is associated with the levels of siltstone and clay. Consequently the origin of this kaolinite is probably detrital and translates sloping reliefs under warm climates and relatively hydrolyzing.

The smectite: it can be inherited or neo- formed from other minerals or ions in solution, but with the usual method of treatment, it wasn't possible to establish the heritage and neo-formation. However, according to, the majority of these minerals can be currently formed in vertisols, under warm climates with strong seasonal contrasts of moisture.

In conclusion, the clay procession presents an almost identical mineralogical composition dominated by illite. This abundance of illite and the constant presence of chlorite testify to the importance of the mechanical erosion undergone by the source rocks composing the ante-jurassic series. These detrital minerals result from the ancient massif and the triassic siliciclastic series of the High Atlas. The smectite at the base attests to an attenuation of erosion due to the Aplains reliefs, stable and favorable to the confinement.

Keywords: Sedimentology, paleogeography, Red formation, Ouanina basin, Hight Atlas, Morocco.

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NATURAL FIBRE-REINFORCED GEOPOLYMER CEMENT FOR PASSIVE COOLING SYSTEMS

Mazen Alshaaer (1,2)*, María Martín Morales (3), Montserrat Zamorano Toro (3), Fernando Rocha (2)

(1) Plasma Technology and Material Science Unit (PTMSU), Physics Department, College of Science and Humanitarian Studies, Prince Sattam bin Abdulaziz University, Alkharj 11942, P.O 83, Saudi Arabia, (2) Geobiosciences, Geotechnologies and Geoengineering Research Center, Aveiro University, Campus de Santiago, 3810-193 Aveiro, Portugal, (3) Department of Civil Engineering, Granada University, 18071 Granada, Spain

This study reports on the synthesis and characterization of new functional geopolymer composites that are reinforced with crushed natural Luffa Cylindical Fibres (C-LCF). The precursor of the geopolymer matrix was derived from kaolin. The natural fibres volume percentage is 10% of the overall composite volume. It is found that by using these natural Fibres as reinforcement, the compressive of the end geopolymeric products increases from 13 MP up to 31 MPa. The geopolymer composite exhibits ductile-like failure, unlike the brittle matrix. In addition, the bulk density decreases from 1.5 g/cm^3 to 1.34 g/cm^3. In terms of microstructure, a greater amount of geopolymer gel is formed after introducing the LFC into the geopolymer matrix. This could be a result of transporting and distributing the alkaline solution with controlled release throughout the geopolymer mixture during the setting reactions, and geopolymer hardening by the micro vascular system of the LCF. This study reported that the surface humidity at ambient conditions increases from 30% up to 53% by introducing the natural fibres as reinforcement. This is an indication that the new product is more effective for evaporative cooling systems.

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PRELIMINARY ASSESSMENT OF KAOLINITIC CLAY DEPOSITS AS A SOURCE OF SUPPLEMENTARY CEMENTITIOUS MATERIALS

Adrián Alujas (1)*, Roger S. Almenares (2), Elizabeth cabrera (3), José F. Martirena (4)

(1) Centro de Estudios de Química Aplicada, Universidad Central de Las Villas, 54830, Santa Clara, Cuba, (2) Instituto Superior Minero - Metalúrgico de Moa, 83330, Moa, Cuba, (3) Departamento de Ciencias Químicas, Universidad Central de Las Villas, 54830, Santa Clara, Cuba, (4) Centro de Investigación y Desarrollo de Estructuras y Materiales, Universidad Central de Las Villas, 54830, Santa Clara, Cuba
*adrianad@uclv.edu.cu

Selection criteria for the identification of kaolinitic clay deposits of high industrial value has been traditionally dominated by the requirements of the ceramic or the paper industry [1]. However, the growing interest in calcined clays as Supplementary Cementitious Materials (SCMs), from sources other than relatively pure industrial grade clay deposits [2], demands the development of new tools for the identification and evaluation of the potentialities of a given clay deposit as a source of raw materials for the production of SCMs. In this paper, a methodology for the preliminary assessment of clay deposits as a source of SCMs is presented and discussed. As a case study, the chemical and mineralogical composition of several non industrial grade kaolinitic clay deposits, identified and classified according to the proposed methodology, is related to the pozzolanic reactivity of their calcination products, measured through Isothermal Calorimetry by the R^3 testing protocol [3], compressive strength in standardized mortars, and alkaline solubility of its main constituents. The developed methodology, derived from both theoretical and experimental considerations about main clay minerals and its most common companion minerals, allows to establish preliminary selection criteria based on the chemical composition of the raw material ($\%Al_2O_3>18{,}0$; $Al_2O_3/SiO_2>0{,}3$; $PPI>7{,}0$; $\%CaO<3{,}0$; $\%SO_3<2{,}0$). Comparison of the potentialities between the different clay deposits is determined from its relative position in a plot that relates the content of Al_2O_3 and the weight loss within the range of temperatures that corresponds to the thermal decomposition of clay minerals, which are, in turn, the main parameters affecting the pozzolanic reactivity of calcination products. The presence of thermally active non clay minerals in the sample may also affects negatively the pozzolanic reactivity. Through the observed results, the developed methodology proves to be a practical and useful tool for the identification and evaluation of kaolinitic clay deposits as a source of pozzolans. Its application in current geological survey has allowed doubling the volume of hypothetical resources of kaolinitic clays with good potentialities as SCMs in Cuba.

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PALEOGEOGRAPHIC CONTROL OF THE NEOGENE GUERCIF BASIN (NE MOROCCO)

Jemaa Amakrane (1,2), Kamal El Hammouti (1), Ali Azdimousa (1), Meriam El Ouahabi (2)*, Nathalie Fagel (2)

(1) University Mohammed Premier, Faculty of Sciences, Department of Geology, Applied Geosciences Laboratory (LGA), BP N° 717, 60000, Oujda, Morocco, (2) University of Liège, Department of Geology, Argiles, Géochimie et Environments Sédimentaires (AGEs), B.18, Sart-Tilman, 4000, Liège, Belgium
jemaa.amakrane@student.ulg.ac.be

Clay mineralogical and geochemical study of marine sedimentary deposits from the Guercif Basin (NE Morocco) allows for the reconstruction of paleogeographic evolution over the Neogene. Sedimentary samples were taken from a 900m long geological cross-section located at the Southwestern part of the basin and dated from Tortonian to Messinian. Three lithological units are deciphered from the bottom to the top: biocalcarenite, marl-clay alternations and gypsiferous marls. The sediment was analyzed for mineralogy by XRD on bulk powder and clay <2 µm fraction and for geochemical by XRF.

In absence of any diagenetic evidence, the evolution of the clay mineralogical assemblage mainly depends on paleogeographic conditions. Three intervals, covering upper Tortonian to Messinian, were identified. Warm and wet interval I is attested by the occurrence of illite and chlorite with a low amount of kaolinite. Interval II was still warm but with seasonal contrast characterized by the occurrence of smectite. Interval III was arid as showed by the appearance of palygorskite associated with smectite. Interval IV from the Messinian was hot and arid with contrasted season as attested by a relative increase in smectite, palygorskite and illite/smectite mixed layers in comparison with illite and chlorite. The Tortonian biocalcarenitic sediment contains a higher CaO content (60%) than the Messinian gypsiferous marls (19%). In addition the high SiO_2/Al_2O_3 ratio (average of 4.72) indicate a high detrital input and therefore confirms the arid environmental conditions over the Messinian.

These results attest for a climate control on the paleogeographic evolution of the Guercif basin.

Keywords: Tortonian-Messinian, Northeastern Morocco, Clay minerals, Paleogeography, Climate.

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LAPONITE AN ANISOTROPIC PATCHY PARTICLE

Roberta Angelini*, Barbara Ruzicka, Emanuela Zaccarelli

Institute of Complex Systems - CNR and Dipartimento di Fisica, Sapienza Università di Roma, I-00185, Italy

Recent progresses in the study and design of soft materials have led to the synthesis of new colloidal particles that self-assemble into useful structures and represent the basis of tomorrow's materials [1]. In this context, colloidal clays, characterized by anisotropic shape and complex interactions, give rise to phase diagrams rich of unconventional phases encompassing fluid, gel and glassy states. The investigation of these systems has therefore gained, in recent years, an important role in Material Science.

In this presentation, I will report on the aging behaviour of aqueous suspensions of Laponite®, an industrial synthetic clay made of nanometre-sized discotic platelets with inhomogeneous charge distribution and directional interactions. The anisotropy of the face-rim charge interactions, combined with the discotic shape, makes Laponite a prototype of patchy particle with a very complex phase diagram. Here the microscopic structure and dynamics of Laponite suspensions have been investigated through the combination of several techniques as Dynamic Light Scattering (DLS), dilution experiments, X-Ray Photon Correlation Spectroscopy (XPCS), Small Angle X-ray Scattering (SAXS), rheometry and Monte Carlo (MC) simulations. We found the existence an equilibrium gel and of two different glasses respectively at low and high clay concentrations and of a spontaneous glass-glass transition between a Wigner glass, dominated by long-range screened Coulombic repulsion, and a Disconnected House of Cards (DHOC) glass, stabilized by orientational attractions [2,3]. Furthermore, different dynamical behaviours that occur at the glass transition are observed [4,5].

These findings shows that a careful choice of the density may provide materials that are extremely stable in the long term and may have implications for applications where a fine control of the local order and/or long term stability of materials are required.

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SYNTHESIS OF SS-DNA MODIFIED HEXANIOBATE NANOSHEETS

Anraku Shinya (1)*, Kaneko Yoshiro (2), Hiroyuki Asanuma (3), Miyamoto Nobuyoshi (1)**

(1) Department of Life, Environment and Materials Science, Fukuoka Institute of Technology, 3-30-1, Wajirohigashi, Higashiku, Fukuoka, JAPAN, (2) Graduate School of Science and Engineering, Kagoshima University, 1-21-40, Korimoto, Kagoshima, JAPAN, (3) Graduate School of Engineering, Nagoya University, Furocho, Chikusaku, Nagoya, JAPAN
*presenting author; **corresponding author: miyamoto@fit.ac.jp

Novel nanostructures can be fabricated by using DNA nanotechnology, which utilizes programmable base sequence of DNA. For example, Rothemund reported DNA origami technique with which we can form desired nanostrucutre with the resolution of several nm [1]. However, fabrication of molecular devices in large scale by using only synthetic DNA is not practical due to high cost. The materials made only of DNA is also problematic due to mechanical weakness.

Therefore, combination of DNA with other material is important for practical applications. Colloidal particles modified with single-strand DNA (ssDNA) were synthesized and self-assembled to construct regulated structure in macroscopic scale. Furthermore, the structures and lattice constant of the colloidal crystals are modifiable by detection ion or specific base sequence of linker-DNA [2]. However, in these studies, only spherical particles were used as the colloidal particles. Utilization of non-spherical particles such as nanosheets, which forms liquid crystal phase, are expected to further extend the DNA-based technology to wider range.

Nanosheets having an anisotropic shape with a thickness of 1 nm and a maximum width of several hundred µm are obtained by exfoliation of inorganic layered material such as graphite, layered clay mineral and layered silicate, in a solution. Functionalization and organization of nanosheets with DNA was reported in view of applications as a biosensor, [3,4] stimuli-responsive gelator, [5] and nanocontainer [6]. For example, aggregation of nanosheets triggered by detection of a specific ssDNA was reported [4]. However, in all the reported studies, DNAs are physically adsorbed on the nanosheet surface so that the stability of the composite is not enough and control of the degree of fuctionalization is difficult. Also, although nanosheet colloid has been highlighted that they form intriguing liquid crystal phases with birefringence and structural colors, control of the optical properties by DNA have not been reported.

In this study, we investigated modification of the hexaniobate nanosheet surface with ssDNAs through a covalent bond, aiming at fabrication of nanomaterials that respond to the molecular information of DNA. Amino-functionalized nanosheets were obtained by the reaction of the hexaniobate nanosheets with 3-aminopropyldiethoxymethylsilane. Then, carboxyl-functionalized nanosheets were synthesized by the reaction of amino-functionalized nanosheets with succinic anhydride. Finally, we obtained ssDNA functionalized nanosheets by the reaction of the carboxyl-functionalized nanosheets with ssDNA which have an amino group and fluorescence moiety (FITC) on the 5'- and 3'-ends, respectively.

The formation of modified nanosheets were confirmed by FT-IR. We then observed ssDNA functionalized nanosheets dispersed in water by confocal laser scanning microscopy (CLSM). In the scattering image, the nanosheets and their aggregates with the size of several tens of µm were observed. Similar image is also observed in the fluorescence mode, indicating that the FITC-terminated ssDNA is immobilized on the nanosheets. In contrast, in the cases of the nanosheets without modification or the simple mixture of the ssDNA and nanosheets, the nanosheets are not observable in the fluorescence image. Thus, it is considered that the ssDNA is immobilized on the nanosheet through covalent bond, which is favorable for further application studies.

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TRANSFORMING CLAYS FOR A MATERIAL'S FUTURE

Deeba Ansari*, Anabelle Legrix

Imerys Innovation, St.Austell, PL24 2SQ, UK
*deeba.ansari@imerys.com, anabelle.legrix@imerys.com

In an era of ever greater challenges for many materials, including minerals, how can humble clays still find new uses and opportunities? That is a question that all innovation managers face in the industrial minerals sector and this paper seeks to explore some of the approaches that can be used. On the one hand anyone who has designed and defined new products knows that one must seek to exploit what nature has provided, and forgets this at their peril. On the other hand we can manipulate these materials to change size, shape, colour, purity, chemistry and thus functionality by many established and some novel processes.

The starting point for defining a clay of choice must be to understand what problem or need is being addressed. If this is not specific enough then the new product will have to go through many iterations before it may either ultimately succeed or fail. Thus the innovator must speak the language of their counterpart, or industry with whom they are seeking a novel solution. In specifying an extender for an interior coating, for example, it needs to provide the right balance of opacity, rheology, colour and mechanical properties. An understanding of the material's use, the demand of the particular industry and its length of use are all essential at the start of the process. From these points the mineral developers must transform the requirements into their own specifications more familiar to them. This should be considered firstly as a functionality, such as refractive index, light scattering capability, surface coverage and so on and then translated back to the material's fundamental characteristics such as particle size, shape and structure of which we are more familiar.

Several case studies are included in this paper that serve to illustrate the development of clays for a diverse range of industrial uses including the agricultural, cosmetic, inks, polymers and coatings sectors. When incorporated into lithographic inks hydrous clays can assist with the stability of the ink-fount solution emulsion. Their addition in facial cosmetics can give matting, surface coverage and blending effects. Calcined clays are added to a range of polymeric and elastomeric systems for impact and dimensional modification. And clays, as well as other industrial minerals, give structure and opacity to many types of architectural and industrial coatings. The manner in which the products are developed is discussed and the outcomes relative to the various approaches is considered in further detail.

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IN SITU HIGH TEMPERATURE X-RAY DIFFRACTION AND ELECTRON MICROSCOPY STUDY OF BAUXITIC CLAYS

Patricia Aparicio (1), Domingo Martin (1), Emilio Galán (1), Adolfo Miras (1), Isabel Guerrero (1), Blanca Bauluz (2), Alfonso Yuste (2), Maria Jose Mayayo (2)

(1) Departamento de Cristalografía, Mineralogía y Química Agrícola, Universidad de Sevilla (Spain), (2) IUCA-Facultad de Ciencias, Universidad de Zaragoza, Zaragoza (Spain)

One of the most important traditional refractory materials are made of aluminum- rich raw clays and bauxites. Depending of the alumina and silica contents, the most important high-temperature phases formed after firing are corundum, mullite and siliceous glass, being mullite the main component formed from bauxitic clays. In this case, the structure of the material consists of needle-like mullite crystals in a siliceous and vitreous matrix with some impurities, being the mullite the responsible of the refractory properties. The aim of this study is to analyze the mineral evolution during the firing of two Al-rich materials, considered as bauxitic clays.

Two samples were selected for the study come from Lower Cretaceous karst bauxite deposits that outcrop to the SE of the Iberian Range (Maestrazgo zone) [1] [2] [3]. Bauxites constitute bodies filling karst cavities developed in Jurassic limestones. The mineralogical composition of the bauxitic materials and their behaviour after heating were followed using a diffractometer with reaction camera from ambient temperature to 1400 ºC, also a set of 5 mm-diameter cylinders were made with the milled raw clay by pressing, and then heated from 1000º to 1400 ºC and sudied by field scanning microscopy (FESEM) and transmission electron microscopy (TEM).

The XRD study of the lower alumnium content sample (48% SiO_2, 43% Al_2O_3) was composed of kaolinite (90%) and minor proportions of hematite, anatase, rutile and chlorite. With firing, the kaolinite contents decrease and its (001) reflection was broader probably because of the dehydroxylation process. Kaolinite disappeared at around 600 ºC. The anatase content also decreased with temperature and disappeared at 1050 ºC. Hematite is present at all temperatures and its content increases from 1250 ºC. At 650 ºC a ϒ spinel structure is detected and lasts up to 1150 ºC. The ϒ spinel formation coincides with the kaolinite disappearance. Finally, mullite and cristobalite growth from 1050ºC and the increase of the XRD patterns background with temperature suggests the formation of a vitreous component.

The XRD study of the higher alumnium content sample (51% SiO2, 45% Al2O3) was composed mainly of kaolinite with traces of anatase and rutile. With firing at 600 ºC, kaolinite disappeared and the only crystalline phases present were anatase and rutile, that were decreasing with temperature and disappeared at 1250 ºC and 1350 ºC respectively. Mullite and cristobalite appear at 1250ºC as the only newformed phases. The increase of the XRD patterns background with temperature also suggests the formation of vitreous component.

Electron microscopy images show that the fired samples are formed by rock fragments and matrix, probably as a consequence of the manufacture process of the cylinders. From 1100º to 1450 ºC, the fragments show reation edges and, in general, evidences of vitrification. Both fragments and matrix have Al- and Si- rich composition and they consist of needle- like mullite crystals embedded in a Si-rich matrix. The length of the mullite crystals, randomly oriented, increases with temperature, from less than 100 nm at 1100º to more than 1100 nm at 1400 ºC. The chemical analyses of the mullite show that it is non-stoichiometric. In comparison with theoretical mullite, with an Al/Si ratio of 2.9, our analyses show less aluminium than expected and also appear minor proportions of Fe and Ti (Fe>Ti) which are probably replace Al in the mullite structure. The (Al+Fe+Ti)/Si ratio increases with temperature from 1.05 at 1100 ºC to 1.33 at 1400 ºC. The content of Fe+Ti increases with temperature from 0.3% at 1100 ºC to 2% at 1400 ºC.

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SYNTHESIS OF ISOMORPHIC STRUCTURE IMOGOLITE TYPE BASED ON PARTIAL REPLACEMENT OF SILICATE FOR ARSENITE

Nicolás Arancibia-Miranda (1,2)*, Mauricio Escudey (1,2), Karen Manquían-Cerda (1)

(1) Facultad de Química y Biología, Universidad de Santiago de Chile, Av. B. O'Higgins, 3363, Santiago, Chile, (2) Center for the Development of Nanoscience and Nanotechnology, CEDENNA, 9170022 Santiago, Chile

The obtaining of isomorphic imogolite structures through total or partial substitution of Si by Ge (Al-Ge imogolite) and Al by Fe ((Al+Fe)-Si imogolite) has been successfully synthesized [1,2], however, recent theoretical work done by Guimarães et al., suggests that based on structural and geometric similarities is possible to obtain similar imogolite structures of type $\mathbf{(OH)_3Al_2O_3XOH}$, (where X = As (III), As (V), P (III), P (V)) [1]. The synthesis of these new materials should consider aspects such as pK_a and solubility of the starting reagents, since these properties could have significant effects on the kinetics of growth and yield of the synthesis. This paper proposes the preparation of an isomorphic structure of imogolite, called Imo-As-ite, based on the partial replacement of $Si(OH)_4$ (equivalent to 10% w/w) by H_3AsO_3. The material obtained was characterized by FT-IR, IEP and TEM.

The analysis of the FT-IR showed differences among the studied materials, highlighting, two characteristic signals of the -OH, in the imogolite, the 3500 and 3224 cm^{-1} were observed, corresponding to the hydroxyl belonging to ≡Al-OH and ≡Si-OH groups, respectively. For Imo-As-ite the hydroxyl signal corresponding to the Al-OH (3474 cm^{-1}) groups was observed, whereas bands associated with internal hydroxyls were not detected, because the formation of the tubular structure of Imo-As-ite involves all the As-O bonds of arsenite. The FT-IR spectrum of Imo-As-ite, two bands were observed at 1050 and 981 cm^{-1}, which may possibly be attributed to the development of a tubular structure (stretching vibration As-O), which is displaced and attenuated, if compared with what was reported for imogolite, for the stretching vibration of Si-O (990 and 939 cm^{-1}). Other bands were identified at 1646, 1384, 545, 388 and 372 cm^{-1}, which refer to different variations of Al-OH [3].

The value of the IEP for Imo-As-ite was lower than the imogolite, reaching values of 8.09 ± 0.02 and 9.50 ± 0.02, respectively. This displacement can be explained because As is more electronegative than Si (2.1 for As and 1.8 for Si), generating the H^+ of aluminols groups that form the outer surface of Imo-As-ite, more acid.

The morphology of the samples of Imo-As-ite and Imogolite were evaluated using transmission electron microscopy (TEM). The TEM images showed differences in the dimensions of both materials. The average external diameter determined for Imo-As-ite was 2.80 ± 0.4 nm, whereas for imogolite reached the 2.1 ± 0.2 nm, these values were determined based on measurement of various samples at different scales (n = 25). A decrease in length was observed for Imog-As-ite in comparison to Imogolite, suggesting that substitutions involving an increase in diameter affects the one-dimensional nanotube growth, similar results have been reported for aluminogermanates [3]. Imo-As-ite synthesis were observed in two types of by-products, spherical morphology and type needles, which would indicate that the process of obtaining of Imo-As-ite is not entirely clean.

This work successfully demonstrated the synthesis of imogolites with structural arsenite, with a theoretical percentage of 10%, with different morphological and superficial characteristics. The present results demonstrate the potential of inexpensive synthesis protocol for obtaining nanotubular structures with a variety of compositions adapted for specific applications.

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EFFECTS OF K_2CO_3 ADDITIONS ON PHYSICAL PROPERTIES OF CERAMIC BODIES DERIVED FROM BALLCLAY-ALUMINA MIXTURES ACTIVATED BY HIGH ENERGY BALLMILLING

Aydin Aras

YuzuncuYıl University, Geological Engineering Department, Van, Turkey
aras5549@yahoo.com

In the previous works high temperature phase changes were investigated in ceramic bodies derived from Westerwald ball clay HB and their mixture with illitic clay or feldspar[1] and alkali and alkali-earth flux [2]. In this present work, the effects of 5 wt% K_2CO_3 addition and grinding with planetary ball mill (Turbula) on physical properties of ceramic bodies derived from same Westerwald ball clay (HB) containing of three different concentrations (20,40, 60 wt%) alumina were investigated by measuring modulus of elasticity (E) and densities and calculating porosities from these densities. It was found that wet-mixed HB- 60 wt% alumina with K_2CO_3 and HB-60 wt% alumina without K_2CO_3 had maximum and minimum E modulus respectively. But, the reverse behaviors were observed in the HB - 20 wt% alumina bodies with K2CO3 and without K2CO3. Grinding 2 h, 4 h and 8 h decreased the E modulus in all studied bodies. Grinding 2 h of mixture of 20 wt% alumina bodies with or without K_2CO_3 resulted well developed secondary mullite formations, but further grinding decreased mullite formation in all bodies, but completely inhibited mullite formation in the bodies with K_2CO_3. Furthermore, the glassy phase of the alumina rich body with K_2CO_3 and milled 8h was more efficient due to lack of mullite nucleation-crystallization which can lead to less viscous liquid and high wettability, than those of v the bodies without K_2CO_3andcaused well sintered body which had highest E modulus of all the studied bodies. The measured E modulus of ceramic bodies derived from above compositions shows that the changes of E modulus dependent on microstructure, i.e. the type and amount of glassy and crystalline phases which is determined by their optimal distribution of these flux or flux cations are largely controlled by the extent of the mixing, i.e. different milling times. In this present work, the changesand evolution of the measured physical properties of ceramic bodies derived from HB-alumina-K_2CO_3mixtures was discussed on the basis of the result of previous works on phase change of Westerwald ball clay and review of several theories on elastic properties of brittle solids [1,2,3,4,5,6].

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SOLID LIPID NANOPARTICLES IN ASSOCIATION WITH LAPONITE: A TOOL FOR DRUG DELIVERY

Marianna Araújo Ferreira, Aliana Monteiro Leite, Fernanda Nervo Raffin, Túlio Flávio Accioly de Lima e Moura*, Raquel de Melo Barbosa*

Department of Pharmacy, Federal University of Rio Grande do Norte, 59010-180 Natal, RN, Brazil

Nanotechnology applied to medicines is a growing area due to technological advances over the last decades. Solid lipid nanoparticles (SLN) are lipid carriers, composed of one or more solid lipids dispersed in the presence of a colloidal stabilizer [1]. These systems can be used as drug delivery systems and can promote improvements in the effectiveness of the drug, by the drug protection and the modification of the pharmacokinetics profile, while decreasing the drug's adverse side effects [2]. As lipid systems, clays have also gained attention for their ability to carry drugs. Laponite (LAP), a synthetic hectorite clay, of the empirical formula $Na^{+}_{0.7}[(Si_8Mg_{5.5}Li_{0.3})\ O_{20}(OH)_4]^{-0.7}$, is formed by lamellae, composed of tetra and octahedral plates, which favour the packaging of several compounds [3,4].

The objective of this study was to evaluate the influence of Laponite on two distinct SLN models, which differ in their lipid compositions. The production of SLN was by the fusion-emulsification´s method, where the structural lipids cetyl palmitate (CP) or myristyl myristate (MM), with the colloidal stabilizer Poloxamer 188 were used. Hybrids systems were obtained by mixing SLN´s colloidal dispersion with 3% (w/w) of LAP, homogenized for 24 hours and stored at 25 ºC.

The nanoparticles (SLN_{CP} and SLN_{MM}) and the hybrids systems ($SLN_{CP}LAP$ and $SLN_{MM}LAP$) were evaluated by hydrodynamic diameters, zeta potential (ZP), and polydispersity index (PDI). Thermal behavior was obtained by thermogravimetric (TG) analysis and differential scanning calorimetry (DSC) to evaluate the thermal stability and crystallinity of the samples respectively. X-ray diffraction (XRD) analysis, was also useful to reveal polymorphic structural changes of compounds that were used in the study of SLN dispersions and hybrids samples [2].

The hydrodynamic diameters of the SLNs produced using CP and MM lipids were 145.9±2.6 and 110.5±1.2 nm, respectively, the polydispersity of the nanoparticles was equal to or less than 0.2. Zeta potential values provide valuable information about the stability of a colloidal system, and can be influenced by factors including electrical conductivity, pH, and the nature of the reagents. The increase in the ZP value (in module) of the hybrids systems ($SLN_{MM}LAP$, -24.4±0.7, $SLN_{CP}LAP$, -27.8±0.9) was observed in relation to the nanoparticles (SLN_{MM}, -13.4±2.1, SLN_{CP}, -5.7±2.0) without LAP. The TG results provided information about the physical stability of the lipid nanoparticles and hybrids systems that were observed, only around 200ºC degradation of all samples. The calorimetric analysis by DSC showed a reduction of crystalline state in samples containing LAP. XRD measurements were carried out for SLN_{MM}, SLN_{CP}, $SLN_{MM}LAP$, $SLN_{CP}LAP$, raw lipids and Poloxamer 188. The diffractograms of pure lipids, Poloxamer 188 and nanoparticles without LAP (SLN_{MM} and SLN_{CP}) confirmed their high crystallinity. The diffractogram profile with hybrid systems showed a noticeable structural change with amorphous forms in both formulations ($SLN_{MM}LAP$ and $SLN_{CP}LAP$), these results agree with those obtained by DSC. Low crystallinity of the solid lipid core of the SLN and hybrid systems is desirable because it is associated with a reduced rate of loss of the active agent from the carrier system, which increases the shelf life of the product [2].

These experimental works showed that it was possible to obtain the SLNs by the fusion-emulsification method. LAP favoured the formation of a carrier system by reducing the crystallinity of nanocarriers, which can contribute to the storage of drugs. In addition, a physically stable system was shown to be a promising system for drug delivery.

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NANOHYBRID SILICATE-BASED MATERIALS AS ADSORBENTS FOR WATER REMEDIATION

Jeovan A. Araujo, Ana C. S. Alcântara*

Centro de Ciências Exatas e Tecnologia, LIM- Bionanos, Universidade Federal do Maranhão, Av. dos Portugueses, 1966, 65080-805, São Luís, MA, Brazil
*ana.alcantara@ufma.br

The assembly of organic-inorganic nanohybrid materials has been widely investigated in clay science and nanotechnology related applications. Resulting from the combination in which the organic and inorganic parts interact at a molecular level, such nanostructured hybridsprovide unique physico-chemical and mechanical properties and new functionalities [1,2]. When the organic constituent originates from a natural source, such as a biopolymer, these materials are frequently described as biohybrids. Generally, hybrid and biohybrid materials present new properties that make them suitable for a range of applications, for instance, the adsorption of pollutants in water treatment or remediation, including heavy metals [3] and organic compounds [4,5]. In that regard, hybrid and biohybrid materials can be prepared by combining monomers or polymers, which act as organic component, with lamellar and fibrous silicates as inorganic counterpart to explore intercalation and grafting reactions, respectively [6]. Indeed, layered silicates (e.g. montmorillonite) have received a great deal of attention due to their intercalation properties, whereas fibrous clay minerals (e.g. palygorskite) exhibit other attractive features, namely their microporosity, high specific surface area and density silanolgroups, giving rise to their use in grafting synthetic approaches [1,2]. Under these circumstances, this work introduces the preparation and characterization of nanohybrids materials based on two natural silicates: montmorillonite and palygorskite. Such clay minerals were organically modified with a surfactant (i.e. 3-aminopropyltriethoxysilane, APTES) and a biopolymer (i.e. gelatin) to prepare hybrid and biohybrid materials, respectively. The functionalization of both layered and fibrous clay minerals was studied by varying the amount of gelatine in biohybrids, and by using three different types of synthetic procedures for preparing hybrids through silylation reactions involving APTES. The nanohybrids were characterized by several physico-chemical techniques. Accordingly, it was observed that modifications on montmorillonite based materials showed an intercalated structure which are mainly driven by ion exchange mechanisms, regardless of the organic modifier. On the other hand, nanohybrids based on palygorskite are functionalized through mechanisms that are induced by interaction forces between residual gelatinchains or APTES silane groups with silanol groups located on the mineral surface. In either case, we synthesized APTES-based nanohybrids in solvents exhibiting unlike relative polarity (toluene, water/ethanol and water/acetone), which would affect the hydrophilic/hydrophobic character of the resulting nanohybrids. Both hybrid and biohybrid materials were applied as adsorbents for the removal of organic contaminants from aqueous solution. For this purpose, we selected a hydrophilic and a hydrophobic compound as model molecules (i.e. caffeine and curcumin, respectively). Biohybrids based on montmorillonite and gelatine resulted in good adsorption capacities for caffeine, while hybrids based on APTES and montmorillonite orpalygorskite displayed different adsorption profiles, depending upon the pH at the equilibrium and the solvent employed in the synthesis. This implies that the solvent plays a crucial role in silylation reactions on silicate surfaces. Hence, these materials showed selectivity for the removal of organic pollutants with different polarity, in this case, caffeine and curcumin. In brief, silicate-based nanohybrids showing enhanced physical and functional properties can be designed to interact with specific organic molecules, which makes this class of versatile materials very promising in different field of applications, such as water remediation.

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EFFECTS OF THERMAL AND ACID ACTIVATION ON SPECTROSCOPIC PROPERTIES OF ATTAPULGITE FROM BRAZIL

Lyghia Maria Araújo Meirelles*, Túlio Flávio Accioly de Lima e Moura, Fernanda Nervo Raffin

Post- Program on Development and Technological Innovation in Medications, Federal University of Grande do Norte, Natal, Brazil

Attapulgite is a hydrated magnesium aluminum silicate with a fibrous structure, formed by tetrahedral and octahedral sheets in a ratio of 2:1. Periodic inversion of the tetrahedral sheet of the clay results in the formation of channels along the fiber whose restricted dimensions allow the adsorption of small molecules [1,2]. A way to optimize the reactivity and adsorptivity of this and other clays consists of activation in an acid medium and by heating or the addition of organic modifiers. Thus, this study aimed to evaluate the effect of treatment acid, heat and the combination of both on attapulgite characteristics obtained in Guadalupe-PI (Brazil). Samples were previously washed and sieved in a 200 mesh, and then treated. Structural characterization was performed by Fourier transform infrared spectroscopy, crystallinity was determined by X-ray powder diffractogram and its chemical composition was defined by X-ray fluorescence. Acid activation was performed by dispersing solid 1% (w/v) in 5M H_2SO_4 at 70 °C for one hour, resulting in the solubilization of some contaminants contained in the clay, such as carbonates. This removal was confirmed by the disappearance of the characteristic band of this impurity seen between 1550 and 1300 cm^{-1} [3]. The same result was not observed in the activated sample under heating at 250 °C for 3 hours, since the decomposition of this impurity only occurs at temperatures above 500 °C [4]. Therefore, the elimination of carbonates by thermal activation is impractical, because excessive heating causes the collapse of the three-dimensional structure of the clay due to dehydroxylation. Characteristic diffraction peaks of attapulgite ($2\theta = 8.3°$, 19.8° and 20.8°) were identified in all samples tested. Diffractive profiles of the acid-treated clays corroborate the effect of the concentrated acid solution observed in the infrared spectroscopy, with the disappearance of the peak at $2\theta = 31°$ for carbonates such as calcite [5]. Heating attemperatures above 300 °C can cause amorphization of the material due to the removal of structural water, with reduction of peak intensity, however the results showed that there were no pronounced changes in the crystallinity of the thermally activated samples, since the temperature adopted corresponds mainly to the loss of water adsorbed and zeolitic [6]. Untreated clay is composed mainly of SiO_2 (49.53%), MgO (12.31%) and Al_2O_3 (10.30%), which has its composition altered at each applied treatment, emphasizing the reduction of MgO and CaO in the samples exposed to sulfuric acid, reduction of organic matter after heating and increased SiO_2 ratio of all activated samples. So, based on the analyses, it can be said that the treatments employed were effective in removing organic and /or inorganic impurities inattapulgiteand simultaneous thermal and acid activation was the most efficient of the conditions adopted to purify and benefit raw attapulgite without causing crystal damage.

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CLAY MINERALOGY OF INLAND EPHEMERAL ALKALINE ENVIRONMENTS (CABALLO ALBA LAKE, SPAIN)

Xabier Arroyo (1)*, Pablo Del Buey (2), Óscar Cabestrero (2), Esther Sanz-Montero (2)

(1) CAI de Técnicas Geológicas, Facultad de CC. Geológicas (UCM), C/ José Antonio Nováis, 12, 28040, Madrid, Spain, (2) Departamento de Petrología y Geoquímica, Facultad de CC. Geológicas (UCM), C/ José Antonio Nováis, 12, 28040, Madrid, Spain
*xarroyo@ucm.es

There are approximately 50,000 playas or playa lakes on Earth. These are intracontinental, small, shallow basins which frequently evaporate to dryness. Most of the European ephemeral and shallow water bodies are found in Spain. These are concentrated in four major closed-drainage areas. One of these closed drainage areas, the Duero Basin, is located in the center of Spain approximately 150 km north of Madrid and consists of highly alkaline(pH values 8-11), brackish to salinelakes (1-9 g L^{-1}) containing a high concentration of chloride with dominant carbonate over sulphates. This complex lies over Miocene sediments being mainly comprised of dark grey sandy clays and silts enriched with organic matter. According to Cabestrero and Sanz-Montero (2016) the sediments of these playa basins consist of up to 50% of detrital grains (clays, feldspars, quartz and carbonates) as well as authigenic minerals (up to 80% from spring to summer) containing carbonates, sulphates and chlorides. Particularly, CaballoAlba Lake has a general type water composition Na^{+}-Cl^{-}-(SO_4^{2-})-(HCO_3^{-}). The Mg^{2+}/Ca^{2+} ratio is 6.1, while Na^{+}/Cl^{-} ranges from 1.64-2.94. Up to 40% of gypsum is present in the shore areas of Caballo Alba, due to the highest Ca^{2+} values among the rest of the lakes of the basin. The smooth surface of the lake hosts a veneer of microbial mats showing a green, occasionally purple layer. Microbes induce changes in the chemical composition and mineralogy. The aim of this work is to analyse the clay mineralogy (XRD, TEM and AEM characterization) in order to understand accurately the genesis of authigenic clay mineral assemblages.

Representative surficial and core samples with nearly 50% of phyllosilicates have been taken to analyse the clay mineralogy of Caballo Alba Lake. The XRD study of <2 μm fractions in oriented mounts reveals that the clay mineral phases are composed of approximately 30% of smectite and 65-70% of dioctahedral detrital micas with subordinate kaolinite. The absence of palygorskite and sepiolite minerals is remarkable. TEM-AEM preliminary results, obtained from powders dispersed on holey C-coated formvar Cu grids; show that smectite particles appear as plates with the typical flaky and wavy morphology poorly developed. The calculated structural formulas (from 45 analyses), normalized to $O_{10}(OH)_2$, show smectitic particles with a trioctahedral character (closer to 3.00 cation p.f.u) with Mg as the dominant cation in the octahedral positions and minor amounts of Al, Fe, Mn and Ti. Thetrahedral substitution of Si for Al ($Si_{3.87}$, $Al_{0.13}$) to ($Si_{3.01}$, $Al_{0.99}$) has been found, indicating a tetrahedral location of layer charge. These data indicates a saponitic nature of the smectites with compositions located in the discontinuity between dioctahedral to trioctahedral smectite system. The interlayer cations are K, Ca, Mg and Na in order of abundance. Na interlayer occupancy tends to increase with the depth of the sample.

The physicochemical conditions, the clay mineral assemblage, the textural features and the presence of saponite with intermediate chemical composition, which points out its metastable character (Yamada et al. 1999); allow us to consider this example as an important analog for understanding brine evolution, smectite formation pathways and biological activity influence in shallow water settings that have existed since the Archean on Earth and perhaps on Mars.

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HYDROTHERMAL SYNTHESIS OF ZEOLITE T FROM KAOLIN USING TWO DIFFERENT STRUCTURE DIRECTING AGENTS

Sazmal E. Arshad (1)*, M. Lutfor Rahman (1), Shaheen M. Sarkar (2), Eddy F. Yusslee (3), Siti Z. Patuwan (1)

(1) Faculty of Science and Natural Resources; (3)Preparatory Centre for Science and TechnologyUniversiti Malaysia Sabah, 88400 Sabah, Malaysia, (2) Faculty of Industrial Sciences and Technology, University Malaysia Pahang 26300 Pahang Malaysia
*sazmal@ums.edu.my

Zeolite T were synthesized from molar chemical composition of $1SiO_2$: 0.04 Al_2O_3: 0.26 Na_2O: 0.09 K_2O: 14 H_2O in form of homogenous milky solution in presence of two different structure directing agents of TMAOH and TEAOH respectively. Modification for composition of silica were using metakaolin from calcined kaolin at 750 °C in 4 h while molar composition of each different SDA were variated from 0.05, 0.10, 0.15, 0.20 and 0.25. The homogenous mixture was left at room temperature for 24 h before undergoing hydrothermal synthesis at 100 °C for 168 hours. Synthesized samples filtered and aged at 120 °C for 2 h and each samples were calcined at high temperatures (545 °C for TMAOH and 520 °C for TEAOH) for templates removal before characterization using XRD and SEM. Crystallization of zeolite T in major form were only at molar ratio of 0.10 of TMAOH while in TEAOH showed species evolution of zeolite T into zeolite L and W for the other molar ratios.

Keywords: zeolite T; offretite; erionite; hydrothermal; kaolin; metakaolin; SDA; TMAOH; TEAOH.

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AGGREGATION OF PRENUCLEATION CLUSTERS OF "HIDDEN PHASE" (QUATARONS) AS MECHANISM FOR FORMING OF AMORPHOUS NANO-MICRO PARTICLES

Askhab Askhabov, Dmitry Kamashev

Institute of Geology of Komi SC UB RAS, Syktyvkar, 167982, Russia
xmin@geo.komisc.ru

By advanced analytical techniques globular internal structure is often found in natural nanomaterials. However, the mechanism of formation the nanoparticles, composing such materials, hitherto remains unclear. This report gives general principle of building nano-micro particles, developed on base of the quataron concept of self-organization of matter at nanolevel [1].

The main idea of the quataron concept is that in supersaturated media specific nanoclusters - clusters of "hidden" phase or quatarons - are formed. Quatarons represent an intermediate phase at nanolevel. They are special pre-nucleation clusters with quite unusual properties. Quatarons are amorphous formations with dynamic structure with oscillating interatomic distances. Atoms and molecules inside quatarons move and rotate, remaining "connected" with each other. Quatarons are high-energy clusters - a part of energy, which could be discharged at their formation remains in quatarons as stored energy. The circumstance that only quatarons, which radius exceeds 4δ, where δ is diameter of cluster-forming atoms (molecules), can be potential centers of crystallization, has fundamental importance for forming amorphous nano-micro particles. Quatarons of smaller sizes are the base (primary) particles for forming structural units of nanostructured natural amorphous materials. The main mechanism for forming self-assembled materials is an aggregation of quatarons sized from δ to 2δ. Quatarons in interval from 2δ to 4δ are capable to form larger secondary clusters by merging.

Different variants of aggregation of quatarons are considered. It is found that forming structural units in opal-like materials (globules) is related with fractal aggregation of primary particles (quatarons). Typical sizes (150-450 nm) of structural units are reached at the third level of fractal aggregation of quatarons, rarer at the second one.

This general rule for formation of particles is confirmed by study the internal structure of the units of natural and synthetic opals, other amorphous materials. It also applies to the case of aggregation of nano-sized particles of clay minerals.

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CLAY-ATMOSPHERE INTERACTION IN A HIGH RISK OF SHRINKAGE AND SWELLING ZONE

Hossein Assadollahi (1,2)*, Hossein Nowamooz (1), Alain Tabatabai (2)

(1) ICUBE, UMR 7357, CNRS, INSA de Strasbourg, 24 boulevard de la Victoire, 67084 Strasbourg, France, (2) Determinant France R&D, 32 Boétie avenue, 75008 Paris, France

Natural clayey soils, and their associated risk of shrinkage and swelling are considered as a natural hazard in France. This natural hazard causes structural damage to lightweight constructions (e.g. residential and industrial buildings and roads) due to differential settlements. Since this has been a big concern for the government and particularly for the insurance companies in terms of indemnity, extensive research has been carried out to predict and prevent this hazard [1]. The interaction of natural clayey soils with the environment and the atmosphere is one of the major tasks to be taken into account. Changes in the climatic parameters along with the presence of clayey soils could increase the risk of damage.

The aim of this paper was to study the interaction of a clayey soil region with the environment in a high risk of shrinkage and swelling zone. To study the problem, energy and water balance were used to determine the clayey soil surface conditions. Climatic data such as air temperature, rainfall, relative humidity and global solar radiation, were used in the balance equations. The energy balance equation was solved along with other equations for the energy balance terms. A new theoretical method was proposed by combining three different methods to calculate the clayey soil surface temperature in time [2,3]. On the other hand, the water balance equation gives the clayey soil surface water flow in time which can be used to determine the flow condition in the soil. The energy balance equation also gives the energy balance terms, G (soil heat flux), Rn (net solar radiation), H (sensible heat) and LeE (Latent heat of evaporation). These atmospheric parameters are essential for the clay-atmosphere interaction analysis. The geotechnical properties of the clayey soil were considered and the retention properties were adjusted by using a suitable soil water retention curve (SWRC). In addition to surface condition, a coupled hydro-thermal analysis [4] was carried out to determine the changes of the clayey soil parameters (such as temperature, suction head, water content) in depth and time. The soil surface temperature and surface water flow were used as initial boundary condition in the analysis. Simulations were compared to the experimental data and the results were coherent. Results also show that the changes and variations in the matrix suction value are at the origin of this kind of hazard. Even though natural clayey soils can perform well as environmental barriers, but they can also be sensitive to climatic variation.

Keywords: Natural Clay, Shrinkage and Swelling hazard, Energy balance, Water balance, Hydro-Thermal analysis.

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CLAY WOR(L)D

Attila Terbócs (1), Tibor Németh (2)*

(1) Hungarian Ethnographical Society, Budapest, Hungary, (2) Eötvös Loránd University, Department of Mineralogy, Budapest, Hungary

World-wide linguistic diversity and affinity of the word ‘clay’ is presented on a map as a playful patch of colour. It is indicated in all European and several other languages spoken in the world, and a flow chart typifying etymological roots and historical evolution of the word is also performed.

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CLAY-MEDIATED COMPATIBILIZATION IN POLYETHYLENE/POLYAMIDE/NANOCLAY BLENDS

Thierry Aubry*, Jacques Huitric, Pascal Médéric, Julien Ville

Université de Bretagne Occidentale, Institut de Recherche Dupuy de Lôme FRE CNRS 3744, 29200 Brest, France
*thierry.aubry@univ-brest.fr

Since the early 1900s, adding fine particles to low viscosity liquid immiscible phases is known to be an efficient route to stabilize droplet morphology [1]. More recently, the same strategy was used to refine and stabilize the nodular morphology of immiscible polymer blends by adding nanoparticles (carbon black, silica, clay) [2].

In the present work, the apparent compatibilizing effect of clay nanoparticles in immiscible polymer blends was studied for polyethylene/polyamide (PE/PA) blends with droplet morphology, filled with organically modified montmorillonite (OMMT) having a selective affinity towards PA. Scanning electron microscopy was used to characterize the blends morphology, clay structure was investigated using wide-angle X-ray diffraction, and transmission electron microscopy observations were used to characterize clay localization and dispersion. Besides, the melt-state and solid-state mechanical properties of PE/PA/OMMT ternary blends were studied: rheological tests were carried out in order to characterize the linear viscoelastic properties of the melts, and tensile tests were performed in order to characterize the solid-state mechanical properties of the blends at small and large deformations.

PE/PA blends compositions exhibiting droplet morphology were first determined, for different OMMT fractions, and different PE/PA polymer couples. In the case of a low viscosity PA minor phase and a high viscosity PE matrix, clay nanoparticles were shown to be exclusively located at PE/PA interface, forming a more or less developed PA-intercalated OMMT nanocomposite interphase [3,4].

The structural characterization revealed the presence of numerous and various defects in the PA-intercalated OMMT nanostructured interphase, and the linear rheological characterization of the blends highlighted the soft character of this interphase, whose viscoelastic properties were shown to be governed by a long relaxation time increasing with clay fraction [5].

At low clay fractions, for which a small clay interfacial coverage was observed, the decrease of the interfacial tension with increasing OMMT content was inferred from fitting the linear viscoelastic properties of PE/PA/OMMT blends with the simplified Palierne's model [6]. At higher clay fractions, for which a fully developed interphase was observed, the full Palierne's model [7] was used to investigate the complex viscoelastic properties of the PA-intercalated OMMT nanostructured interphase [8].

Finally, addition of OMMT to PE/PA blends was shown to strongly influence both linear and non-linear solid-state tensile mechanical properties of PE/PA/OMMT ternary blends. Quite interestingly, the tensile properties at break were shown to be improved by clay addition, possibly due to the ability of the PA12-intercalated OMMT interphase to dissipate energy through different deformation-induced interphase restructuration mechanisms.

All results highlight the prominent role played by the soft PA-intercalated OMMT nanocomposite interphase in the morphology refinement and stabilization, as well as in the solid-state mechanical properties of PE/PA/OMMT blends.

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EVALUATION OF THE POTENTIAL OF CALCINED KAOLINITIC CLAYS USED AS CLINKER SUBSTITUTE IN LIMESTONE CALCINED CLAY CEMENT (LC3)

François Avet, Karen Scrivener*

Laboratory of Construction Materials, EPFL, Lausanne, Switzerland

Limestone calcined clay cements (LC^3) are a promising approach to reduce the clinker content of cement. In LC^3-50 systems, the clinker content is reduced to 50%, with 30% of calcined clay, 15% of limestone and 5% of gypsum. Among the different classes of clays, kaolinitic clays show the highest pozzolanic potential after thermal activation[1]. The higher reactivity of kaolinitic clays can be explained by the higher amount and the position of hydroxyl groups in the kaolinite structure. During calcination, this leads to more disorder and to the presence of Al^{V} exposed at the surface of the material.

In this study, the influence of the kaolinite content of clays (defined as calcined kaolinite content for calcined clays) is investigated, since middle grade kaolinitic claysare inexpensive and abundant on earth. First, a benchmark test of calcined clay mortar strength is launched in order to establish criteria of feasibility for suitable clays in cement. Moreover, due to the large number of calcined clays available worldwide, a new Rapid, Relevant and Reliable (R^3) pozzolanic test was developed to get a quicker indication of calcined clay reactivity. This test is carried out on portlandite/calcined clay/limestone model systems. The reactivity is assessed by measuring the heat release by isothermal calorimetry and by determining the bound water using simply an oven.

Concerning the benchmark test, strong linear correlations between LC^3-50 strengths and the calcined kaolinite content of the calcined clays are obtained. Other parameters of calcined clays such as fineness, specific surface and secondary phases only play minor role in strength development. From the R^3 pozzolanic test, linear correlations are obtained between strength results on mortars and the heat release on model systems after only 24 h of testing by isothermal calorimetry and 72 h by thermal treatment in oven. Thus, the R^3 test permits to predict the strength development of LC^3-50 mortars.

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THERMAL PROPERTIES OF SOME EGYPTIAN KAOLIN PASTES FOR PELOTHERAPEUTIC APPLICATIONS

M. E. Awad (1,3)*, A. López-Galindo (2), R. Sánchez-Espejo (2), M.M. El-Rahmany (1), C. Viseras (2,3)

(1) Department of Geology, Faculty of Science, Al Azhar University in Cairo, 11884, Egypt, (2) Instituto Andaluz de Ciencias de la Tierra (IACT), CSIC-Universidad de Granada, Spain, (3) Departmento de Farmacia y Tecnología Farmacéutica, Universidad de Granada, Spain
*mawad@correo.ugr.es; mawad@azhar.edu.eg

Thermotherapy is a recognized medicinal strategy based on the analgesic and anti-inflammatory effects that heat application produces on the human body. Pelotherapy, or mud therapy, has received much attention because clays are ubiquitous, cheap, and exhibit good heat retention capacity [1,2]. The present study aims to evaluate the potentiality of 7 selected well-crystallized kaolinite-rich samples (namely, K: Wadi Khaboba; H: Gabal Hazbar; N: Wadi Abu Natash) from Egyptian Carboniferous sedimentary deposits (located at the Abu Zenima district, west central Sinai peninsula; [3]) to use them in medicinal semisolid formulations as peloids. The effect of particle size is studied to check their influence on thermal dosage performance.

The studied samples exhibit a variable mineralogy. Kaolinite is the main constituent (ranging from 81 to 94%), followed by quartz (up to 14%), lesser amounts of anatase and halite, and traces of hematite, magnetite, alunite and gypsum. The kaolinite Hinckley Index varies from 1.28 to 1.50. 1:1 (w/w) kaolin mud pastes were prepared with purified water in Eppendorf tubes using a touch vibration vortex mixer for 2 minutes. The cooling kinetics of pastes were measured by using a differential scanning calorimetry equipment (Shimadzu DSC-50Q). Specific heats were calculated, following [4]. The granulometry and geometric surface area were measured by laser diffraction (Mastersizer 2000LF, Malvern Instruments) in the range 0.02 and 1500 µm.

All analyzed samples showed a clear predominance of particles under 4 µm (ranging from 82 to 94%), with median size (D_{50}) ranging from 0.93 to 1.35 µm. The heat retention time during cooling from 50 °C to 32 °C reached up to 30.82 minutes, oscillating around an average of 28.72 minutes, and the temperature corresponding to the minimal dosage time (T_{20}) was not exceed below 34.7 °C. A good correlation ($R^2 = 0.875$) was found between heat retention time and specific heats. There is no correlation between kaolinite content and thermal properties, but R^2 values around 0.6 are found with granulometry (finer the particles, greater the heat retention time t_{32} and the specific heat). Even if sample H5 (Gabal Hazbar deposit) is not the richest in kaolinite, it exhibits the best thermal dosage performance, in accordance with the granulometry ($D_{50} = 0.93$ µm), and geometric surface area (3.73 m^2/g).

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MOLECULAR MODELING OF INTERACTIONS BETWEEN ENVELOPE GLYCOPROTEIN E1 OF HEPATITIS C VIRUS AND KAOLINITE SURFACES

Mahmoud E. Awad (1,2)*, César Viseras (2), Ana Borrego-Sánchez (2,3), Elizabeth Escamilla-Roa (3), C. Ignacio Sainz-Díaz (3)

(1) Department of Geology, Faculty of Science, Al Azhar University in Cairo, Nasr City, 11884, Egypt, (2) Facultad de Farmacia. Universidad de Granada, 18071, Granada, Spain, (3) Instituto Andaluz de Ciencias de la Tierra, CSIC-UGR. Av. de las Palmeras 4, 18100 Armilla, Granada, Spain
*mawad@correo.ugr.es; mawad@azhar.edu.eg

The Hepatitis C virus (HCV) is a worldwide health challenge; so new strategies should be enhanced to develop the anti-viral drugs, including the use of natural materials like kaolinite [1]. Transmembrane domains (TMD) of envelope glycoproteins (TMDs-E1 and E2) play a direct role in heterodimerization and supposed to be essential for the formation of the viral envelope. In particular, the N-terminal peptide sequence [E1-(350-370)] of this TMD might be acted as receptor for binding and connecting to the host cells and is responsible for virus fusion. Therefore, if any alterations occurred in the charged residues of TMD structure, could lead to inhibition of the virus by disabling the functions of E1 and E2[2]. This work intends to explain the expected pathways and mechanism of kaolinite surfaces as inhibitory effect against HCV particles, and to facilitate a new trial of therapeutic strategy for hepatitis C virus treatment with kaolinite derivatives. The molecular structure of the protein segment TMD (350-370) of the HCV envelope glycoprotein E1 and its adsorption on surfaces of kaolinite have been studied by means of molecular modeling methods, in both dry and hydrated conditions, using on atomistic force fields based on empirical interatomic potentials [3] and molecular dynamic (MD) simulations. Our calculations indicate that the studied protein segment is likely to be adsorbed on the kaolinite with an exothermic process. This adsorption is more exothermic with the kaolinite aluminol (001) surface than with the siloxane (001) one. The results predict that the kaolinite can be considered in an exploratory research for a therapeutic treatment against HCV.

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HYPERSPECTRAL REMOTE SENSING AND SPECTRAL ANALYSIS FOR MAPPING AND DETECTION OF KAOLIN QUALITY

M. E. Awad (1,3)*, R. Amer (1,4), A. López-Galindo (2), H. M. El-Desoky (1),
M. M. El-Rahmany (1), L. García del Moral (5), C. Viseras (2,3)

(1) Department of Geology, Faculty of Science, Al Azhar University in Cairo, 11884, Egypt, (2) Instituto Andaluz de Ciencias de la Tierra (IACT), CSIC-Universidad de Granada, Spain, (3) Departmento de Farmacia y Tecnología Farmacéutica, Universidad de Granada, Spain, (4) Department of Earth and Environmental Sciences, Tulane University, USA, (5) Departamenteo de Fisiología Vegetal, Universidad de Granada, Spain
*mawad@correo.ugr.es, mawad@azhar.edu.eg

This study aims to use spectral analysis and hyperspectral Hyperion remote sensing images for mapping and evaluating the quality of kaolin deposits. Five EO-1 Hyperion Level 1 GST radiometrically and geometrically corrected images of April and May 2011 were used to study the spatial distribution of kaolin mineral in Abu Zenima district, Sinai Peninsula, Egypt. Samples were collected from the Carboniferous and Cretaceous kaolin beds in the study area. The spectral analysis were carried out on both, bulk and powdered samples, by using an Analytical Spectrometer Device (ASD) Portable Spectroradiometer Field Spec Pro JR (A109200), with spectral ranges 350-2500 nm. The position, depth, full-width-half-maximum (FWHM), and SP Index of absorption features were calculated for all of the continuum-removed spectra. X-ray diffraction (XRD) was used to measure the kaolinite degree of crystallinity Hinckley index (HI). Results of XRD analyses show that the kaolinite degree of crystallinity in the study area varied widely where Hinckley Index (HI) ranges from to 0.27 to 1.50. The Carboniferous kaolin has higher crystallinity than the Cretaceous kaolin (Awad et al, 2017). Spectral analysis indicated that the prominent absorption features of kaolin spectra occur around ~1400, ~1900, ~2200 and 2300 nm. Results show that there are shifting and changes in the morphology of the absorption features with both the kaolinite abundance (wt%) and the Hinckley index (HI). Spectral Angle Mapper (SAM) supervised classifications was used to identify kaolin distribution on the Hyperion images using the measured spectra of samples with different crystallinity. Field sampling and mapping indicated that SAM classification proved successfulness for identification of spatial distribution of kaolin mineral based on the HI crystallinity.

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NOVEL LAYERED DOUBLE HYDROXIDE (LDH) FOR THE OXIDATIVE VALORISATION OF LIGNIN

Iqra Zubair Awan (1,2)*, Nathalie Tanchoux (2), Francoise Quignard (2), Stefania Albonetti (1), Didier Tichit (2), Fabrizio Cavani (1), Francesco Di Renzo (2)

(1) Dipartimento di Chimica Industriale Toso-Montanari, Università di Bologna, Bologna, 40136, Italy, (2) Institut Charles Gerhardt Montpellier, UMR 5253 CNRS-UM-ENSCM, ENSCM, Montpellier, 34296 France
*iqra-zubair.awan@enscm.fr

The idea of biomass valorisation evolved when fossil resources were found not sufficient to meet the energy demands of the developing industry. Lignin, being an abundant and under valorised bio resource, became the centre of interest for scientists in order to have fossil-fuel like aromatic compounds. However, the natural complexity of lignin is the major challenge to be addressed before its valorisation. To understand the reactivity pattern and effective parameters required for the process, we synthesized lignin model molecules containing β-O-4 linkage which mimic the linkages present in real lignin. The model molecules were well characterised by GCMS, NMR and MALDI-TOF prior studying their oxidative depolymerisation. The study of reactivity of these molecules will provide an insight for tailoring the development of heterogeneous catalysts be able to expand prospective market for bio-based product. In this framework, Layered Double Hydroxides (LDH) are efficient precursors having finely dispersed mixed metal oxides which have not been extensively studied so far for the depolymerisation of lignin. To address this problem, aiming at high surface area and redox properties, we synthesized and characterised Ni-Cu-Fe, Ni-Fe and Cu-Fe based systems of mixed oxides in different ratios and calcined them at different temperatures. The catalysts will be used to study hydrolysis and oxidation of β-O-4 linkage in the model molecules. In Ni-Cu-Fe System, the phases formed were NiO, CuO, and spinel ($NiFe_2O_4$). The spinel formation is delayed at 500 °C or more. The calcinations of Ni-Cu-Fe and Ni-Fe system catalyst at 400 °C do not exhibit any Fe-bearing crystalline phase and the presence of amorphous iron oxide is an important feature of the system [2]. The surface area properties were studied as a function of temperature however no significance difference was observed once spinel phases were formed.

Early reports have suggested that Copper does not form an LDH with only Iron due to geometrical distortion by Jahn-Teller's effect [3]. In the attempt to understand the threshold value of Cu needed for formation of the LDH phase, the Ni/Cu ratio was changed which concluded as the catalysts having least amount of Ni^{+2} is unable to form a LDH phase. To study the phase transformation of LDH to oxide phases, the ratio of divalent Cu^{+2} and to Fe^{+3} were altered. Following predicted thermodynamic stability of Cu-Fe LDH, various attempts with different ratios and in different conditions are made to approach the subtle target of this single phase [1].

The formation of finely intermixed oxide phases from LDH can provide promising catalysts aimed at the depolymerisation of lignin and the selectivity of bond cleavage of β-O-4 linkages or Carbon-Carbon bonds. The significance of copper in the redox behaviour of iron cations could not only provide useful explanation for the oxidation pathways in lignin model molecules but also for the reactivity trend in different conditions [4].

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SIMULTANEOUS REMOVAL OF INORGANIC AND ORGANIC CONTAMINANTS FROM WATER BY INORGANIC-ORGANIC CLAYS

Suramya I. Rathnayake, Wayde N. Martens, Yunfei Xi, Ray L. Frost, Godwin A. Ayoko*

School of Chemistry, Physics and Mechanical Engineering, Queensland University of Technology, Brisbane, QLD 4001, Australia

Many methods are available for the removal of organic and inorganic contaminants from water. Of these, adsorption is one of the most widely used methods. While the adsorptive properties of naturally occurring clay minerals are well- known, unmodified clay minerals are rarely used for the simultaneous removal of organic and inorganic contaminants. The aim of this work is to explore the use of inorganic-organic clays (IOCs) as effective adsorbents for the removal of inorganic and organic pollutants from water. The IOCs were synthesised by intercalating the cationic surfactant, octadecyltrimethylammonium bromide (ODTMA), and inorganic cation, metal hydroxy polycations (hydroxy aluminium, Al_{13}) into Ca-montmorillonite (Ca-Mt). Three intercalation methods were employed and different ODTMA concentrations were used [1,2]. The obtained IOCs were fully characterised by X-Ray diffraction (XRD), Thermogravimetric analysis (TG), Fourier Transform Infrared spectroscopy (FTIR), and Brunauer, Emmett and Teller (BET), and their abilities toremove both organic (bisphenol-A) and inorganic (Cr (VI)) water contaminants from binary systems were investigated, and the mechanism explored [3]. The results of the Cr(VI) removal were particularly interesting because both adsorption and partial reduction of Cr (VI) occurred. This was attributed to the presence on Fe(II) in the natural form of the montmorillonite sample used. Overall, the work contributes to the understanding of the adsorption properties of IOCs as potentially efficient materials for the simultaneous removal inorganic and organic pollutants from contaminated waters.

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ADSORPTION OF RAIOIODINE FROM WATER BY CLAY-LIKE LAYERED DOUBLE HYDROXIDES

Frederick L. Theiss, Ray L. Frost, Godwin A. Ayoko*

School of Chemistry, Physics and Mechanical Engineering, Science and Engineering Faculty, Queensland University of Technology, Brisbane, Australia

^{131}I is used widely used in nuclear medicine and medical imaging but is also generated during uranium fission in the atomic energy industry [1,2]. It is clear that new technologies need to be developed to remove and store radioiodine. Layered double hydroxides (LDHs), are a class of layered clay-like minerals based on the brucite like ($Mg(OH)_2$) structure, that carries a net positive charge. The positive charge of the cation layers are balanced by exchangeable anions intercalated into the interlayer regions [3-5]. Further detail on the structure and composition of LDH materials has been reported by many groups in numerous publications [6-8] while the nomenclature and composition of the hydrotalcite supergroup has been reviewed more recently by Mills et.al [9].

LDHs were prepared by a conventional co-precipitation method, thermally activated by calcination at around 500 °C and used to treat synthetic wastewater solutions containing, iodide, iodate or iodide/iodate mixtures [10]. The adsorption kinetics of iodide (I^-) and iodate (IO_3^-) over 28 days was a rapid process, and could be described by the pseudo second order model. Thermal activation temperature was found to have a significant impact on the adsorption of iodine species. The adsorption of iodide (I^-) by a sample of LDH thermally activated to only 350 °C was successfully fitted to the Langmuir isotherm; while a sample calcinedat 500 °C showed better fit to the Freundlich isotherm. In contrast the adsorption of iodate (IO_3^-) could only be described by the Freundlich isotherm. It was proposed that the incomplete dehydroxylation and decarbonation of the LDH thermally activated to 350 °C meant that adsorption on the surfaces of the LDH has a greater impact on these samples, resulting in more Langmuir-like characters in the observed result. There appears to be significant difference between the adsorption mechanisms of iodide (I^-) and iodate (IO_3^-).

Due to the nature of the adsorbant-adsorbate interactions in LDHs, the leaching of intercolated anions over time through an anion exchange process cannot be discounted. Surprisingly little iodide (I^-) or iodate (IO_3^-) appeared to be leached from the LDHs in most experiments. The maximum amount of iodate leached from any sample was approximately 21% of the iodate (IO_3^-) originally present, and just under 3% of the iodide (I^-) originally present, though the addition of 0.1 M carbonate solution did significantly increase the leaching. Compared with the relatively short radioactive half-life of the ^{131}I isotope, this suggests that LDHs may indeed be a practical and cost effective means of removing and temporarily storing radioiodine in a range of situations.

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INVESTIGATION OF THE ADSORPTION OF GMP AND DGMP NUCLEOTIDES ONTO NA-MONTMORILLONITE SURFACE BY MOLECULAR DYNAMICS SIMULATION

Pauline Bacle*, Sébastien Le Crom, Virginie Marry

PHENIX UMR 8234, Université Pierre et Marie Curie, Paris 75005, France

The concentration of prebiotic organic building blocks may have promoted the formation of biopolymers in the environment of the early Earth. Therefore, the adsorption of RNA and DNA monomers, called nucleotides, on minerals that were abundant in the early Earth environment has been largely investigated both theoretically [1,2] and experimentally [3,4]. In particular, adsorption studies on swelling and non-swelling clays have shown that DNA monomers adsorb much more strongly than RNA monomers [4]. Yet, the only difference between deoxyribonucleotides and ribonucleotides is the hydroxyl group on the 2' carbon of the deoxynucleotide's pentose which has been reduced to just a hydrogen atom. Moreover, experimental results showed that even if adsorption of nucleotides occurs primarly on the lateral surfaces of clay particles, adsorption on the basal surfaces might happen at low pH for swelling clays, which are negatively charged.

In the present study, we focused on the adsorption of both guanosine monophosphate GMP and its deoxy- version, dGMP, on the basal surface of montmorillonite, a swelling clay. Molecular Dynamics simulations were performed on systems constituted of a clay sheet, water molecules and a nucleotide, using ClayFF force field for the clay and AMBER's GAFF force field for the biomolecules [5]. For dGMP, two adsorption configurations were found whereas only one was observed for GMP. The relative stabilities of these two adsorbed configurations were then further studied by Metadynamics simulations, which allowed us to obtain free energy surfaces corresponding to both cases using as collective variables the distances between two atoms of the base and the clay surface. Finally, kinetics were investigated using a Markovian model. Our results were discussed in the light of experimental data obtained with similar systems [4].

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INFLUENCE OF SOIL SUCTION ON THE VOLUME CHANGE BEHAVIOUR OF MONTMORILLONITE, ILLITE AND KAOLINITE CLAYS

Wiebke Baille (1)*, Snehasis Tripathy (2), Tom Schanz (1)

(1) Chair of Foundation Engineering, Soil and Rock Mechanics, Ruhr-Universität Bochum, 44780 Bochum, Germany, (2) Geoenvironmental Research Centre, Cardiff University, Cardiff, CF24 3AA, Wales, UK
*wiebke.baille@rub.de

Most naturally occurring clayey soils are composed essentially of one or more of the clay minerals from the kaolinite, illite, and montmorillonite groups [1]. Unsaturated clayey soils possessing such clay minerals exhibit swelling or compression when inundated with fluids. Similarly, saturated clays composed of these clay minerals usually undergo a significant volume decrease during the drying process and due to an increase in the externally applied stress.

The volume change and shear strength behaviour of soils are controlled by the effective stress. The influence of positive pore water pressure on the effective stress has been widely adopted as the design basis in geotechnical engineering practice associated with saturated soils. The influence of negative pore water pressure on the engineering properties of unsaturated soils has been explored [2,3]. Both two stress state variables and single stress variable approaches have been implemented in analyzing the engineering behavior of unsaturated soils [4,5,6,3,7,8]. In either of these approaches, determination of the soil-water characteristic curve (SWCC) has been shown to play a crucial role [2,8]. The suction stress approach [3,7,8] was used in this study to calculate the development of effective stresses during drying process. The suction stress forms a part of the effective stress in the case of unsaturated soils. The suction stress is manifest in the tensile strength of soil, which originates from the available interaction energy at the soil solid surface and can be conceptualized to exist in the forms of van der Waals attractive force, double-layer repulsive force, surface tension, and solid-liquid interface forces due to pore water pressure.

The effective stress in clays possessing a significant proportion of one of the clay minerals kaolinite, illite, or montmorillonite was determined based on the suction stress characteristic curves (SSCCs) of the clays. The SSCCs were determined based on the drying soil-water characteristic curves of the clays for a suction range of 0.03 to about 219.0 MPa. One-dimensional compressibility behaviour of initially saturated clays was also studied by loading clay specimens up to a maximum vertical stress of 21.0 MPa [9];[10]. The effective stress-void ratio responses of the clays during the drying process were compared with their saturated counterparts. The shapes of SSCCs and the magnitudes of minimum and maximum suction stress were strongly dependent on the mineralogy and the properties of the clays. For the clays with kaolinite and illite as the dominant clay minerals, the suction stress decreased, remained nearly constant, and then increased with an increase in the applied suction, whereas it decreased monotonically with increasing suction for the montmorillonite clay. A decrease in the suction stress caused an increase in the effective stress, which in turn reduced the volume of the clays. For applied suctions smaller than the air-entry value of any clay, equal magnitudes of suction stress and effective stress produced a similar volume change of the clay. The study clearly showed that suction changes beyond the air-entry value are less effective in producing volume changes in unsaturated soils, primarily because of a decrease in the effective stress due to an increase in the suction stress.

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MODIFICATIONS OF SOIL CLAY MINERALOGY RESULTING FROM CONTINUOUS AGRICULTURE - EFFECT OF DIFFERENT AGRONOMIC PRACTICES

Eleanor Bakker (1)*, Bruno Lanson (1), Fabien Hubert (2)

(1) Univ. Grenoble Alpes, ISTerre, CNRS, IRD, IFSTTAR, Grenoble, France, (2) Univ. Poitiers, IC2MP, CNRS - Poitiers, France
*eleanor.bakker@univ-grenoble-alpes.fr

Potassium (K) is an essential nutrient for plant growth. Clay minerals in soils represent a reservoir of K, some of which is available to plants. However, the long-term effects of plant uptake of Kon soil clay mineralogyhave not yet been determined. Field experiments such as the Morrow Plots represent a unique opportunity to determine the effects of 110-years of continuous agriculture on the fate of K-containing clay minerals in the field.

Available samples correspond to plots under continuous corn (C) and corn-oats-hay (R) seeding rotations, with fertilised (F) and non-fertilised (N) subplots. Selected samples date from 1904, 1957, 1980, 1997 and 2012-2014, allowing investigation of historical cropping practices, the introduction of high-level L-NPK fertilisation in 1954, and short-term alterations resulting from the crop rotation. Size fractionation was carried out both by sedimentation and centrifugation to isolate<0.05, 0.05-0.2, 0.2-2, and 2-50 µm fractions, and X-ray diffraction (XRD) was performed on fractions in the Ca-saturated state. Full-pattern modelling of XRD data was carried out to determine the structure model and the quantitative contribution of each phase.

The proportion of <0.05 µm fraction was found to increase with time for all samples with a simultaneous decrease in 0.05-0.2 and 0.2-2 µm fractions for the period 1904-2014, whilst the overall proportion of <2 µm fraction remained constant. Results of CHNS analysis show a slight decrease in the amount of organic matter for the same period, whilst cation exchange capacity was shown to increase dramatically between 1957 and 2014. Quantitative analysis of the 2-50 µm fraction demonstratesconstantmineralogy of this fractionover the period 1904-2014.

For <0.05, 0.05-0.2, 0.2-2 µm clay fractions, asix-phase model containing discrete illite, chlorite, kaolinite, and randomly-interstratified illite-expandable (illite-exp), kaolinite-exp and chlorite-exp was established as a basis for fitting all fractions and samples. For the 2012-2014 rotation, there is little apparent difference between samples, indicating that short-term modification of soil clay minerals is not a significant factor, at least when sampling at the end of the cropping season. Strong differences exist in the proportion of phases between size fractions for each subplot and year, discrete illite prevalent in 0.2-2 µm fractions, whereas illite-exp and kaolinite-exp are dominant in the finestfractions.

Further changes in relative proportions of phases during the period from 1904-2014 can be observed, such as a decrease in discrete illite in the 0.2-2 µm fractions as compared to finer fractions. Finer fractions also contain fewer illitic layers in illite-exp, and this illite-exp has become progressively more illite-poor during the period sampled. When considering both illite and illite-exp, the dominant K-bearing clay phases, R-subplots have a higher proportion of both phases than the respective C-subplots. Furthermore, when considering the total proportion of illitic layers - the sum of discrete illite plus the illitic layers in illite-exp - differences appear when comparing plots with the same crop rotation history. F-subplots appear to have fewer total illitic layers in comparison to N-subplots. This is thought to be an effect of higher yields and thus higher K- uptake and export in cropped material, which is sufficient to impact clay mineralogy despite fertiliser input on F-subplots. Overall, the results from the Morrow Plots show degradation of illitein a different manner according to the size fraction and nature of the K-bearing phase.

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STRUCTURAL, MICRO- AND NANO-CHARACTERIZATION OF ZN-CLAYS IN NONSULFIDE SUPERGENE ORES (PERU AND NAMIBIA)

Giuseppina Balassone (1), Gennaro Ventruti (2), Doriana Vinci (2), Maria Lacalamita (2), Ernesto Mesto (2), Emanuela Schingaro (2), Matteo Leoni (3), Nicola Mondillo (1), Giuseppe Arfè (1), Fernando Nieto (4), Maria Boni (1)

(1) Dipartimento Scienze della Terra, dell'Ambiente e delle Risorse, Università di Napoli Federico II, 80134, Napoli, Italy, (2) Dipartimento di Scienze della Terra e Geoambientali, Università degli Studi di Bari Aldo Moro, 70121, Bari, Italy, (3) Dipartimento di Ingegneria Civile Ambientale e Meccanica, Università di Trento, 38123, Trento, Italy, (4) Departamento de Mineralogía y Petrología and IACT, CSIC, 18002, Granada, Spain

Zn-clay minerals worldwide are associated with a variety of base metal ores, as the supergene nonsulfide supergene deposits [1]. In these occurrences, sauconite (the Zn-bearing triocthaedral smectite) is either the prevailing economic mineral or minor component of the weathering-derived mineral assemblage. The best example of supergene nonsulfide zinc deposit, where sauconite predominates over the other Zn-oxidized minerals is the world-class Skorpion mineralization (Namibia). Skorpion ore is hosted in Neoproterozoic rocks and sauconite predominates over the other Zn-oxidized minerals [2]. Among other worldwide occurrences, the Yanque (Zn)-Pb nonsulfide supergene deposit is also sauconite-dominated [3]. This study deals with a detailed characterization of sauconite from Skorpion and Yanqueusing XRPD, WDS, FTIR and TEM-HRTEM, to determine composition, structural and textural features of Zn-clays in the two deposits. Taking into account that the mineralogical data on sauconite are limited [i.e. 4,5], this study provides property information to constrain the genesis of the ore deposits, as well as to plan a correct metallurgical processing. Chemical data of the studied sauconite samples indicate that octahedral sites are occupied by Zn cations with minor contents of Al, as well as Fe and Mg, while the interlayer contains predominantly Ca^{2+} cations. The IR spectra show a distinctive band at about 3644 cm^{-1}, assigned to the $Zn(OH)_3$ stretching vibrations. For the Skorpion sample it was possible to separate a small fraction of pure smectite, whereas the Yanque sample contains small amounts of quartz, illite, kaolinite, chlorite, K-feldspar and goethite. The XRDP pattern of the Skorpion sample shows the (001) basal reflection at about 14.72 Å, characteristic of di-hydrated Ca^{2+} rich-smectite, and the diagnostic peak d_{060} at 1.533 Å, indicative of the trioctahedral nature of this smectite. The pattern exhibits broad and asymmetric diffraction maxima that are typical effects of disorder, stacking faults and/or fine grained crystallite dimension. To overcome these issues a suite of crystallographic programs are employed for a thorough microstructural characterization of these mineral phases. The TEM-HRTEM study shows that the microtextures of the Zn-clays observed at size below 10 μm are of two types, i.e. compact clay packages and porous clay aggregates. The first type is represented by straight and almost oriented packets, as an epitaxial growth onto mica crystals or rarely as void fillings. The packets can locally pass to slightly curved fibres coexisting with the straight packets. The second type consists of very fine-grained packets, with sizes lower than the compact clay packages types, ca. <400 nm. Electron diffraction patterns show that sauconite has a turbostratic arrangement. As reported in literature, it is difficult to obtain lattice-fringe images of very hydrated clays, as sauconite, due to the structural damage caused by the electron beam and the vacuum of the TEM environment and/or electron irradiation, which cause dehydratation and collapse of smectite. For the investigated samples, the measured smectite spacing is from 10 Å, in the case of a complete collapse, to ≈14 Å in case of an incomplete collapse (for example d_{001} of 13 Å in the Skorpion sauconite). TEM-AEM study demonstrated that the Skorpion sauconites are mainly Ca-rich varieties, in comparison to the Peruvian samples, which contains also significant quantity of K. In Skorpion, the dioctahedral smectite (beidellite) is very subordinate respect to its Zn-triocthaedral counterpart, and finely intergrown with sauconite (as in Peru samples, where beidellite is clearly more abundant). The occurrence of Zn-beidellite and other phyllosilicates (chlorite, baileychlore, etc.) at the micro- and nanoscale in the studied samples confirms the complex mineralogical nature of the Zn-nonsulfide smectite-rich (micro)systems, with remarkable implications for mineralogical evaluation and processing.

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SORPTION OF LEAD AND COPPER IN HYDROMORPHIC SOILS: INFLUENCE OF CLAY AND IRON MINERALOGY ON METAL RETENTION

Réka Balázs (1)*, Viktória Kovács Kis (2), Peter Sipos (1), Tibor Németh (1)

(1) Institute for Geological and Geochemical Research, Research Centre for Astronomy and Earth Sciences, Hungarian Academy of Sciences, Budapest, H-1112, Hungary, (2) Institute for Technical Physics and Materials Science, Centre for Energy Research, Hungarian Academy of Sciences, Budapest, H-1121, Hungary

Meadow soils are seasonally or permanently saturated by water, resulting in enhanced mineral weathering, variable redox processes and diverse clay and iron mineralogy. Ferrous compounds are characteristic of predominantly reductive soil environments, whereas alternation of oxidizing and reducing conditions promote ferric minerals. Several studies suggested that iron (oxy)hydroxides control the distribution of trace elements and also the immobilisation of potentially toxic metals [1,2]. Moreover, iron (oxy)hydroxide coatings increase metal sorption in soil clay minerals [3]. The sorbed elements are released to soil solution if iron minerals dissolve by reduction. Also, iron(II)- iron(III) hydroxides (green rust) of wet soils are supposed to reduce many agricultural pollutants. As a result, wetland soils provide a unique environment for trace element cycling and potentially toxic metal transport. Investigation of such varying mineralogical and geochemical features of wetland soils may provide better understanding of these processes.

We have studied meadow soil profiles from an 8 ha wetland developed on alluvial carbonate sediments between the rivers Danube and Tisza. Due to seasonally and spatially variable water table, the study area indicates diverse clay and iron mineralogy in a soil profile or in different pedons within short distances. Goethite and ferrihydrite are the characteristic iron oxyhydroxides of the periodically aerated horizon, whereas samples of reductive soil environments contain vivianite, siderite and non XRD detectable iron minerals, probably green rust. Based on detailed clay mineralogical studies, soil samples contain low and high-charge smectites. Swelling clay minerals are beidellitic and montmorillonitic according to Green-Kelly test. Beidellitic smectite formed likely due to the reduced iron-rich soil pore water.

Metal sorption capacity of the bulk soils was investigated by batch adsorption experimentation. Maximal Cu and Pb uptake were found as follows: soil with vivianite and high-P iron oxyhydroxides > soil of iron accumulation horizon > soil of gleyic horizon without XRD detectable iron oxides. Similar sorption capacity was observed for each metal on the studied samples. Chemical composition of the soil mineral phases was analyzed by TEM-EDS in order to understand their varying contribution to potentially toxic element immobilization processes. The highest Cu sorption was observed on iron oxide particles with high P content, whereas low-P iron oxyhydroxide and clay mineral particles from oxidized or reductive soil samples adsorbed a lower amount of Cu.

In summary, our laboratory adsorption experiments denoted that the iron mineralogical character of meadow soil samples strongly influences metal soprtion capacities. Phosphorus content of iron oxides play an important role in the observed differences.

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RELATIONSHIP BETWEEN SURFACE PROPERTIES OF SMECTITES AND RHODAMINE 123 MOLECULAR AGGREGATION

Tímea Baranyaiová (1)*, Juraj Bujdák (1,2)

(1) Comenius University in Bratislava, Department of Physical and Theoretical Chemistry, Faculty of Natural Sciences, 842 15 Bratislava, Slovakia, (2) Institute of Inorganic Chemistry, Slovak Academy of Sciences, 845 36 Bratislava, Slovakia
*baranyaiova6@uniba.sk

Probing the surface properties of clay minerals based on dye molecular aggregation represents a perspective analytical method. The formation of dye molecular aggregates in colloids leads to the significant changes in dye spectral properties. This phenomenon is known as metachromasy. Numerous studies have reported a close relationship between the layer charge of clay minerals and metachromatic behaviour of dyes [1]. Moreover, knowledge on dye metachromasy in clay mineral colloids may be useful for designing hybrid materials of proper photophysical properties.

In this work, the mechanism of rhodamine 123 (R123) molecular aggregation was investigated and applied for probing the surface properties of smectites. The kinetics of R123 molecular aggregation in the dispersions was measured for the series of Na^+-smectites, including four trioctahedral smectites and six montmorillonites. The R123 loading was kept constant ($0.1\ mmol \cdot g^{-1}$). The UV-Vis spectra were recorded in the combination with a thermostatic stopped-flow rapid mixing device. Spectral and concentration profiles of different dye species were identified using chemometric method - *Multivariate Curve Resolution-Alternating Least Squares* (MCR). Adsorbed monomers, oblique J-aggregates/dimers, H-dimers and higher H-aggregates could be distinguished. The reaction mechanism models were tested by non-linear regression analysis of the concentration profiles of respective spectral species.

Very fast dye adsorption followed with the formation of molecular aggregates occurred for all tested smectites. Significant differences in time spectral evolution apparently related to the smectites' properties. The fraction of R123 cations taking part in molecular aggregation increased with increasing layer charge of smectites. The largest amounts of initially formed molecular aggregates were observed in the colloids of smectites with high layer charge. Aggregation occurred also in the colloids of smectites with lower layer charge, but was much slower. The formation of higher H-aggregates was observed for the smectites with high layer charge, whereas H-dimers and oblique J-aggregates were identified as the main products in the colloids of smectites with low layer charge.

The mechanism of R123 molecular aggregation was described by two main parallel processes, both proceeding by first-order reaction kinetics, but different in their reaction rate. Additional processes may also have occurred in dependence on the smectite layer charge, and involved mainly the redistribution or structural changes of initially formed molecular aggregates.

The methodology developed in this work represents a sensitive and effective analytical tool for the characterization of surface properties of smectites. Moreover, it can be potentially applied also for probing the surface properties of nanomaterials, biopolymers and other substances promoting dye metachromasy. Understanding details on dye/clay mineral interaction can be useful in designing hybrid materials for specific applications.

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ENHANCING AFLATOXIN ADSORPTION IN SIMULATED GASTRIC SOLUTION WITH ORGANIC NUTRIENTS-MODIFIED MONTMORILLONITE

Ana Luisa Barrientos Velazquez*, Youjun Deng

Soil & Crop Sciences Department, Texas A&M University, College Station, TX, 77843, USA
yjd@tamu.edu

Smectites have shown to effectively adsorb aflatoxins in the gastro intestinal tract when incorporated into an aflatoxin contaminated feed. Yet, a complete animal recovery has not been observed. Smectites' adsorption capacity for aflatoxin was significantly reduced by the presence of large protein molecules, such as pepsin in simulated gastric fluid. The proteins restricted the adsorption sites on the smectite available for aflatoxins. The objective of this study was to enhance the aflatoxin B_1 adsorption of smectites by restricting the influence of proteins such as pepsin. Organic nutrients were selected to occupy part of the interlayer space of smectites to achieve a more desired environment for aflatoxin adsorption but not for the large protein molecules.

The interlayer of a Ca-montmorillonite was exchanged with five organic nutrients respectively: arginine, histidine, choline, lysine, and vitamin B_1 (thiamine). To confirm the intercalation of the organic compound on the smectite, X-ray diffraction patterns of the organic-montmorillonite complexes were recorded. The samples were heated from 50 to 300 ºC at 25 ºC intervals and a XRD pattern recorded at each temperature. Aflatoxin adsorption isotherms in pepsin solution were performed for each organic-montmorillonite complex. X-ray diffraction patterns and FTIR spectra were recorded for the organic-montmorillonite plus aflatoxin samples.

The variable temperature XRD patterns of vitamin B_1-montmorillonite and choline-montmorillonite showed a constant interlayer of 14 Å and 13 Å, respectively, up to 250 ºC. Arginine-montmorillonite and histidine-montmorillonite had an initial d-value of ~13 Å at room T, after heating to 150 ºC the interlayer was reduced to ~11.5 Å, and collapsed to 11 Å at 250 ºC. At 300 ºC, vitamin B_1-montmorillonite was the only sample that maintained the expanded interlayer at 12.7 Å. The FTIR spectra of the organic-montmorillonite complexes showed bands of the organic compounds and some band shifts due to the interaction of the organic compounds in the smectite. The FTIR spectra of the aflatoxin-pepsin-organic-montmorillonite complexes showed distinctive bands of aflatoxin, but there was also presence of a broad band at 1640 cm^{-1} attributed to pepsin. This band appeared to be narrower in the vitamin B1-montmorillonite complex, indicating that less pepsin was present in the interlayer. The XRD results also indicate that less pepsin was adsorbed in the vitamin B_1 modified clay as the d-value only expanded to 14.5 Å in the presence of pepsin, compared to ~17 Å as in arginine and lysine clay complexes. The aflatoxin adsorption capacity of the unmodified montmorillonite in a pepsin solution was 0.2 mol/kg. Vitamin B_1-montmorillonite complex showed a significant improvement in the affinity and increased the aflatoxin adsorption to 0.56 mol/kg. Choline-montmorillonite and histidine-montmorillonite also improved the affinity and showed a maximum AfB_1 adsorption of 0.41 mol/kg and 0.36 mol/kg, respectively. Arginine-montmorillonite and lysine-montmorillonite showed a slight increase in the adsorption capacity but the affinity was still low.

The results indicated that intercalating polar organic nutrients into the interlayer space of montmorillonite improved the AfB_1 adsorption by restricting the adsorption of pepsin. Yet, pepsin was not completely blocked. Among the five tested nutrients, vitamin B_1 was the most effective in blocking the adsorption of pepsin and increasing the adsorption capacity and affinity of aflatoxin in the simulated gastric solution.

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SYNTHESIS AND CHARACTERIZATION OF PMMA AND ORGANIC MODIFIED MONTMORILONITES NANOCOMPOSITES VIA *IN SITU* POLYMERIZATION ASSISTED BY SONICATION

Julio Roberto Bartoli*, Bruna Rosa Prado

Department of Materials Engineering and Bioprocess, School of Chemical Engineering, State University of Campinas, Campinas, 13083-970, SP, Brazil

Exfoliated nanocomposites of polymer/clay are considered as high performance materials. This is due to the high aspect ratio of the exfoliated clay that offers a large superficial area of interaction with the polymer. There are many challenges to obtain a high degree of exfoliation of the clay in the polymer matrix, different methods of preparation such as, in situ polymerization, melt intercalation and solution blending, have been used in academia and in the industry [1,2]. The *in situ* polymerization assisted by sonication is the most promising method to prepare exfoliated nanocomposites. The acoustic cavitation in the reaction medium help the dispersion of the nanoparticles and could promote sonochemical reactions, creating physicochemical interactions between the polymer chains and the organoclay [3].

In this work, polymethylmethacrylate (PMMA) and organic modified montmorilonites nanocomposites were synthetized by *in situ* polymerization of MMA monomer, in chloroform, using a sonication probe. The parameters of the syntheses were reviewed from the literature and the boundary conditions for a systematic experimental study were defined using the design of experiments methodology. The following variables were studied: type of organic modifier (surfactant) of the clay and energy of sonication during the reaction. Different commercial organoclays (OMMT) containing the hydroxyl groups (Cloisite® 30B), aromatic (Cloisite® 10A) or aliphatic (Cloisite® 25A) were used in this work.

The PMMA nanocomposites, with 3% by weight of organoclay, were characterized by XRD, TGA, TEM, FTIR, UV-Vis, DSC, GPC, parallel plate rheometry and refractometry analysis. The changes in the rheological behavior associated with clay nanolayer dispersion could be assessed from curves of the complex viscosity at low frequency.

The statistical analysis of factorial design indicated (95% of confidence) that the only significant factor was the “Flory-Huggins interaction parameter” for the following PMMA/OMMT nanocomposites response variables:

-the power law index of the complex viscosity for PMMA/C25A nanocomposite indicated a better organoclay dispersion, among the others, and a trend to a percolating network structure;

- the UV-visible transmittance of PMMA/C25A was similar as the pristine PMMA; the refractive index of the PMMA/C25A showed a reduction of 10^{-3} (accuracy of 10^{-4}) which could be a potential application for optical electronic devices, such as new materials for core/cladding of polymeric optical waveguides or fibers;

- an improvement of thermal stability of the nanocomposites was measured by TGA due to an increase of 35 to 50 °C compared to the pristine PMMA.

As the “sonication energy” was not significant, then the *in situ* polymerization could be performed at the lower energy level, considering the boundary conditions studied to improve organoclay dispersion.

The enhancements in the properties verified for the PMMA/C25A nanocomposites are attributed to the Flory-Huggins interaction parameter (χ) between “OMMT surfactant- chloroform solvent”. The long alkyl chain and bulky surfactant of C25A organoclay could contribute for the diffusion of the chloroform/MMA solution into the gallery space of that clay due to the better affinity to the chloroform (χ~1,2); taking account that the three grades of OMMT studied presented the same, ~1,9 nm, interlamelar distance.

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ANALYSIS OF THE SPECTRAL RESPONSE (V-NIR) APPLIED TO THE STUDY OF CLAYS IN SEDIMENTARY MATERIALS

ARTURO BÁSCONES (1,2)*, EDUARDO GARCÍA-MELÉNDEZ (2), MERCEDES SUÁREZ (1), JAVIER GARCÍA-RIVAS (1)

(1) Department of Geology. University of Salamanca. Plaza de la Merced s/n. 37008. Salamanca. Spain, (2) Department of Geography and Geology. Faculty of Environmental Sciences. University of León. Campus de Vegazana s/n. 24071. León. Spain

The study is focused on the relationship between mineralogy and the spectral response produced by the sedimentary materials that are rich in clays located in the northwest area of the Duero Basin, in the province of León (Spain).

For that purpose, samples were taken on the top soil surface from the different sedimentary units. We separated the fraction smaller than 4 mm in order to study it by X-ray diffraction and characterize both its mineralogy in bulk-rock and its clay minerals content through oriented aggregates of the fraction smaller than 2 µm (in normal environment, solvating with ethylene glycol and heating at 550 ºC for two hours).

We measured the spectral response (V-NIR) in the laboratory on different grain-sizes (bigger and smaller than 4 mm and on the powdered sample). Differences in porosity and the presence of interlayer water or hydroxyl groups in the clays will affect the spectral response, generating quantifiable absorption features in certain wavelengths. The alteration processes suffered by the sediments, which produced textural and compositional changes, will also be reflected in the absorption features of the reflectance spectral curves both in the visible and the near infrared.

The absorption features produced in the spectral curves at the wavelengths of 1.4 and 1.9 µm are mainly related to the vibrations of the hydroxyl groups and the water molecules. These absorption features are not detected or have a low intensity when we only have structural OH^{-}, producing absorption features at the wavelengths of 2.2 - 2.4 µm, related to the combination of basic modes of tension (O-H) and flexion (Metallic ion-O-H) (Hunt & Salisbury, 1970). The proportion of the different types of clays present in the samples obtained by X-ray diffraction has been compared to the data obtained by laboratory reflectance spectroscopy. Thus, the samples with a high chlorite/illite content produce low absorption features at 1.4 and 1.9 µm, related to the low molecular water content in these samples. However, they have two absorption features at 2.34 and 2.46 µm, typical of mica group (Clark et al., 1990). The opposite happens in the samples with a high vermiculite/smectite content, which have intense absorption features at 1.4 µm and mainly at 1.9 µm. The electronic processes that produce absorptions in the visible are related to the charge transitions between electronic levels of different energy, as with the ferrous/ferric ion, present in surfaces of alteration of sedimentary materials (Hunt & Ashley, 1979).

All the mineralogical differences seen in the studied sediments will allow us to subsequently map, with the aid of satellite images, the geological units with different geochemistry and mineralogy.

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LAYERED DOUBLE HYDROXIDES AS MULTIFUNCTIONAL EXCIPIENTS FOR TOPIC FORMULATIONS

Maria Bastianini*, Michele Sisani, Annarita Petracci, Roberto Spogli

Prolabin & Tefarm, via dell'acciaio 9, 06134 Ponte Felcino, Perugia, ITALY

Layered double hydroxide compounds (LDHs) are a class of layered materials with positively charged layers and charge-balancing exchangeable anions located in the interlayer region. The general formula is $[M(II)_{1-x}M(III)_x(OH)_2]_x+(A_{n-})_{x/n}$ yH_2O, where M(II) is a divalent metal like: Mg^{2+} or Zn^{2+}, M(III) is a trivalent metal like: Al^{3+}, A is an organic or inorganic anion of charge n- and y is the number of moles of water per formula. The counter-balancing anions are located in the interlamellar region together with the water molecules.

Synthetic layered double hydroxides have attracted particular attention because of their biocompatibility and lack of toxicity. Moreover their chemical composition can be finely tuned. Recently many works have been published on the use of LDHs as a carrier of active molecules, proving their effectiveness.

LDHs has been used as carrier [1] of drugs, aminoacids and antibiotics, DNA, showing good results in terms of controlled release, drug loading and protection of labile biomolecules.

Prolabin & Tefarm has developed an innovative and green method of synthesis that allows the production of easily exchangeable LDHs. The properties of this innovative LDH were determined by x-ray powder diffraction (XRPD), inductively coupled plasma atomic emission spectroscopy (ICP-OES) and field emission scanning electron microscopy (FE-SEM).

The LDH was used as a support for an anti-inflammatory drug that was intercalated by anionic exchange. The LDH-drug hybrid obtained was characterized by XRPD, thermogravimetrical analysis, HPLC.

The hybrid was formulated in a gel provided for topical use. The gel possesses very good organoleptic properties, due to the multifunctional effect of LDHs, which also acts as a rheological modifier.

In *vitro* release studies on the gel were carried out using a vertical Franz Diffusion Cell, PermeGear, Inc., Bethlehem, P.A., 20 mm diameter, equilibrated at 32 °C (skin temperature) by an external circle bath. The amount of drug released was determined by HPLC. Tests were carried out in triplicate and the results were reported as an average and normalized on the basis of the total drug content.

The hybrid-containing formulation has been compared to a commercial reference, showing a higher and prolonged release. The release mechanism is strictly linked to the nature of LDHs and is based on the ion exchange mechanism; it allows a prolonged release with an increase of the local bioavailability of the drug.

The preliminary results obtained show that LDHs are able to improve drug release in formulations for topical applications. This technology enables a modified and prolonged release of active ingredients. LDHs also exert interesting effects on the topical formulations (i.e. rheological and texturizing properties).

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XRD MICROSTRUCTURAL ANALYSIS OF MULLITE IN TRIAXIAL PORCELAIN COMPOSTIONS

Angel Sanz (1), Joaquín Bastida (1)*, Angel Caballero (2) Marek Kojdecki (3)

(1) UD. Geología. Universidad de Valencia, 46100- Burjasot, Valencia, Spain, (2) Instituto de Cerámica y Vidrio (CSIC), Campus Cantoblanco, 28049 -Madrid, Spain, (3) Instytut Matematyki i Kryptologii, Wojskowa Akademia Techniczna, 01-476 -Warszawa, Poland
*bastida@uv.es

XRD microstructural analysis of mullite by the Warren - Averbach method [1] was performed in a set of industrial triaxial porcelain compositions [2] with two different modalities of each triaxial constituent (quartz of d50= 3 mm or d50= 10 mm, feldspar lithium bearing or without lithium and kaolinite of high or low “crystallinity”), at 4 maximal temperatures of firing in the range 1270 - 1340 ºC and two types of firing cycles (fast or slow).

The analysed direction of diffraction was [110], corresponding to slower crystal growth velocity, and greater development of the corresponding faces (form {110}) [3] using the 110 and 220 diffraction peaks. Experimental and instrumental peaks were fitted to pseudo-Voigt functions [4] using the Profile program (Bruker AXS-Socabim) and the Warren-Averbach method calculation was made with WinCrysize V.3.0 program (Bruker AXS-Sigma).

The graphical representations of average crystallite size versus firing temperature grouped by formulation variables and firing cycles showed increasing sizes with temperature. For the different type of firing and type of triaxial constituent at each temperature, in the range 1300 - 1340 ºC, greater sizes were found for slow firing, for low “crystallinity” kaolinite, for smaller particle size of quartz as well as for Li-bearing flux (some exceptions were found at 1270 ºC). However, the observed differences (considering the instrumental error obtained as 7%) were not significant in fast firing, except for the influence of the type of flux.

Formulations with Li bearing flux showed more frequently bimodal frequency distribution and greater increases of maximum frequency crystallite size with temperature in slow firings than in fast firings, whereas the found increases were greater (but with small difference) in fast firings than in slow firings for compositions with no Li bearing flux.

The positive influence of lower “crystallinity” of kaolinite, lower quartz particle size and use of Lí bearing flux to produce greater crystallite growth with increasing temperature can be deduced for the relatively slow firngs.

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ASSESSMENT OF CLAYEY PELOIDS FORMULATIONS FOR CLINICAL USE IN EQUINE REHABILITATION

Carla Marina Bastos*, Fernando Rocha, Angela Cerqueira, Cristiana Costa, Denise Terroso

GeoBioTec, Department of Geosciences, University of Aveiro, Portugal

Injuries to the musculoskeletal system of horses are very common, especially in sport horses. Veterinary clinical practice is supported by an uncertainty about the total recovery of the animal mainly because it is necessary a long time recovery and the animal must be withdrawn from the sporting activity and undergo a complex and long treatment programs. This lack of sporting activities may in some cases exceed one year.

Veterinarians are using less complex and traumatic methods for the injured animal, developing new therapeutic protocols, using clays in combination with hydrotherapy, cryotherapy and specific exercises.

The use of hot clay cataplasms in the injured areas, involved in impermeable bands on the external side, acts as a thermal adjuvant and prolongs the action effect of clays. The clays are prepared with water and sometimes with other substances, like acetic acid. These empirical methods have demonstrated fast and effective results in the decrease of the inflammatory response and the formation of edemas. A few studies were performed on commercial clays used by the veterinarians in horse musculoskeletal injuries treatments.

Several analyses were carried out: grain size distribution (wet sewing and sedigraph), mineralogical composition (X-ray diffraction), geochemical (major and minor elements) analyses (X-ray fluorescence), abrasivity, plasticity, cation exchange capacity and exchangeable cations, specific surface area, expandability, oil absorption and cooling rate.

These important properties, in particular cation exchange capacity and cooling kinetics and the physical, chemical and mineralogical characterization may contribute for the establishment of healing criteria for veterinarian clays.

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AMMONIUM-RICH ILLITES IN VERY LOW GRADE METAPELITES: MICROTEXTURE AND COMPOSITION

Blanca Bauluz (1), Fernando Nieto (2)

(1) IUCA-FACULTAD DE CIENCIAS, Universidad de Zaragoza, Zaragoza (Spain), (2) Departamento de Mineralogía y Petrología and I.A.C.T., Universidad de Granada-CSIC, Granada (Spain)

The illite interlayer contains K as a fixed cation by definition, but illites from different environments also have ammonium reported in the interlayers. The content of ammonium can vary between several hundred parts per million to 100% for pure ammonium illite, the end-member called tobelite. The ammonium often comes from decomposition of organic matter in diagenetic environments or from coal in anchimetamorphic environments ([1] and references therein).

In this study we described the occurrence of ammonium-rich illites in Silurian black metapelites of the Iberian Range (NE Spain). Some of these outcrops had been previously described [2]. The aim of this study is to characterize the microtexture and composition of these NH_4-rich illites using X-ray diffraction, infrared spectroscopy and transmission electron microscopy (TEM). Samples were treated with L.R. White resin [3] in order to prevent the collapse of smectite-like interlayers in the vacuums of the ion milled and TEM, as well as to facilitate the differentiation of illite and smectite interlayers in TEM images. Typical areas were removed for TEM observation via attached Cu washers, thinned in an ion mill, and carbon coated.

In these metapelites NH_4-rich illites are associated to other phyllosilicates such as K-illite, mixed layer I/S (R1), pyrophyllite and kaolinite. X-ray powder diffraction shows an expanded $d_{(001)}$ spacing for ammonium-rich illites in comparison to K illites. The basal spacing varies from 10.052 to 10.088 Å for ammonium illites, in contrast with the typical value for K illites (~9.99 Å). These $d_{(001)}$ indicate contents in ammonium around 15 to 30% in the interlayer position. Infrared spectra of the samples exhibit pronounced absorption at 1430cm^{-1}, the resonant-banding frequency for NH_4^+ coordinated in the illite interlayers.

TEM images show parallel to subparallel packets of NH_4^+ and K- illites; they are 15-30 nm thick with relatively well-defined boundaries. Selected area diffraction patterns show that disordered polytypes occurs in both types of illites. High-resolution TEM images show that they are formed of nearly straight lattice fringes with constant 10-Å spacings for K illites and 10.2-10.8 A Å for ammonium rich illites. In occasion fine intergrowths of smectite layers (12 Å) and R1 I/S (21 Å) phases with the illites have been observed.

Chemical compositions, determined in the TEM, show that all the illites are dioctahedral and the interlayer positions are mainly occupied by K and minor Na contents. The interlayer compositions, calculated on the basis on 11 oxygens, vary considerably in these phases, with values ranging from 0.25-0.70 a.p.f.u, corresponding the highest values to K illites and the rest to ammonium rich illites. This continuous trend suggests large variation in K and NH_4 contents in the illite interlayer that probably produce the variation in $d_{(001)}$ spacing measured in the TEM images.

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SYNTHESIS OF IMPREGNATED BENTONITE BY USING ULTRASOUNDFOR THE PURPOSE OF ITS APPLICATION IN THE FENTON PROCESS

Milena Bečelić-Tomin, Đurđa Kerkez, Aleksandra Kulić, Dragana Tomašević Pilipović*, Božo Dalmacija, Vesna Pešić

University of Novi Sad, Faculty of Science, Department of chemistry, biochemistry and environmental protection, 21000 Novi Sad, Serbia
milena.becelic-tomin@dh.uns.ac.rs

Modified clays are often used as catalysts for application in heterogeneous Fenton process for removing of dyes from coloured effluents. The impregnation with iron salts is one of the simplest techniques for preparation of clay for this application. However, this method, as well asmany other methods usedin the preparationof the catalyst, requiresa certain period of catalyst ageing, which is adrawbackforits industrial scale application [1]. Using ultrasound is one of the ways for improving the method for preparation and properties of solid catalysts. The results fromsome studies [1], [2], [3] show that the use of ultrasonic techniques save time and water in the synthesis of solid catalyst while preserving the physical and chemical properties of materials and also improve thecatalytic activity.

Investigation of the effect of preparation methods of Fe-loadedbentonite on its stability and efficiency in a heterogeneous Fenton process was carried out in aqueous solution of synthetic Reactive Blue 4 (RB4) dye. We useda Na-bentonitethat was supplied by the "Bentoproduct" company, Šipovo (Bosnia and Herzegovina). Two catalyst synthesis methods were used in the study. In both cases, clay suspension was prepared under vigorousstirring of 1 g of clay in 50 ml of distilled water for 30 min. For the preparation of the impregnation solution, sodium carbonate powder was added to a 0.2 M solution of $Fe(NO_3)_3.9H_2O$ in order to achieve a molar ratio $[Na^+]/[Fe^{3+}]=1$. We prepared seven different ratios of Fe^{3+}/clay i.e. 0.6; 1.25; 3; 5; 7; 9 and 11 mmol Fe^{3+}/g. For catalyst preparation three methods were used. Firstly, the conventional method of impregnation (sample B_{Fe} CMI) that involves mixing of Fe-polycation with the hydrated clay suspension for a period of 4h.the other two methods used an ultrasound (Ultrasonic Homogenizer Sonopuls HD 2200, Bandelin) preparation of Fe-polycation (5 min) and its mixing with the clay suspension for 5 min (sample B_{Fe} UMI5) and 10 min (sample B_{Fe} UMI10). Samples prepared using the traditional and ultrasound methods were dried at 100 °C for 24 h, then washed with distilled water several times and centrifuged, again dried for 24 h at 100 °C and calcinated at 350 °C (2 h). The calcined materials were applied as catalysts in the Fenton process. The effectiveness of decolourization of syntheticRB4 dye solution was monitored by measuring the absorbance at a wavelength 594.78 nm using UV/VIS spectrophotometer (PG Instruments Ltd T80+ UV/VIS, model: Shimadzu UV-1800, Japan). The content of leached iron was examined with an atomic absorption spectrophotometer (Perkin Elmer Analyst 700). Experimental conditions of the Fenton process were: [RB4] =50 mg/l, $[H_2O_2]$ = 20 mM, pH 3, reaction time 3h.

All three catalysts with a ratio of ≥ 3 mmol Fe^{3+}/g showed high decolourzation efficiency (91-97%). Iron content in the leachateat the end of the reaction was not dependent on the concentration of Fe^{3+} in the clay suspension. Iron concentration in the solutions after Fenton process varieddepending on the applied catalyst, with 0.43, 0.47 and 0.16 mg/L Fe for B_{Fe} CMI, B_{Fe} UMI5 and B_{Fe} UMI10, respectively. The difference in Fe concentration for the catalysts can be explained by better incorporation of iron ions in the interlayers of Na-bentonite by using ultrasound in the synthesis of the catalyst [4], and a longer period of exposure time (10 min). Our results confirm the earlier findings in terms of shortening the ageing time and therefore the entire preparation procedure while retaining the necessary catalytic activity. The synthesis of a stable catalyst requires optimization of exposure time to ultrasonic waves.

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ENCAPSULATION OF THIOXANTHONE, A FLUORESCENT DYE IN AN ORGANIC-INORGANIC HYBRIDS HAVING A TALC-LIKE STRUCTURE: INFLUENCE ON ITS PHOTOPHYSICAL PROPERTIES

Adrian Beda (1,2), Jocelyne Brendle (2)*, Christian Ley (1)

(1) Laboratoire de Photochimie et d'Ingénierie Macromoléculaires, EA 4567, ENSCMu, Université de Haute Alsace, Mulhouse,68093, France, (2) Institut de Science des Matériaux de Mulhouse, UMR CNRS 7361, ENSCmu, Université de Haute Alsace, Mulhouse, 68093, France
*Jocelyne.Brendle@uha.fr

Organic-inorganic hybrids having a talc like structure (TLH) can be prepared by a process based on sol-gel chemistry which enables the formation of the materials under mild conditions in a one-step method. In this case, the organic groups are linked directly to the inorganic framework by covalent bonds.

In this study we focused first on the synthesis of (TLH) in the presence of *thioxanthone (TX) (Fig. 1),* a chromophore which has often been used as triplet sensitizers and photoinitiators of polymerization and has interesting photophysical properties [1,2] and then on the influence of the confinement on its photophysical properties.

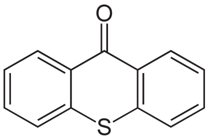

Fig. 1. Structure of Thioxanthone

A series of TLH having the following chemical formula: (TX)-$Mg_3(RSi)_4O_8(OH)_2$ (where R stands for the organic part) was prepared starting from organotrialcoxysilanes having different functionalities (mercaptopropyl, phenyl, and mixture of both), an ethanolic solution of a magnesium salt and TX. The key parameters governing the synthesis were finely tuned for each system. It was shown that room temperature (20 °C) and short aging times lead to the formation of lamellar structures as confirmed by X-Ray diffraction. The chemical formula of the obtained materials were determined by X-Ray fluorescence spectrometry and thermogravimetric analysis. The stability of the Si-C bond was checked by IRTF. ^{13}C and ^{29}Si NMR shed respectively light into the structural investigations of the attachment of pendant organic chains to the inorganic framework as well as on the integrity of TX and the degree of polycondensation of silicon species. Femtosecond pump-probe and steady state UV-Visible measurements were carried out to check the photophysical properties. This set of experiments showed that this the combination of TX and TLH leads to very interesting hybrid materials showing original properties.

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FTIR SPECTROSCOPY AND HEAT EVOLUTION STUDIES OF LOW GRADE KAOLIN CLAY POZZOLAN IN GHANA

Mark Bediako

CSIR-Building and Road Research Institute, Materials Development Division, Kumasi, Ghana
b23mark@yahoo.com

The use of low grade clays as a supplementary material is known to be suitable as the high grade kaolin [1,2]. In view of this, researchers have channelled a significant amount of attention on low grade kaolin and their suitability as pozzolans. In this work a Ghanaian low grade clay was used and calcined at a temperature of 800C [2]. The raw and calcined clay were evaluated based on the functional groups using FTIR spectroscopy [3]. The hydration of Portland cement incorporated with the calcined material at optimum level was evaluated using FTIR spectroscopy and Isothermal calorimetry. Calcined low grade clay indicated a change of their structure from crystalline to amorphous from the FTIR spectroscopy results. The calorimetric results indicated that the accumulated heat evolved in the Portland cement was higher than the pozzolan mixture. The heat evolution curve for the two binders were similar with the exception of the acceleration period where the Portland cement indicated a higher acceleration period than the pozzolan binder. The study recommends the use of pozzolanic binders for low heat construction works than Portland cement.

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RHEOLOGICAL AND THERMAL PROPERTIES OF CARBOXYMETHYL CELLULOSE AND BENTONITE-CARBOXYMETHYL CELLULOSE DISPERSIONS

Benslimane Abdelhakim (1), Bahlouli I. Mohamed (2), Bekkour Karim (3)*, Hammiche Dalila (4)

(1) Laboratoire Mécanique Matériaux et Énergétique, Département Génie des Procédés, Université A. Mira, Bejaïa, Algeria, (2) Université des Sciences et de la Technologie d'Oran — Mohamed Boudiaf, Oran, Algeria, (3) ICUBE, UMR 7357 CNRS — Université de Strasbourg. 2, rue Boussingault, 67000 Strasbourg, France, (4) Laboratoire des Matériaux Polymères Avancés. Département Génie des Procédés. Université A. Mira, Bejaïa, Algeria
*bekkour@unistra.fr

The aim of this work was to investigate the rheology and the thermal behavior of carboxylmethyl cellulose (CMC) aqueous solutions and bentonite-CMC mixtures. The rheological properties of aqueous CMC solutions and bentonite-CMC dispersions were investigated at different temperatures (20, 40, 60 and 80 °C) and different mass concentrations of CMC (0.1, 0.5, 1.0 and 2.0 wt%).

It was found that all the studied fluids exhibit a non-Newtonian shear thinning behavior. The flow behavior of CMC solutions was described using the Cross model which allowed the determination of the critical concentration c* that can be regarded as the concentration at which microstructural evolution occurs, i.e. transition from a semi diluted non-entangled solution to a semi diluted entangled network [1]. A viscosimetric analysis of the viscosity-temperature flow curves showed a decrease of viscosity up to a critical value, i.e. the well-known gelation temperature (or cloud point), ranging between 60 °C and 80 °C for CMC solutions and between 40 °C and 60 °C for bentonite-CMC dispersions. Afterwards, a sudden dramatic jump above the so-mentioned critical temperature was observed. The cloud point is generally viewed as the temperature at which macroscopic phase separation in the polymer solution occurs, as a result of complex interactions between the polymer chains. In practice, using high shear rates, i.e. in the non-Newtonian behavior region, prevents gelation or at least, yield a translation to higher temperatures [2,3].

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SYNTHESIS AND CHARACTERIZATION OF AN ALGERIAN MONTMORIOLLINITE CLAY AND ITS APPLICATION IN THE ENVIRONMENT

Saliha Belal*, Fatiha Mokhtari

Laboratoire des Eco-Matériaux et Nanostructurés, Faculté de Chimie, Département de Génie des Matériaux, Université des Sciences et de la Technologie d'Oran Mohamed Boudiaf, BP 1504 El-Mnaouar, 31000 Oran, Algeria
*belal.saliha2016@gmail.com

The objective of this study is to determine the power adsorbing of a material aluminosilicate of origin Algerian (Montmorillonite), to eliminate a cationic colouring agent which is the methylene blue in aqueous environment. Materials were characterized by various techniques; BET, MEB, DRX, XRF and FTIR. The experiments were carried out in the bath mode. The influence of some parameters on the adsorption of the colouring agent on our solid supports, specifically, the contact time of adsorbing adsorbate, the pH of the solution and the initial concentration of the BM, was determined. The kinetic study showed that the process of adsorption of the BM on the montmorillonite is carried out in a fast step. The exploitation of adsorption isotherms using various classic models showed that the adsorption can be governed by the isotherms of Langmuir and Freundlich. The thermodynamic parameters were determined from the values of the maximal capacities of adsorption and the equilibrium constants. The phyllitic material (Clay of Maghnia) used in this work is proven effective in the elimination of cationic colouring agents and could be a very interesting alternative material.

Keywords: Adsorption; Isotherms; Methylene blue; Kinetics; Montmoriollinite.

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MODIFICATIONS OF AN ALGERIAN PALYGORSKITE FOR THE IMPROVED REMOVAL OF PESTICIDES FROM POLLUTED WATERS

Lala Setti Belaroui (1,2)*, Affaf Ouali (1), Abdelkader Bengueddach (1),
Alberto López Galindo (3), Aránzazu Peña (3)

(1) Lab. of Chemistry of Materials (LCM), Fac. of Applied and Exact Sciences, University of Oran 1, BP 1524 Oran El M'Naouer, Oran, Algeria, (2) Dep. of Pharmacy, Fac. of Medicine, University of Oran 1, BP 1510 Oran El M'Naouer, Oran, Algeria, (3) Instituto Andaluz de Ciencias de la Tierra (CSIC-UGR), Avda. de las Palmeras 4, 18100 Armilla, Granada, Spain

Palygorskite is amagnesium aluminum non-planar hydrous 2:1 phyllosilicate with modulated structure. The mineral exhibits a fibrous morphology, has largeinternal surface area and contains exchangeable cations and reactive Si-OH groups on its surfacethat may interact with many different compounds.

A Tertiary sedimentary palygorskite-rich sample, located near the town of El Ghoufi (East Algeria) [1] was used in this study. The samplewas ground, sieved through 90 µm and purified to remove carbonates (mainly dolomite and minor calcite). The purified sample (Raw Pal) was further modified either with magnetic iron oxides or subjected to hydrothermal treatments to increase its adsorption capacity. The obtained products were studied for adsorption of two pesticides, a fungicide, fenarimol and aherbicide, linuron. Both pesticides are frequently detected in environmental waters [2]. The modifications consisted in a) mixing two iron precursors in an alkaline medium with purified palygorskite, which gives black nanoparticles (FeO Pal_1); b) dark black nanoparticles (FeO Pal_2) obtained by the same protocol plus a hydrothermal treatment; and c) red nanoparticles (Fe_2O_3 Pal) [3], synthesized as FeO Pal_1, and then oxidized by adding nitric acid at 50 °C. All three develop a strong magnetic character in contact with a magnet. The palygorskites were characterized using infrared spectroscopy, X-ray diffraction and fluorescence, and electron microscopy. The adsorption and kinetic behavior of the palygorskites was evaluated by the batch method, fitting the experimental results to different mathematical equations.

The TEM photographs of the four samples are depicted in Figure 1. Fig. 1(a) corresponds toRaw Pal needleswith a length of 2000- 5000 nm and 10-50 nm in diameter [1]. Figs. 1(b) and (c) show Fe_2O_3 Pal and FeO Pal_1, respectively, in which the iron oxide particle size varies between 7 and 21 nm;the samples present a heterogeneous distribution of spherical particles without obvious aggregation and dispersed onto the palygorskite needles' surface, being the distribution for Fe_2O_3 Pal denser than for FeO Pal_1. Fig. 1(d), corresponding to FeO Pal_2, clearly shows an oxidenanoparticle surface pattern differentfrom Fe_2O_3 Pal and FeO Pal_1, with a hexagonal shape and a molecule size 1000 times bigger.

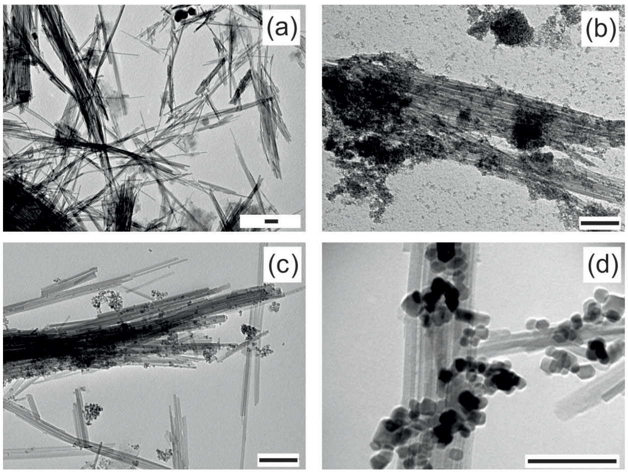

Fig.1. The TEM images of the Algerian palygorskite/iron oxide samples. In each case the bar corresponds to 2000 Å.

The retention of the pesticides increased by a factor of 4for fenarimol by Fe_2O_3 Pal and up to 20 times for linuron by FeO Pal_2. The results show that chemically modified palygorskites have a good potential for the remediation ofpesticide-polluted waters.

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GEOLOGICAL POSITION AND CHARACTERISTICS OF RUSSIAN BENTONITE CLAY DEPOSITS

Peter Belousov (1), Sergey Zakusin (1,2), Victoria Krupskaya (1,2)

(1) Institute of deposits, petrography, mineralogy and geochemistry, Moscow, Russia, (2) Lomonosov Moscow State University, Moscow, Russia

The ability of bentonite clay to swell, its binding capacity, high thermal stability and sorption properties make bentonite an indispensable raw material for industry. In Russia, the main bentonite consuming sectors of industry are metallurgy, foundry and drilling. Estimated reserves of bentonite clays in Russia are about 240 million tons ($A+B+C_1$-grade) [1]. The biggest mined deposits are Biklyanskoe with explored reserves of 13.5 mln.t. (Republic of Tatarstan), Ziryanskoe with explored reserves of 10 mln.t. (Kurgan region) and “10th Khutor” with explored reserves of 6 mln.t. (Republic of Khakassia).

Russian classification of bentonites based on their origin has some special aspects. Deposits of bentonite clay are divided into following groups: volcanic-sedimentary (devitrification of volcanic ash in slightly alkaline waters); hydrothermal (hydrothermal transformation of volcanic and sedimentary rocks); sedimentary (redeposited clay) and eluvial (weathering crust). However, the main bentonite types presented in Russia are sedimentary and volcanic-sedimentary ones.

In structural terms, major Russian deposits of bentonite clay are located in the East-European Platform, Urals, West Siberian Plate, the Altai-Sayan and the Far East folded zones. In stratigraphic terms, almost all Russian deposits are associated with Lower Carboniferous and Neogene-Paleogene system. Sedimentary type is associated with the edge parts of cratons and shield in the era of tectonic movement stabilization. Volcanic-sedimentary deposits of bentonite clay are associated with foldbelts (continental margin orogenes, with zones of deep fault and active volcanism).

Sedimentary Deposits are usually characterized by a simple geological structure, large reserves and poor quality of bentonite. Montmorillonite content ranges from 40 to 70%.

The largest Russian deposits of bentonite clay belong to this type and are located in the Republic of Tatarstan (Biklyanskoe, Verhne-Nurlatsky, Tarn-Varskoe and Berezovskoe) with total reserves of 45 mln.t., Kurgan region (Ziryanskoe deposit: alkaline-earth type, CEC - 66 mg-eq/100 g) with reserves of 10 mln.t., Omsk region (Lubinskoe virgin field) with reserves of about 20 mln.t. and Orenburg region (more than 20 deposits - Sobolevskoe, Zheltoe, Aktivnoe, Sarinskoe, Izhberdinskoe etc.) with reserves of about 25 mln.t.

Volcanic-Sedimentary Type. They are of high quality and have complicated geological structure. Montmorillonite content ranges from 50 to 80% (both alkaline and alkaline-earth type).

The deposit of bentonite clays “10th Khutor”, located in in Rep. Khakassia with reserves of 6 mln.t. belongs to the volcanic-sedimentary type. The deposit is localized within the continental tuff-sand-clay coal-bearing formation of Carboniferous age. Average montmorillonite content is 70% (alkaline-earth type, CEC - 45 mg-eq/100 g). Besides 10th Khutor deposit, this coal-bearing formation contain at least four smaller deposits of bentonite clay and appears to be an area of interest for exploration.

Another important region is Sakhalin island where bentonite clay genetically and spatially associated with Miocene tuff-terrigenous coal-bearing deposits of Lower Neogene. Montmorillonite is of alkaline type and its content is about 40-85%. The main deposits are Tihmenevskoe, Vahrushevskoe and Makarovskoe with total reserves of about 4 mln.t.

As a result of the study of Russian bentonite clay deposits it can be concluded that volcanic-sedimentary type of bentonite origin tends to form bentonite-bearing provinces. Moreover, the majority of these provinces have a characteristic feature - they are associated with fold belts and lay conjoint with coal-beds and are located in coal-bearing basins. It is also worth noting that Wyoming deposit, one of the largest and high quality bentonite deposits in the world, located in the United States also belongs to this type, and occurs in conjunction with the coal-bearing strata.

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CASCADE RESONANCE ENERGY TRANSFER IN HYBRID NANOCOMPOSITES BASED ON LASER DYES AND SAPONITE

S. Belušáková (1)*, J. Bujdák (1,2), K. Lang (3)

(1) Comenius University in Bratislava, Department of Physical and Theoretical Chemistry, Faculty of Natural Sciences, 842 15 Bratislava, Slovakia, (2) Institute of Inorganic Chemistry, Slovak Academy of Sciences, Dúbravská cesta 9, 845 36 Bratislava, Slovakia, (3) Institute of Inorganic Chemistry of the Czech Academy of Sciences, v. v. i., Husinec-Řež 1001, 250 68 Řež, Czech Republic
*belusakova3@uniba.sk

Förster resonance energy transfer (FRET) is a nanoscale phenomenon taking part in the photosynthesis process in green plants. The resonance between two dye molecules with suitable photophysical properties is essential for FRET. Excitation energy transfer from an initially excited molecule representing the energy donor (ED) to the second molecule, representing the energy acceptor (EA) is then the fundamental step of the energy transfer. The objective of this work was to characterize FRET in hybrid systems based on the mixture of laser dyes adsorbed or intercalated in synthetic saponite (Sap). Six cationic dyes (xanthene and oxazine types) were chosen to match energy transfer conditions. Fluorescence spectra proved cascade, multistep FRET in the experiments based on hybrid colloids. The colloids were used as precursors for the preparation of hybrid thin films, which were characterized by the X-ray diffraction, absorption spectroscopy and linearly-polarized absorption spectroscopy. Dye molecular aggregation was relatively low and the photoactive forms such as monomers and J-aggregates prevailed. Steady-state fluorescence spectroscopy, fluorescence anisotropy and time-resolved fluorescence spectroscopy confirmed the occurrence of very efficient, multi-step FRET also in the thin solid films. The concentration affects intermolecular distances between dye molecules intercalated in Sap film thus controlling FRET efficiency. Relatively low dye/Sap ratio led to an optimal average distance sufficient for efficient FRET. Saponite with a low layer charge represents a suitable inorganic template for the construction of photoactive hybrid materials. The hybrid materials with laser dyes can be used as light harvesting systems and for light energy manipulations on the molecular level. They can be precursors of more complex materials as components for solar cells mimicking a cascade energy transfer processes occurring in photosynthesis systems of green plants. Besides that, the application of FRET in probing smectites, clay minerals or related materials is also considered.

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A COLLOIDAL PATHWAY TO Ag/ TiO_2-ZnO/CLAY MATERIALS FOR PHARMACEUTICALS PHOTODEGRADATION

Carolina Belver (1)*, Jorge Bedia (1), Montserrat Tobajas (1), Ariadna Álvarez (1), Mariana Hinojosa (2), Vicente Rodríguez (2), Juan José Rodríguez (1)

(1) Sección de Ingeniería Química, Universidad Autónoma de Madrid, Madrid, Spain, (2) División de Materiales Avanzados, Instituto Potosino de Investigación Científica y Tecnológica, San Luis Potosí, S.L.P. Mexico

Modification of layered clays with different type of nanoparticles (NPs) has been a topic of intense research focused on the development of porous catalysts, thanks to their special features like their nanometer-scale and their capacity for versatile tuning of their components. Among the catalytic applications, clay materials have been widely used for the development of novel photocatalysts [1]. Photocatalysis is a useful technology for environmental remediation that has demonstrated its efficiency in degrading emerging contaminants present in water. This technology employs seminconductor catalysts (TiO_2, ZnO, etc) that generate radicals thanks to their activation by light, yielding the oxidation of organic species. Nevertheless, these semiconductors have several drawbacks related with their low surface area, difficult recovering and lower efficiency under visible light. In this scenario, clay materials are used as supports of active semiconductors with the purpose of improving the porous network, the adsorption capacities and the rheological properties of the photocatalysts.

In our prior research, we synthesized titania-clay photocatalysts with high activity for phenol degradation, following a sol-gel route that allowed the exfoliation of a layered clay at the same time as the assembling of TiO_2 nanoparticles [2]. Herein, we have extended the study through a new approach to improve the visible photoactivity of titania-clay materials, preparing novel Ag/TiO_2-ZnO/clay materials. These photocatalysts are based on a three-heterojunction between Ag nanoparticles (NPs), TiO_2-ZnO semiconductors and a delaminated layered clay. Firstly, a series of TiO_2-ZnO/clay materials were prepared by a sol-gel approach, varying the amount of ZnO (0.1 to 2%), that were further used as supports of highly dispersed AgNPs. AgNPs were photodeposited in 1.0 wt% and its incorporation helps to improve the generation of radicals during photocatalytic process. The structural, electronic and textural features of the photocatalysts were characterized by different techniques. In all cases, the clay was delaminated by the incorporation of the oxide matrix between the layers, improving the textural properties of the materials with respect to the starting clay. All photocatalysts were constituted by anatase particles (15-20 nm) anchored to the layered clay and a homogenous distribution of AgNPs.

The Ag/TiO_2-ZnO/clay materials were tested for the photodegradation of model pharmaceuticals (atenolol and acetaminophen, among others) under solar light. The degradation rate was checked under different conditions. The photodegradation was favoured at low concentrations of the target compound and atenolol showed the lower degradation rate. Although the target compounds were removed during the reaction, some TOC was remaining in solution due to the presence of short-chain carboxylic acids and unidentified by-products, although with very low significance in terms of ecotoxicity. The results of this study prove the ability of these novel photocatalysts to promote the degradation of these pollutants under solar light irradiation.

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ULTRASONIC *VS* HYDROTHERMAL METHOD. APPROACHES TO CONVERT WASTE MATERIAL INTO USEFUL PRODUCT

Claudia Belviso*, Francesco Cavalcante, Antonio Lettino, Pietro Ragone

Laboratory of Environmental & Medical Geology, IMAA-CNR, Tito Scalo (PZ) 85100, Italy

Layered double hydroxides (LDH) are compounds with a brucite structure showing a high specific surface area, a catalysis character and ion-exchange capability. These properties allow a wide application of LDH in many contexts mainly related with environmental remediation.

Layered double hydroxides have been synthesised by co-precipitation process in aqueous solution [1], hydrothermal method [2], mechanochemical approaches [3], microwave heating and ultrasound technique [4]. Moreover, literature data document hydrotalcite and hydrotalcite-like compounds synthesis by different aluminium hazardous wastes and among these, red mud has been largely used [e.g. 5].

Red mud (RM) is a waste material formed during the production of alumina when the bauxite ores are subject to caustic leaching. Due to its chemical and mineralogical composition mainly characterized by the presence of iron-based oxides, red mud was also used to induce magnetic properties in different materials [6]

In this paper, the action of ultrasonic process in synthesizing a large amount of layered double hydroxides (hydrotalcite) *vs* conventional hydrothermal process has been investigated. A sample of red mud was used as raw material. The results indicate that RM was converted in LDH applying both ultrasonic and hydrothermal methods. However, the comparison between the two processes shows that the action of sonication energy is more effective than hydrothermal heating in improving the reactivity of raw material and in accelerating the reaction to form hydrotalcite-like compounds.

The synthetic products were characterized by X-ray powder diffraction (XRD) and scanning electron microscopy (SEM). Magnetic properties were also investigated.

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INFLUENCE OF PRESENCE OF AMMONIUM IN THE HYDROTHERMAL ILLITIZATION OF SMECTITE

María Bentabol (1)*, Daniel Lamarca-Irisarri (2), Eduardo Flores (2), F. Javier Huertas (2)

(1) Department of Inorganic Chemistry, Crystallography and Mineralogy. University of Málaga. Campus de Teatinos s/n, 29071, Málaga, Spain, (2) Instituto Andaluz de Ciencias de la Tierra-IACT (CSIC-University of Granada). Avda. de las Palmeras 4, 18100 Armilla, Granada, Spain

During diagenesis, several reactions induce changes both in phyllosilicates and organic matter, which in basins associated to the production of hydrocarbons leads to ammonium fixation in illite and micas [1] and to dissolution induced by organic acids [2] [3]. Dissolution processes may contribute to the smectite-to-illite transformation, stabilized by fixation of K (and NH_4^+). Ammonium is a weak acid in solution. Under neutral conditions where the concentration of hydronium is very low (<10-7 M), ammonium contributes to smectite dissolution. The effect of organic acid on silicates dissolution is partially known, but the potential role of ammonium is completely novel.

In order to study the possible influence of NH_4^+ in the smectite-to-illite transformation reaction, a series of hydrothermal experiments were carried out at 100, 150 and 200 ºC, for 15 to 90 reaction days and two NH_4^+ concentrations (0.1 and 0.01 M). Solids were characterized after alteration by XRD and FTIR.

The results show that in these conditions, the smectite incorporates NH_4^+ in the structure, and smectite dissolution is corroborated by the formation of K- and NH_4^+-zeolites, at pH basic, and of K-feldspars and buddingtonite. Nevertheless, the XRD patterns reveal that, in addition these phases, the solid products include a small peak at ~10 A, suggesting formation of illite

Thus, presence of NH_4^+ seems to promote smectite-to-illite transformation reaction through the mechanism: NH_4^+-smectite → interstratified I/S → illite.

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APPLICATION OF NORTHEASTERN BRAZIL'S PALYGORSKITE FOR ADSORPTION OF MERCURY IN AQUEOUS EFFLUENTS

Luiz Carlos Bertolino (1), Vitor Schwenck Brandao (1), Rayssa Paula Paz Furlanetto (1,2), Patricia Viana Rodrigues (1,2)

(1) Center for Mineral Technology (CETEM), Av. Pedro Calmon, 900 Cidade Universitária, 21941-908, Rio de Janeiro, RJ, Brazil, (2) Chemistry Institute (IQ), Federal University of Rio de Janeiro (UFRJ), Av. Athos da Silveira Ramos, 149 Cidade Universitária, 21044-020, Rio de Janeiro, RJ, Brazil

Palygorskite is a hydrated silicate of aluminium and magnesium that has decolorizing power, thixotropic properties, high specific surface area and high sorption capacity. It is considered 2:1 clay with an octahedral layer of aluminium and magnesium between two tetrahedral layers of silica. The elongated and fibrous crystals give it suitable aspects for various industrial uses [1]. The mineral has high adsorption capacity for metals due to the isomorphic substitutions that can occur in the crystalline lattice. The most common substitutions are for Si^{4+} by trivalent cations (e.g. Al^{3+} or Fe^{3+}) in the tetrahedral sheet, and for Al^{3+} by divalent cations (e.g. Mg^{2+} or Fe^{2+}) in the octahedral sheet, which lead to a charge deficiency and a negative potential on the surface of the clay mineral [2]. In recent decades the contamination of water bodies by mercury discharge from mining activities in Brazil has prompted research to remove this metal in order to minimize environmental and human health impacts. This study involved the use of palygorskite from the state of Piauí, in the northeast region of Brazil, for mercury adsorption from aqueous effluents. The mineral underwent several stages of beneficiation and mineralogical characterization. The beneficiation stages consisted of comminution through a jaw crusher, wet bar milling, followed by wet granulometric classification and magnetic separation in the BOXMAG Rapid separator in a field of 15 kGauss. The mineralogical characterization was performed using XRD, XRF, SEM and TG-DTG methods. The CEC was determined by the methylene blue method. The results indicated that the beneficiation stages were efficient because an increase of palygorskite concentration and decrease of impurities such as quartz and kaolinite were observed in the sample. The fraction smaller than 44 µm indicated 54.70% SiO_2, 8.41% Fe_2O_3, 15.15% Al_2O_3 and 5.69% MgO. The CEC of the sample was $31 cmol_c/kg$, which is within the range of reported values in the literature. SEM analyses showed the palygorskite grains maintained their fibrous appearance. The extracted sample in the <44 µm fraction was pelletized through the addition of binders, 10% WAX and 20% Portland cement 32. The pelletisation process using the binding agents prevented the segregation and migration of fine particles, and increased the contact area of the clay mineral. The pellets were dried at 35 °C for 12 hours and were immersed in solutions of pH 2, 5 and 10 to test their stability. The granulometry of the pellets used for the adsorption test ranged from 2.8 to 4.75 mm. Mercury adsorption tests with the pelletized palygorskite were carried out in a fixed glass column with a layer of 60 g of the sample for percolation of 200 ml of the $Hg(NO_3)_2$ solution with the aid of peristaltic pump with a 2.4 L/h flow rate, at a predetermined time of up to 120 minutes. The analyses of low concentrations of mercury in the solutions were performed using an RA-915 + LUMEX mercury analyzer. The results showed that after 5 and 30 minutes of testing, the pellets adsorbed about 11% and 22% mercury (on mass basis), respectively. The main adsorption range occurred in the 60-minute test, where 83% of the total mercury mass was adsorbed, after which there was no significant change with the maximum value (86.79%) reaching at 120 minutes. These results showed palygorskite was very efficient in the adsorption of mercury, adsorbing mostly within the first 60 minutes. Solutions of 180 ml of $Hg(NO_3)_2$ were percolated with concentrations of up to 800 mg/L of mercury in fixed layer of a glass column with approximately 60 g of the sample, in order to evaluate the thermodynamic mechanism that controlled the adsorption, by using Langmuir and Freundlich models. The solutions with high concentrations of mercury were evaluated by atomic absorption spectroscopy. Analysis of the coefficient of determination indicated that the Freundlich model, $R^2 = 0.9978$, fitted the experimental data better. The tests demonstrated the efficiency of the palygorskite from Piauí to adsorb mercury in aqueous effluents, indicating its applicability in industrial processes for the removal of this metal.

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MINERALOGY, MICROMORPHOLOGY, CHEMISTRY AND STUDY OF BENEFICIATION OF KAOLIN FROM BORBOREMA PEGMATITE PROVINCE, NORTHEASTERN BRAZIL

Luiz Carlos Bertolino (1)*, Victor Matheus Joaquim Salgado Campos (1,2), Odivaldo Cambraia Alves (3), Ana Valéria Freire Allemão Bertolino (3), Vitor Schwenk Brandão (1)

(1) Sector for Technological Characterization, Coordination of Mineral Analysis, Center for Mineral Technology, Avenue Pedro Calmon, 900 - University City, 21941-908, Rio de Janeiro, Rio de Janeiro, Brazil, (2) Rio de Janeiro State University, (3) Department of Physicochemistry, Chemistry Institute, Fluminense Federal University, Outeiro de São João Batista Street, without number - Center, 24020150, Niteroi, Rio de Janeiro, Brazil

Kaolin is a rock composed principally by kaolinite [1]. Because of its properties, it is widely used in different industrial segments, such as paper and ceramics. For its use, the mineral must satisfy certain industrial standards, which can involve processes of granulometric classification, magnetic separation and chemical bleaching. Brazil is the sixth major world producer of kaolin [3] and most of its reserves can be found in the country's northern region [4]. There are also occurrences of kaolin deposits in pegmatites of the Borborema Pegmatite Province (BPP), northeastern Brazil [5]. However, further studies of its mineralogical and technological features and the determination of methods to remove iron oxides and hydroxides, which decrease the whiteness index, are still necessary for the suitable exploitation of the ore. Therefore, this article reports the mineralogical and technological characterization of kaolin samples from BPP, and also the results of its beneficiation, aiming to determine the most suitable method to remove iron oxides and hydroxides. Three samples were obtained in the southern region of Borborema Pegmatite Province. Clay size (2 µm) and industrial fractions (44 µm) were obtained by suspension and wet vibratory sifting, respectively. Clay-size fractions were prepared from each sample, then air dried, ethylene glycol solvated and calcined at 350 ºC and 550 ºC for diffractometric studies. Industrial fractions were processed in two routes. The first involved magnetic separation followed by chemical bleaching and the second only entailed chemical bleaching. The fractions were analyzed by X-ray diffraction, X-ray fluorescence and scanning electron microscopy (for chemical analysis), granulometric analysis, determination of whiteness index and electron paramagnetic resonance. It was verified that the clay-size fractions are composed principally by kaolinite and, in two of the cases, by illite. In industrial fractions, it was possible to identify well crystalized kaolinite in the form of booklets and muscovite, quartz and feldspar, in gangue form. The industrial fractions' chemical compositions indicated a high content of kaolinite. The magnetic separation was responsible for small increases of whiteness index and just 30 minutes of chemical bleaching was necessary to achieve increases from 78.2 to 90.2%, 91.3 to 95.7% and 86.9 to 90.4% in the whiteness indexes. The quantitative and qualitative analysis of the electron resonance paramagnetic spectra indicated that although magnetic separation was responsible for removal of iron oxides and hydroxides, it was inefficient in comparison to the chemical bleaching results for removal of the impurities from kaolin, and consequently improving the whiteness index [6]. Therefore, the kaolin samples tested were essentially kaolinitic and through the suitable beneficiation processes, it was possible to increase the quality of the ore, enhancing it for use in many industrial segments, adding value to this Brazilian ore.

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USE OF BRAZILIAN PALYGORSKITE AS ADSORBENT OF LEAD AND CADMIUM IONS FROM AQUEOUS SOLUTIONS

Luiz Carlos Bertolino (1), Fernanda Arruda Nogueira Gomes da Silva (2), Vitor Schwenck Brandão (1), Karla Mayara Arguelles Simões (1,2), Bruna de Lemos Novo (1,2)

(1) Center for Mineral Technology (CETEM), Av. Pedro Calmon, 900 Cidade Universitária, 21941-908, Rio de Janeiro, RJ, Brazil, (2) Chemistry Institute (IQ), Federal University of Rio de Janeiro (UFRJ), A. Athos da Silveira Ramos, 149, Cidade Universitária, 21044-020, Rio de Janeiro, RJ, Brazil

Industrial development and the emergence of new technologies have had harmful consequences for the environment, for example the contamination of soils, rivers and seas by the disposal of heavy metals. Sustainable and economically favourable alternatives have been sought for the treatment of these effluents, one of them being adsorption by means of clay minerals [1]. Palygorskite is a hydrated lamellar clay with fibrous morphology. It is a phyllosilicate where two tetrahedral sheets composed of silicon and oxygen are connected by an octahedral sheet with magnesium ions [2]. The presence of micropores and channels in the mineral structure, as well as the elongated nature of the particles and their fine granulometry, give palygorskite a high specific surface area and sorption capacity for different species [3]. The objective of this work was to evaluate the ability to remove Pb (II) and Cd (II) ions in synthetic effluents using palygorskite from Guadalupe, state of Piauí, Brazil. The clay was characterized by XRD, XRF, SEM, TG-DTG, surafec area by the BET method. Cation exchange capacity was measured by the methylene blue method and zeta potential measurements were done to determine the surface charge potential. Batch adsorption experiments were performed by equilibrating 2 g palygorskite with 40 ml of $Pb(NO_3)_2$ or $Cd(NO_3)_2$ for 1 h at pH 5. The removal efficiency of the metal ions was determined by atomic absorption analysis of the supernatants. The relationship between the concentration of the effluent and the amount of adsorbed ions (adsorption isotherm) was studied, and the results obtained in the adsorption tests were evaluated with the objective of understanding the maximum capacity and type of adsorption, and also if this process is favorable or not. Characterization techniques revealed that the sample is essentially composed of palygorskite, kaolinite, quartz and goethite and has SiO_2, Al_2O_3, MgO and Fe_2O_3 concentrations of 58.0% 15.80%, 4.2% and 7.6%, respectively. The images obtained through SEM allowed the identification of the maintenance of the fibrous structure of the material. The results of the analysis of cation exchange capacity (35.5 $cmol_c$/kg), associated with the measurement of surface area (71.3 m^2/g) and negative surface charge over the whole pH range studied, explain palygorskite's high adsorption capacity for Pb and Cd. The results of the adsorption tests were efficient for both cations studied, with adsorption percentages of 99.0% and 91.0% for lead and cadmium, respectively. The Langmuir isotherm model proved to be the most adequate in describing the batch adsorption data for both metal cations, since the R^2 values were greater than those obtained for the Freundlich model. The results indicate that the adsorption process occurs in a monolayer, which is a reversible process. The free energy of Gibbs from the reactions of palygorskite with the studied cations occurs spontaneously, and the more negative value of ΔG is relative to the reaction with the lead ions. Thus, the reaction is more spontaneous for this cation, corroborating the greater interaction observed in the adsorption tests. The results of the characterization techniques (FRX and EDS) obtained after the batch adsorption process confirmed the presence of the adsorbed lead and cadmium ions in palygorskite.

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ADOBES FROM THE AGUADA CULTURE (c. 300-1100 BC) AND THEIR POSSIBLE CLAY SOURCES AT AMBATO VALLEY (CATAMARCA, ARGENTINA)

Silvana R.A. Bertolino (1)*, Marcos Gastaldi (2), Udo Zimmermann (3)

(1) IFEG-CONICET. Medina Allende s/n, Ciudad. Universitaria, X5000HUA Córdoba, Argentina, (2) IDACOR-CONICET. Museo de Antropología, Universidad Nacional de Córdoba. Hipólito Irigoyen 174, X5000JHO Córdoba, Argentina, (3) University of Stavanger, Department of Petroleum Engineering, 4036 Stavanger, Noway
*silvanarbertolino@gmail.com

Although the studies of pre-hispanic architecture in northern Argentina are widespread, very little is known of the adobes used in architectural elements (walls, seats, etc.). During the first millenium of the Cristian era at the Ambato Valley (Catamarca, Argentina), the residential buildings were made combining adobe walls and stone colums. The walls were covered with either rock, clay plaster or red paint. Adobes from Piedras Blancas (PB) and Cerco de Palo 065 (CP65) residential sites of the Aguada Culture (4th to 12th c. AC) have been examined as well as local possible raw materials within the Ambato valley. Based on the size, building complexity and other features that reflect the social status of the inhabitants, PB is the site with higher hierarchy and complexity. CP65 on the other hand, locates 800 m north of PB and represents one of low hierarchy.

This investigation will help to characterize these materials, to identify the clay source and to evaluate the availability, consumption and procurement of raw materials in the ordinary life of the Aguada people. Mineralogical and geochemical studies were conducted by XRD, FE-SEM-EDS, XRF and lithium metaborate/tetraborate fusion ICP combined with ICP/MS method on both the adobes and the possible source materials. The latter were also preliminary evaluated on basic physical and technological properties; their mineralogy, geochemistry and properties have been previously reported [1].

There are no commercial clay deposits in the area. Local clay sources were selected as possible candidates from: clays of fault gouges derived from crystalline Precambrian to Low Paleozoic basement rocks (Humaya y Los Escobales), altered epiclastic rocks (Los Escobales) and Quaternary loessic sediments (Cerco de Palos 65a-b, El Rodeo, Los Varela, La Aguada, Los Escobales) that filled the valley and crop out close to the archaeological sites.

At PB the adobes are fairly homogeneous in mineralogy and composed of quartz, micas (phlogopite, muscovite and biotite) and plagioclase along with hornblende, hypersthene, scarce chlorite and a clay suite of dominant illite, irregular I/S, and traces of kaolinite associated with minor calcite. Only the adobe from the perimeter wall (PB802) do not contain amphyboles and hypersthene but higher proportions of expandable clays (I/S). The adobe from CP65 is similar but with lower proportions of hornblende.

This mineralogy matches that of the Quaternary loessic sediments one of which is nowadays used to make adobe. Particularly minerals like hornblende, hyperthene, phlogopite and kaolinite are present in both the adobes and the sediments.

Comparing the chemical composition of the adobe material with the sampled clays then all but the samples from the fault gouge are possible candidates for the origin of the adobe. These clay samples are strongly enriched in Bi, Sb, Pb and Cs. The adobe samples do match nearly perfectly the Quaternary sediments and source material samples, besides one fractionated sample (a gravel) from El Rodeo. Slight differences can be observed only in a minute depletion in the adobe samples for Fe_2O_3 and TiO_2 and enrichment in K_2O (which is variable in the sources), Th and Cs - besides the significant enrichment in Nb and Ta. Hence, these source samples have been most probably used for the manufacturing of the adobe material. However, the mentioned source samples are not covering the entire composition of the adobe material as those are enriched in Cs, Nb and Ta; a certain additional input of Cs, Nb and Ta enriched material is necessary as all indicated source samples here show lower concentration of those three elements than the adobe, yet a mixing with the highly enriched samples from the fault gouge is not possible as then other trace elements should be enriched in the adobe, like Sb, Bi, Pb and Zr.

The trend of using local Quaternary sediments for the adobe is strongly suggested by the mineralogy and the geochemistry. There are no significant differences in the use and supply of raw materials between sites of different hierarchy.

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HALLOYSITE-BIOPOLYMER SYSTEM IN AQUEOUS SOLUTION: NANO-ITC INVESTIGATION

Vanessa Bertolino, Giuseppe Cavallaro, Giuseppe Lazzara, Stefania Milioto, Filippo Parisi

Dipartimento di Fisica e Chimica-Università degli Studi di Palermo, Viale delle Scienze pad.17, Palermo I-90128, Italy
giuseppe.lazzara@unipa.it

Studies on stability of halloysite nanotubes (HNTs) in aqueous polymer dispersions are conducted. HNTs are interesting for recent research because they are considered "green" materials and have versatile properties such as hollow tubular morphology, large specific area, tunable surface chemistry, high mechanical strength and thermal stability [1,2]. They are already used in the preparation of polymer systems as transport/drug delivery and in treatment wastewater, or as reinforcing agents. Selective absorption inside or outside nanotubes can be controlled by electrostatic force [3]. Three polymers with different surface charge, an anionic (pectin), a neutral (hydroxypropylcellulose, HPC), a cation (chitosan), are chosen. HNTs and polymers concentrations are respectively 1 and 0.1 wt% in all dispersions. Turbidimetric technique is used to evaluate the stability of functionalized nanotubes in water. Turbidimetry shows that aqueous dispersion of HNTs in presence of HPC is more stable than others. Viscosity measurements prove that dispersed particles stability in solution was not due to a kinetic effect. Polymer adsorption onto HNT surface is investigated by isothermal titration calorimetry (ITC). The experimental data are interpreted on the basis of a model of adsorption of the polymer on the nanoparticle and they allowed the calculation of the standard variation in free energy, enthalpy and entropy of the process. ITC was used to interpret turbidimetric data. ζ-Potential clarifies surface charge properties of functionalized nanotubes upon polymer absorption. Measurements are conducted by varying polymer concentration or pH, respectively. Different trends are obtained for the various systems. This behaviour confirms different interaction mechanism between the components (HNTs-polymer). Chitosan, with its positive charges, could prefer to interact to negative external nanotube surface; pectin, instead, could interact with the inner nanotube surface. Both polymers, however, stabilize HNT particles in water according to electrostatic mechanism. A trend of ζ-potential almost constant is obtained with HPC, so the better stability of this system could be attributed to a steric rather than electrostatic stabilization. Modified nanotubes by interactions with polymers may lead to the formation of colloidal systems with controlled stability and it offers different perspectives of new applications (area of cosmetics and medical implants) of these dispersions such as good carriers for substances to be released in response to external stimuli.

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CHARACTERISATION OF CLAYS AND CLAY MINERALS FROM BOREHOLES IN THE IRRUPUTUNCU AND OLCA VOLCANOES HYDROTHERMAL SYSTEMS, CHILE

Christian Betancourt*, Diego Morata

Department of Geology and Andean Geothermal Centre of Excellence (CEGA), Faculty of Physical and Mathematical Sciences, Universidad de Chile, Santiago, Chile

The Irruputuncu and the Olca are active volcanoes located in the Chilean Altiplano, where both of them present fumaroles at their craters and hot/warm springs at their bases. Previous geothermal explorations carried out on the zone conducted the drilling of 5 exploratory wells; two slim boreholes at the Irruputuncu (~800 m and ~1430 m depth) and three exploration water wells at the Olca (<700 m depth), from which numerous samples were taken at different depths for this study. The Irruputuncu is a dacitic stratovolcano with a sequence, as seen on the boreholes, dominated by tuffs, breccias and minor lava flows, with bottom hole temperatures close to 150 °C and 195 °C (at 700 m and 1371 m depth, respectively). On the other hand, the Olca is an andesitic volcano in which shallow drillings at its base confirm de occurrence of hot water aquifers of up to 70 °C and a zone dominated by smectite clays. This work aims to study the current hydrothermal systems associated to this volcanoes through different means, one of them being the recognition and characterization of clays and clay minerals and their variation in relation to different depths in each well.

The first approach to analyse the different clays and clay minerals present in the samples will be through the use of XRD and other traditional means, aiming to approach challenges such as their reaction progress with temperature and depth. Likewise, we aim to study the whole-rock control on clay mineral formation, analysing contrasting lithologies with different primary volcanic-related structures. After the results from the XRD have been obtained, the analysis on this minerals will continue afterwards through the use of methods like SEM, EMPA and TEM.

Since this study is a work in progress that is just beginning, the data from this analysis has not yet been obtained, but the preliminary results regarding the XRD will be ready in time to be exposed during the congress. Nevertheless, we expect to find clay sequences more commonly associated to acidic hydrothermal systems.

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MECHANICAL AND THERMAL PROPERTIES OF POLY(ε-CAPROLACTONE) NANOCOMPOSITES WITH CLAY-SUPPORTED CARBON NANOTUBE HYBRIDS

Zoe Terzopoulou (1), Dimitrios Bikiaris (1)*, Konstantinos S. Triantafyllidis (1), Georgia Potsi (2,4), Dimitrios Gournis (2), George Z. Papageorgiou (3), Petra Rudolf (4)

(1) Department of Chemistry, Aristotle University of Thessaloniki, GR-54124 Thessaloniki, Greece, (2) Department of Materials Science and Engineering, University of Ioannina, GR-45110 Ioannina, Greece, (3) Chemistry Department, University of Ioannina, P.O. Box 1186, 45110 Ioannina, Greece, (4) Zernike Institute for Advanced Materials, University of Groningen, Nijenborgh 4, 9747 AG Groningen, the Netherlands

In the recent study poly(ε-caprolactone) (PCL) nanocomposites with hybrid clay-supported carbon nanotubes (Clay-CNT) in concentrations 0.5, 1.0 and 2.5 wt% have been prepared by melt mixing. Emphasis was given to study the effect of nanoadditive on mechanical and thermal properties of PCL/Clay-CNT nanocomposites. All nanocomposites exhibited similar stress-strain patterns to those of neat PCL but with many differences. It was found that increasing nanofiller content tensile strength at yield point and Young's Modulus values increased. This is an indication that used hybrid acts as reinforcing agent. Tensile strength at break has also a similar trend and enhanced for nanofiller concentration 0.5-1 wt%. After that a small decrease was observed. As was found by XRD the fillers were exfoliated in the polymeric matrix, but no covalent interactions were detected based on XPS and FTIR measurements. Concerning thermal properties it was found that the crystallinity of PCL/Clay-CNT nanocomposites is the same as for neat PCL, but the nanofiller acts as nucleating agent which promotes the crystallization and also allows it to occur at higher temperatures. Under isothermal conditions, the rate of crystallization decreased drastically with increasing the temperature. Crystallization half-times were also decreased for the nanocomposites, which show that isothermal crystallization proceeds faster since filler particles cause heterogeneous nucleation. Under isothermal conditions, the rate of crystallization decreased drastically with increasing the temperature. Crystallization half-times were also decreased for the nanocomposites, which show that isothermal crystallization proceeds faster since filler particles cause heterogeneous nucleation. Thermal stability is instead negatively influenced by the nanofiller, since Clay-CNT catalyzes the decomposition of PCL at lower temperature. The presence of hydroxyls on the surfaces of clays and to a lower extent on the CNTs accelerated degradation rates of PCL as found by TG. In all samples degradation occurs mostly via intramolecular transterification reactions, and/or unzipping reactions from the α-carboxylic acid chain-ends at 370 °C, while at 400 °C *cis*-elimination also takes place, thus this secondary mechanism is favored at higher temperatures. The predominant mechanism remains intramolecular transterification in all temperatures. The monomer ε-caprolactone is the main decomposition product.

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THE ARRANGEMENT OF THE OCTYLAMMONIUM CATIONS IN MONTMORILONITE INTERLAYER UPON HYDRATION AND DEHYDRATION PROCESSES

Valéria Bizovská*, Ľuboš Jankovič, Jana Madejová

Institute of Inorganic Chemistry, Slovak Academy of Sciences, Bratislava, Slovakia
*valeria.bizovska@savba.sk

Clay minerals, mainly smectites, saturated with organic cations (organoclays) have attracted a great attention during past decades because of their use as adsorbents in treatment of contaminated waters. Understanding microstructure of organo-montmorillonites under wet/dry conditions is of high importance in clarifying their adsorption characteristics towards hydrophobic organic compounds in water. In this work the arrangement of less-traditional octylammonium cations in the montmorillonite interlayers was investigated at dry and hydrated conditions. The Na-saturated montmorillonite from Jelšový Potok deposit in Slovakia (Na-JP) and dioctylammonium (2C8) and tetraoctylammonium (4C8) salts were used for organoclays preparation. To prepare materials with sufficient hydration potential the loading concentration of hydrophobic organic cations was only 20% of the CEC of Na-JP. The samples were placed in glass vials, dried overnight at 80 °C and stored above P_2O_5 for 48 h. The increase of d_{001} value of dried samples from 12.5 nm (Na-JP) to 12.9 nm for 2C8-JP and 15.3 nm for 4C8-JP indicated the formation of lateral monolayers of the surfactants. The conformation of the 2C8 and 4C8 surfactants was examined by the near-IR (NIR) spectroscopy. The position of the first overtone of the CH_2 groups ($2\nu_{CH2}$) indicated the abundance of ordered *all-trans* and disordered *gauche* conformers in montmorillonite interlayers. The wavenumbers of the $2\nu_{CH2}$ of 2C8-JP and 4C8-JP at 5815 and 5805 cm^{-1}, respectively, suggested dominance of *gauche* conformers in both samples, however, slightly higher number of disordered conformers was detected for smaller 2C8 cations. Dried samples were further hydrated for 96 h over the water vapour providing the 100% relative humidity. The amount of adsorbed water was 8.1 mass% for the 2C8-JP and 7.0 mass% for 4C8-JP. The hydration of the samples evoked a shift of the $2\nu_{CH2}$ band to the lower wavenumber indicating the increasing number of *all-trans* conformers. More pronounced shift, *i.e.* from 5815 to 5799 cm^{-1} was observed for 2C8-JP while displacement from 5805 to 5798 cm^{-1} was found for 4C8-JP. Water molecules are supposed to enlarge the interlayer space and make alkyl chains easier to stretch to *all-trans* conformation. The reverse process, *i.e.* dehydration was followed using a special NIR DRIFT temperate cell allowing in-situ measurement of the NIR spectra in a temperature range 25 - 200 °C. Both hydrated samples showed the shift of the $2\nu_{CH2}$ band to higher wavenumber indicating decreasing amount of *trans* and increasing *gauche* conformers with increasing temperature. For 2C8-JP a marked change was observed mainly in temperature range from 25 - 125 °C (by 15 cm^{-1}), further increase in temperature remained the position of this band unchanged. The $2\nu_{CH2}$ band of hydrated 4C8-JP was shifted by 8 cm^{-1} mainly in temperature range from 25 - 100 °C. Different behaviour was observed for 2C8-JP and 4C8-JP dried before in-situ NIR measurements. Heating up to 200 °C had no effect on the $2\nu_{CH2}$ position remaining almost the same within the whole temperature interval. Moreover, the positions found for dried samples, i.e. 5814 cm^{-1} for 2C8-JP and 5805 cm^{-1} for 4C8-JP, were the same as those detected for hydrated samples heated at/above 150 °C. It is evident, that these wavenumbers reflect the highest possible degree of disorder of octylammonium surfactants at loading level corresponding to 20% CEC of Na-JP.

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TEMPERATURE - COMPOSITION RELATIONSHIPS OF CHLORITE DIVERSITY IN THE W-(CU,MO) ORE DEPOSIT OF BORRALHA, NORTHERN PORTUGAL

Iuliu Bobos*, Fernando Noronha

Instituto de Ciências da Terra - Pólo Porto, DGAOT, Faculdade de Ciências, Universidade do Porto, Rua do Campo Alegre 687, 4169-007 Porto, Portugal

Four assemblages of trioctahedral chlorite were identified in the magmatic-hydrothermal system of Borralha (N Portugal): *i*) Fe,Mn-chlorite joined to scheelite I; *ii*) Fe-minerals joined to wolframite + scheelite II ± sulphide; *iii*) Fe,Mg-chlorite joined to molybdenite + bismuthinite, and *iv*) Mg,Fe-chlorite joined to chalcopyrite. Crystal chemistry of Fe-chlorite $(\mathrm{Al}_{3\cdot01}\mathbf{Fe}^{\mathbf{3+}}_{0.25}\mathbf{Fe}^{\mathbf{2+}}_{7\cdot95}\mathrm{Mn}_{0\cdot26}\mathrm{Mg}_{0\cdot19})$ $(\mathrm{Si}_{5\cdot44}\mathrm{Al}_{2\cdot56})_4\mathrm{O}_{10}(\mathrm{OH})_8$ and Fe,Mn-chlorite $(\mathrm{Al}_{2\cdot69}\mathrm{Fe}^{3+}_{0.02}\mathrm{Fe}^{2+}_{7\cdot54}\mathbf{Mn}_{1\cdot08}\mathrm{Mg}_{0\cdot62})(\mathrm{Si}_{5\cdot31}\mathrm{Al}_{2\cdot68})_4\mathrm{O}_{10}(\mathrm{OH})_8$ corresponds to daphnite. Fe,Mg-chlorite $(\mathrm{Al}_{2\cdot89}\mathrm{Fe}^{3+}_{0.24}\mathbf{Fe}^{\mathbf{2+}}_{6\cdot42}\,\mathrm{Mn}_{0\cdot21}\mathbf{Mg}_{2\cdot08})$ $(\mathrm{Si}_{5\cdot31}\mathrm{Al}_{2\cdot79})_4\mathrm{F}_{0\cdot31}\mathrm{O}_{10}(\mathrm{OH})_8$ corresponds to ripidolite and Mg,Fe-chlorite $(\mathrm{Al}_{2\cdot63}\mathrm{Fe}^{3+}_{0.37}\mathrm{Fe}^{2+}_{1\cdot72}\mathrm{Mn}_{0\cdot01}\mathbf{Mg}_{6\cdot40}\,\mathrm{Ca}_{0.26})$ $(\mathrm{Si}_{6\cdot02}\mathrm{Al}_{1\cdot98})_4\,\mathrm{O}_{10}(\mathrm{OH})_8$ to pychnochlorite.

X-ray patterns of chlorite minerals correspond to a typical Fe-chlorite structure, but the 00*l* intensities show a clear difference related to the relative intensities of 00*l* reflection planes. Higher intensities correspond to Fe,Mn-chlorite due to the presence of heavy metals (e.g., Mn) incorporated between the silicate and hydroxide octahedral sheet. The 060 plane occurs at 1.54 Å indicating a trioctahedral structure of chlorite minerals, which belong to the *II*b polytype. The wavenumber, intensity and shape of infrared (IR) spectra chlorite minerals varied with compositional changes in octahedral sheet well documented by electron microprobe analysis. The Si-O stretching vibration plane ($990\ \mathrm{cm}^{-1}$) of Fe,Mn-chlorite is sharper than in Fe,Mg-chlorite.

Fe-oxidation state of chlorite was determined by X-photoelectron spectroscopy (XPS) and calculated for EPMA data. The $\mathrm{Fe}^{3+}/\sum\mathrm{Fe}$ ratio determined on the basis of XPS is relevant, ranging from 0.04 to 0.07 in Fe,Mn-chlorite and from 0.12 to 0.15 in Fe,Mg-chlorite; lower $\mathrm{Fe}^{3+}/\sum\mathrm{Fe}$ values were obtained using the chemical analytical data.

Chlorite geothermometry was determined using the approaches of Bourdelle et al. (2013), Cathelineau (1988) and also, estimated by varying XFe and $\mathrm{Fe}^{3+}/(\mathrm{Fe}^{3+}+\mathrm{Fe}^{2+})$ (Inoue et al.2009). Accordingly, temperature of Fe,Mn-chlorite (scheelite I) formation ranges from 450 to 500 ºC; for Fe-chlorite (Mn-bearing wolframite + scheelite II ± sulphide), temperature conditions vary from 300 to 400 ºC; for Fe,Mg-chlorite (Mo-mineralization) is about 250 ºC and for Mg,Fe-chlorite around to 150 ºC.

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VERY LOW-GRADE METAMORPHISM OF THE PERMIAN VOLCANISM FROM THE APUSENI MOUNTAINS, ROMANIA

Iuliu Bobos (1)*, Mihai Tatu (2), Juliano Senna (1,3), Ionel Nicolae (2), Ioan Seghedi (2)

(1) Institute of Earth Sciences - Porto, Department of Geosciences, Environment and Land Planning, Faculty of Science, University of Porto, Rua do Campo Alegre 687, 4169-007 Porto, Portugal, (2) Institute of Geodynamic of Romanian Academy, Jean-Louis Calderon 19-21, Bucharest,8 Romania, (3) Federal University of Jequitinhonha and Mucuri Valleys, Brasil
*ibobos@fc.up.pt

The Apuseni Mountains represent a broken exhumed fragment from Apulian promontory located between the Pannonian and Transylvanian basins. The Permian bimodal volcanism (mafic and mafic-intermediate rocks intercalated with rhyolitic rocks were pervasively affected by the Alpine dynamic metamorphism. The mafic-intermediate and felsic rocks represent a specific example of an association of bimodal volcanism rocks within a post-collisional extensional setting (Nicolae et al. 2014).

Deformed mafic-intermediate rocks (i.e. lava flows sometimes as pillow of basalts or basaltic andesites, tuffites, rare spilitic dolerites and andesites) collected from the Moma and Dieva nappes and rhyolitic rocks from the Dieva, Finis, Moma and Gârda nappes were studied by optical microscopy, X-ray diffraction (XRD) and electron microprobe analysis (EMPA).

XRD patterns of the <2 μm clay fractions extracted from deformed basalt and doleritic rocks show the presence of chlorite, whereas illite is the dominant mineral in the coarse fractions extracted from deformed rhyolitic rocks. Chlorite Árkai-index (AI) point to from low- to middle anchizonal conditions for the deformed basalt samples.

Chlorite is ubiquitous in all deformed basalts samples, but the composition is different. EMPA show a typical crystal chemistry composition of Fe,Mg-chlorite $(Si_{5{\cdot}75}Al_{2{\cdot}25})(Al_{2{\cdot}32}Fe^{3+}{}_{0.05}Fe^{2+}{}_{4{\cdot}05}Mn_{0{\cdot}02}\,Mg_{5{\cdot}47})O_{10}(OH)_8$ (pycnochlorite) and Mg-Chlorite $(Si_{5{\cdot}58}Al_{2.42})(Al_{2.49}Fe^{3+}{}_{0.12}Fe^{2+}{}_{1{\cdot}88}Mn_{0{\cdot}04}\,Mg_{7{\cdot}15})\ O_{10}(OH)_8$ (ripidolite) in slowly deformed basalt rocks, whereas the Fe-chlorite $(Si_{5{\cdot}77}Al_{2{\cdot}33})\ (Al_{2.10}\,Fe^{3+}{}_{0.00}Fe^{2+}{}_{6{\cdot}85}Mn_{0{\cdot}12}Mg_{2{\cdot}55})O_{10}(OH)_8$ (brunsvigite) variety was found in strongly deformed basalts. Mineral assemblages identified in deformed basalts are characterized by chlorite + epidote ± calcite ± magnetite. Chlorite geothermometer (Bourdelle et al. 2013) estimated a higher temperature at about 230 ºC for brunsvigite variety.

Illite Kübler-index (KI) pointed also for low-anchizonal conditions for deformed rhyolite. The "*b*" cell dimension parameter measured in illite minerals is about 8.98 Å, characteristics of low-pressure. Illite minerals from deformed rhyolitic rocks show an end-member illite with phengitic and no paragonitic composition $[K_{0.83}(Al_{1{\cdot}63}Fe_{0{\cdot}16}Mg_{0{\cdot}26})(Si_{3{\cdot}38}Al_{0{\cdot}62})O_{10}(OH)_2]$. Also, illite + chlorite (<30%) assemblage was identified in the rhyolitic rocks with small amounts of biotite. Crystal chemistry correspond to Mg-chlorite $(Si_{6{\cdot}11}Al_{1.89})\ (Al_{2.38}Fe^{3+}{}_{0.27}Fe^{2+}{}_{1{\cdot}87}Mn_{0{\cdot}06}Mg_{6{\cdot}77})\ O_{10}(OH)_8$ (pycnochlorite), estimating a temperature at about 170 ºC.

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SOME FEATURES OF MONTMORILLONITE'S SAMPLE PREPARATION TO THERMAL ANALYSIS (DSC, DTG, TG)

Julia Bocharnikova (1), Dmitriy Sivkov (1,2), Natalia Boeva (1)*

(1) IGEM RAS, Moscow, 119017, Russia, (2) MSU, Moscow, 119991, Russia

Montmorillonite is a phyllosilicate. A member of the smectite group. This is a 2:1 clay, meaning that it has two tetrahedral sheets sandwiching a central octahedral sheet. It is rock-forming mineral of bentonite. This mineral very well swells in water. Know about the presence and amount of montmorillonite in rocks or soils necessary for geologist and build-engineering. Also important is content of exchangeable cation, because the swelling depend on not only the amount of montmorillonite, but also the composition of exchangeable cations and surrounding solution.

Researches were carried out using he F1 Jupiter STA 449 instrument («Netzsch», Germany) by heating rate 10 K/min in the closed crucibles in the air atmosphere. Samples weight - 40 mg.

In this work different shapes thermal curves (graphs) of montmorillonite were considered. The first endoeffect which is accompanied by the removing free and interlayer water can has a different intensity. Na^+-montmorillonite is able hold a few layers of water. Therefore we unable use this peak for identification montmorillonite and its type. The unification of sample preparation helps researcher to solve the problem. For the comparability of the curves in some laboratories accepted withstand in the constant humidity desiccators over salts or salt solutions, also use heating up to 105 °C.

Due to remove excess water molecule without complete dehydration in our case makes sense saturate water vapour over a saturated solution of K_2SO_4 (p/p_0=0.97). Although, in nature samples admixture of illite are able give dehydration it same temperature range. Micas dehydroxylation occur together montmorillonite dexydroxylation. This in turn prevents applying dehydroxylation data. For differentiation of montmorillonite from others minerals additionally is proposed saturated clay sample of ethylene glycol vapor. As diagnostic sign of montmorillonite is swelling in ethylene glycol, this allows applying this property during analysis of mineral substances. There are serial of endoeffects on a DSC-curve of ethylene glycol removing: the first at the temperature of 180-210 °C, the second and others - 210 to 400 °C, which are responsible to 1) removing free ethylene glycol and 2) collapsing of "ethylene glycol - interlayer exchangeable cation montmorillonite" complex. Using DTG and TG data F. Nieto [1] determined amount of smectite.

Sometimes it is require studying of organic matter in the structure and in this case it is desirable to remove all moisture, but without pre-oxidation. It impossible to dry this sample by heating, to remove water necessary to hold it over P_2O_5 [2]. For comparison needs curves with wet montmorillonite (p/p_0=0.97). During scanning smectite with organic matter you can extract more information by change oxidation to inert atmosphere and by comparing curves. For example, the behavior of the heat flow of amorphous silica saturated ethylene glycol differs from montmorillonite by the presence of endoeffect in Ar-atmosphere and exoeffect in air at the temperature interval 550-650 °C.

Require deflating the air to vacuum sale before start of program. This curve also shows changes which occur in vacuum during heating. As reduction of dehydration endoeffect due to escape of free water or partially to escape of "Na^+-water".

Thus the choice of the mode of sample preparation and scanning atmosphere allows you to differentiate montmorillonite /smectite from others minerals and substances.

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UNIQUE PHOTOPHYSICAL BEHAVIOR OF THIOCYANINE/CLAY HYBRID SYSTEMS

Peter Boháč (1)*, Adriana Czímerová (1), Juraj Bujdák (1,2)

(1) Institute of Inorganic Chemistry, Slovak Academy of Sciences, Bratislava, SK-845 36, Slovak Republic, (2) Department of Physical and Theoretical Chemistry, Faculty of Natural Sciences, Comenius University, Bratislava, SK-842 15, Slovak Republic
*bohac.peter@gmail.com

Hybrid colloidal dispersions based on cationic cyanine dye 3,3’-diethyl-2,2’-thiacyanine (TCy) and three smectites with different layer charge (synthetic saponite (Sap), hectorite (H), and montmorillonite (M)) were prepared and their spectral properties were investigated by absorption and fluorescence spectroscopies. The photophysical properties of hybrids were compared with the properties of dye solutions. The solution of TCy in ethanol is consist mostly of monomers and exhibits a negligible luminescence.

The dye adsorption on smectite particles led to dye aggregation and to the significant changes of its spectral properties. A detailed analysis of absorption spectra based on chemometric methods (principal component analysis and multivariate curve resolution - alternating least squares) [1] revealed a very complex nature of these hybrid systems. The presence of three relevant components (monomeric form, H- and J-aggregates) were identified in all prepared hybrids.

The formation of a high number of J-aggregates in TCy/M lead to the enhancement of fluorescence and to the narrow shape of the fluorescence spectra. Amount of J-aggregates were increased with interaction time, what can be explained by kinetics of the molecular aggregation of cationic dyes on clay surface [2]. With decrease of layer charge of smectites and TCy/clay loading, amount of formed J-aggregates was decreased.

TCy luminescence was significantly enhanced upon the adsorption on Sap surface, but could not be assigned to a J-aggregation. Strong couplings, such as collective exciton delocalization in dye supramolecular systems formed on saponite surface and weak coupling via excitation energy migration and transfer led to the emission spectra, whose profiles did not depend on the excitation wavelengths. Enhanced luminescence could be assigned to the fixation of dye molecules on Sap surface, thus preventing rotational relaxation of the molecules [3].

These colloidal systems are perspective precursors for other hybrid materials.

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CERAMICS APPLICATION OF ALLUVIALS CLAYS FROM NGWENFON (CAMEROON) IN BULDING CONSTRUCTION

Bomeni Isaac Yannick (1)*, Njoya André (2), Wouatong Armand Sylvain Ludovic (1), Ngapgue Francois (3), YongueFouateu Rose (4), Mache Jacques Richard (5), KamgangKabeyene Véronique (6), Fagel Nathalie (7)

(1) Department of Earth Sciences, University of Dschang, P.O. Box 67 Dschang Cameroon, (2) Department of Plastic Artand Art History, Fine Arts Institute of Foumban, P.O. Box 31, Foumban, Cameroon, (3) Department of Civil Engineering, Fotso Victor Institute of Technology, P.O. Box 134 Bandjoun Cameroon, (4) Department of Earth Sciences, University of Yaoundé I, P. O. Box 812 Yaoundé Cameroon, (5) Department of Technical Support, Local Material Promotion Authority (MIPROMALO), P. O Box 2396 Yaoundé, Cameroon, (6) Department of Earth Science, Higher Teacher Training College, P.O Box 47 Yaoundé Cameroon, (7) Department of Geology, University of Liege, 4000, Liege Belgium
*isaacbomeni@yahoo.fr

Our aim is to characterize four types of alluvial clays from the locality of Ngwenfon at 35 kilometers of Foumban (West Cameroon). X-ray diffraction, chemical composition, particle size distribution, organic matter and plasticity have been investigated in raw clay materials in order to test their suitability for building material and firing bricks in particular. Ceramics properties such as linear shrinkage, water absorption, flexural strength, compress strength and mineral neoformations have been also investigated by firing specimen brick at temperature range to 800 °C at 1150 °C. Kaolinite, quartz, goethite, feldspath and illite represent the dominant mineral phases, associated minor contribution of chlorite, gibbsite, anatase and plagioclase. SiO_2, Al_2O_3, and Fe_2O_3 are the main oxides. The physical parameters of alluvial clays display a continuous and wide spread granulometry with relatively high plasticity (from 20 to 60%) and high organic matter contain (from 9 to 13%). A significant densification has been observed from 1000 °C to1150 °C. It is confirmed by the appearance of new mineral phases like mullite, cristobalite and spinelle, responsible for increased mechanical strength and reduced water absorption. Most alluvial clays from Ngwenfon display suitable ceramic properties at sintering range from 1000 °C to 1150 °C. However, the black clays, with their low ceramic properties at 1150 °C, are inappropriate for firing brick production. Indeed, black clays are characterized by a compress strength ≤16,2 MPa, i.e. a value lower than the required value of 20 Mpa for the standard reference NF P 12-021-2.

Keywords: Alluvial clays; Cameroon; Characterization, Ceramic properties, Building construction.

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SIMULATION OF 3D CRACK APERTURE DISTRIBUTIONS USING ^{14}C-PMMA METHOD

Marine Bonnet (1)*, Paul Sardini (1), Laurent Caner (1), Jukka Kuva (2), Marja Siitari-Kauppi (2)

(1) IC2MP, HydrASA, University of Poitiers, France, (2) HYRL, Department of Chemistry, University of Helsinki, Finland
*marine.bonnet@univ-poitiers.fr

The transport properties of geologic materials are strongly affected by their structure which leads to different weathering processes. Fractures control the global mechanical and transport properties of rocks, thus it is of a crucial importance to better understand and characterize them. To this end, a multi-scale approach is needed because of the highly variable spatial, length and aperture distributions of cracks. The present study proposes a novel approach to characterise aperture distribution of fractures.

SEM or X-Ray computed micro-tomography technics are not enough to well-define the aperture distribution of cracks because their aperture vary over several orders of magnitude (from µm to several mm) which is not accessible with these technics [1]. The ^{14}C-PMMA (PolyMethMethylAcrylate) method was chosen to quantify the connected pore network distribution of samples ranging from 1 to 10 cm in size, and at a spatial resolution of pore aperture lower than µm [2]. This method is based on the total impregnation of connected pore space of materials with ^{14}C-doped resin and allows detecting the connected crack network using autoradiography. An autoradiograph is a 2D scale but an estimate of the 3D crack network can be done and be relevant. To this purpose, a series of artificial cracks with a known aperture (ranging from 0 µm to 270 µm) were created [3]. These artificial samples are created between two glass plates spaced thanks to a mylar or Al-foil of varying thickness, imitating the desired aperture. Optical densities extracted from cracks on scanned autoradiographs are converted into activity profiles, allowing the determination of their aperture.

This methodology was applied on cracks perpendicular to the autoradiographic surface, and then on cracks with different tilts to the autoradiographic surface because of the complexity in shape and inclination of cracks in natural materials. The next purpose of this work is to apply this methodology on natural and weathered samples and to establish a link between the mineralogy and porosity evolutions during weathering.

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ADSORPTION OF PRAZIQUANTEL IN LAYERED AND FIBROUS CLAY MINERALS

A. Borrego-Sánchez (1,2)*, E. Carazo (2), C. Viseras (1,2), C. Aguzzi (2), C.I. Sainz-Díaz (1)

(1) Instituto Andaluz de Ciencias de la Tierra, CSIC-UGR. Av. de las Palmeras 4, 18100 Armilla, Granada, Spain, (2) Department of Pharmacy and Pharmaceutical Technology, University of Granada, Campus de Cartuja s/n, 18071 Granada, Spain

Montmorillonite is a dioctahedral 2:1 phyllosilicate with one octahedral sheet and two tetrahedral sheets (T:O:T) per unit cell. A nanometer interlayer space exists between each triple-sheet-layer. These layers have isomorphic substitutions of Si by Al in the tetrahedral sheet and Al by Mg^{2+} in the octahedral layer. An important part of the physicochemical properties of montmorillonite depends on the isomorphic substitutions that confer a negative residual charge compensated by cations in the interlayer space. Therefore, montmorillonite has high adsorption, cation exchange capacity and swelling properties [1]. Majority of the adsorption-desorption phenomena will be carried out in the interlayer space of the clay mineral, where the interlayer cations play an important role.

Sepiolite is a non-planar phyllosilicate with fibrous morphology. The basal oxygen layer is continuous but the apical oxygens undergo a periodic inversion every 8 octahedral positions. This inversion causes a discontinuous octahedral layer forming long channels, where the organics can be adsorbed [2].

The exchange capacity of these minerals makes that it can be used to adsorb and release organic molecules, being good candidates for the design of modified release systems of drugs, such as praziquantel (PZQ) [3]. PZQ is the drug of first choice for an extended parasitic disease, Schistosomiasis, that worldwide affects 250 million people [4].

Complementary theoretical and experimental studies are being carried out to determine the effective possibilities of some clay minerals as nanomaterials for drug delivery purposes. In particular, interaction of different clay minerals with PZQ is being studied; correlating theoretical results with those obtain experimentally.

With these premises, adsorption of praziquantel in both clay minerals has been studied by computational methodologies using atomistic calculations with force fields based on empirical interatomic potentials. The optimization of the adsorption of PZQ in the montmorillonite interlayer and sepiolite channels were performed using the CVFFH force fields. Accordingly to the results, PZQ is likely to be adsorbed in the silicate surfaces.

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BIOPHARMACEUTICAL IMPROVEMENT OF PRAZIQUANTEL BY INTERACTION WITH MONTMORILLONITE

A. Borrego-Sánchez (1,2)*, E. Carazo (2), C. Viseras (1,2), C. Aguzzi (2), C.I. Sainz-Díaz (1)

(1) Instituto Andaluz de Ciencias de la Tierra, CSIC-UGR. Av. de las Palmeras 4, 18100 Armilla, Granada, Spain, (2) Department of Pharmacy and Pharmaceutical Technology, University of Granada, Campus de Cartuja s/n, 18071 Granada, Spain

Praziquantel (PZQ), is the drug of first choice for the treatment of the human schistosomiasis, a parasitic disease which currently affects 250 million people in 74 developing countries, with about a half million deaths per year [1]. PZQ is administered orally, requiring high doses to overcome adverse biopharmaceutical properties, including high lipophilia and intense hepatic first pass metabolism. According to its biopharmaceutical profile, praziquantel is classified as a Class II drug [2], with very low water solubility and high permeability. Therefore, dissolution is the limiting factor for absorption in the gastrointestinal tract. Improvement in aqueous solubility of the drug would reduce the currently high oral doses [3]. Consequently, complementary theoretical and experimental studies with praziquantel and low cost excipients are being carried out by our group [4], with the aim of improve the biopharmaceutical profile of the drug without increase the final cost of the treatments.

Veegum HS® (VHS) is a pharmaceutical grade clay mainly constituted by montmorillonite, a clay mineral able to effectively interact with diverse drugs, modifying their bioavailability, and in some cases increasing drug solubility [5]. Therefore, VHS, with high adsorption and cation exchange capacity and swelling properties is a peculiar nanostructurated material potentially useful as a good nanocarrier to improve the solubility of lowly soluble drugs, as PZQ.

With these premises, aim of this work was to carry out an experimental study of the interaction between praziquantel and montmorillonite. Briefly, a known amount of the drug was dissolved in absolute ethanol and put in contact with the clay during time enough to ensure the adsorption equilibrium. Then, the solvent was evaporated and the resultant PZQ/VHS products characterized by X-ray Powder Diffraction, Differential Scanning Calorimetry, Thermogravimetric Analysis, Fourier Transform Infrared Spectroscopy and Scanning Electron Microscopy. Official dissolution test were then carried out both to determine the possible improvement in drug solubility and/or drug dissolution profiles.

The results showed the effective loading of the drug in the interlayer of the clay mineral as well as the significant increase of dissolution rate of PZQ induced by the interaction with the montmorillonite.

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COMPUTATIONAL STUDY OF THE ETHOMEEN SURFACTANT ADSORPTION IN PHYLLOSILICATES

A. Borrego-Sánchez (1,2)*, M.E. Gómez-Pantoja (3), E. Morillo (3), T. Undabeytia (3), C.I. Sainz-Díaz (1)

(1) Instituto Andaluz de Ciencias de la Tierra (CSIC-UGR), Av. de las Palmeras 4, 18100 Armilla, Granada, Spain, (2) Department of Pharmacy and Pharmaceutical Technology, University of Granada, Campus de Cartuja s/n, 18071 Granada, Spain, (3) Institute of Natural Resources and Agrobiology (IRNAS-CSIC), Reina Mercedes 10. Apdo. 1052. 41080 Sevilla, Spain

Clay minerals, in particular smectites, are low cost materials being abundant in nature. Phyllosilicates have a nanometric interlayer space accessible to water molecules and other compounds. These interlaminar spaces represent about 90% of the mineral total surface yielding a high adsorption capacity for polar molecules. These properties make the phyllosilicates suitable for environmental applications, such as the retention of organics residues in soils, or their use as nanocarriers for controlled release of agrochemicals and also drugs [1,2].

Ethomeen T/15 is a widely used cationic surfactant. Ethomeen T/15 is an amphiphilic molecule that contains both a hydrophobic and hydrophilic part. In addition, surfactant allows preparing aqueous solutions with a high concentration of substances immiscible or partially miscible with water, due to increase their solubilisation. Surfactant molecules can interact with the interlayer space of clays for improving the adsorbent properties of clays, enhancing the adsorption of organic molecules on the montmorillonite surface. Adsorption of Ethomeen T/15 surfactant on montmorillonite showed several loadings due probably to different arrangements within the interlayer space as determined by XRD and FTIR. However, the distribution of the surfactant molecules on the clay surface has still to be elucidated.

The aim of this work was to study the adsorption of the surfactant Ethomeen T/15 onto montmorillonite by combining experimental data with molecular modeling. Specifically, molecular modeling calculations using force fields based on empirical interatomic potentials [3] have been applied to a montmorillonite model with several relative contents of this surfactant and water molecules within the interlayer space. Molecular Dynamics simulations showed that the surfactant molecules are likely to be adsorbed in the interlayer space of montmorillonite as monolayers and bilayers.

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ANTIBACTERIAL ACTIVITY OF LYSOZYME AND AMYLOID FIBRILS IN LAYERED DOUBLE HYDROXIDE NANOCOMPOSITES

Zaineb Bouaziz (1,2)*, Laurence Soussan (1), Jean-Marc Janot (1), Abdesslem Ben Haj Amara (2), Sebastien Balme (1)

(1) Institut Européen des Membranes, UMR5635 UM ENSM CNRS, Place Eugène Bataillon, 34095 Montpellier cedex 5, France, (2) Laboratoire de Physique des Matériaux Lamellaires et Nanomatériaux Hybrides, Faculté des Sciences de Bizerte Université de Carthage, Tunisie

On one hand, lysozyme has been extensively used for studies on adsorption protein. Indeed, it is inexpensive, globular, monomeric protein and often considered as a hard protein model [1]. On the other hand, lysozyme is a well-known antibacterial protein [2]. It also exhibits the ability to form amyloid fibrils at low pH, 75 °C temperature. Actually, we systematically studied the adsorption kinetics of both native lysozyme and amyloid fibrils on LDH materials as well as their antibacterial activity.

These hybrid materials were characterized by X-ray diffraction and Fourier transform infrared spectroscopy, evidencing that adsorption only occurs on the material external surface. Interestingly lysozyme keeps its antibacterial activity under amyloid form even if it is adsorbed on LHD, suggesting that the active site is not denatured and well oriented. This was confirmed by the Trp fluorescence lifetime characterization by time-resolved fluorescence spectroscopy [3]. The Trp lifetimes are indeed similar for native lysozyme and amyloid fibrils either in solution or adsorbed on LDH.

Keywords: Layered double hydroxide (LDH), Lysozyme, Amyloid fibrils, Adsorption, Fluorescence and Antibacterial activity.

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REMOVAL OF Pb(II) FROM LIQUID EFFLUENTS USING RAW AND ACID-ACTIVATED ALGERIAN CLAYS AS ADSORBENTS. A CASE STUDY OF WASTEWATER TREATMENT

Athman Souad, Mohammed-Azizi Fettouma, Boufatit Makhlouf*

Laboratoire d'Electrochimie-Corrosion, Métallurgie et Chimie Minérale, Faculté de Chimie, Université des Sciences et de la Technologie Houari Boumediene (U. S. T. H. B.), B.P.: 32, El-Alia, Bab-Ezzouar, Alger 16111, Algeria
*maboufatit@yahoo.com ; mboufatit@usthb.dz

In this study, samples of raw Algerian clay materials were acid-activated (0.5M HCl). The characteristics were obtained by FTIR, XRF, XRD and SEM. Batch experiments were conducted to assess the removal of Pb(II) ions from effluent discharged from production process of batteries as an industrial liquid effluents and aqueous systems using the raw clay and acid-activated clay materials as adsorbents under different conditions. The effect of factors including pH, contact time and amount of clay on the adsorption properties of Pb(II) were investigated at T= 25 ˚C. The optimum parameters of our study obtained were pH values range: 5 - 6, mass of acid-activated clay: 1g and 12g, shaking time:1h and initial concentration of metal ions:10mg.L^{-1} in aqueous systems and varying in liquid wastes. The obtained results revealed that the removal percentages of Pb (II) ions, from both aqueous solution and liquid wastes, were varying between 90% and 98% for 40 min of contact time and optimal pH values ranged from 5 to 6. The sorption process was examined in terms of its equilibrium and kinetics. The adsorption kinetics fitted well with the pseudo-second order model because of its correlation coefficients (0.99) and good agreement between q_e and q_{exp}.

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ASSESSMENT OF ADSORPTION BEHAVIOUR OF INORGANIC POLLUTANTS IN AQUEOUS SYSTEMS BY USING NEW ALGERIAN CLAY

Mohammed-Azizi Fettouma, Athman Souad, Boufatit Makhlouf*

Laboratoire d'Electrochimie-Corrosion, Métallurgie et Chimie Minérale, Faculté de Chimie, Université des Sciences et de la Technologie Houari Boumediene (U. S. T. H. B.), B.P.: 32, El-Alia, Bab-Ezzouar, Alger 16111, Algeria
*maboufatit@yahoo.com ; mboufatit@usthb.dz

A new sorbent, a natural Algerian material clay from Meniaa (Ghardaia, S. Algeria) has been chemically treated and characterized by XRD, XRF, SEM and FT-IR spectroscopy. This new sorbent material clay was used as adsorbent for removing heavy metal ions such Pb(II), Ni(II), Cu(II) and Zn(II) from aqueous solutions by mean of batch experiments. The sorption process was examined in terms of its equilibrium and kinetics. The best fit was obtained with the pseudo-second order, in the pH range 5 - 6, for the metal ions considered using adsorption method.

Keywords: Natural Algerian clay, XRD, XRF, SEM, FT-IR, Removal, Heavy metal ions, Kinetic

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INTERACTION OF AMMONIUM WITH BIRNESSITE: EVIDENCE OF A CHEMICAL AND STRUCTURAL TRANSFORMATION

Hella Boumaiza (1,2,3)*, Romain Coustel (2), Christian Ruby (2), Latifa Bergaoui (1,3)

(1) Laboratoire de Chimie des Matériaux et Catalyse, Faculté des Sciences de Tunis, Université Tunis El Manar, Tunisia, (2) Laboratoire de Chimie Physique et Microbiologie pour l'Environnement (LCPME)-UMR 7564, CNRS-Université de Lorraine, 405 rue de Vandoeuvre, 54600 Villers-lès-Nancy, France, (3) Département de Génie Biologique et Chimique, Institut National des Sciences Appliquées et de Technologies (INSAT), Université de Carthage, Tunis, Tunisia

In the last decade, some studies showed disparities in the mass balance between measured rates of denitrification and NO_3^- production in Mn-rich media [1-5]. It has been suggested that in addition to existing coupled bacterial nitrification-denitrification and anammox processes, the conversion of combined nitrogen to dinitrogen might take place via chemical process [6,7]. In this study we examined the interaction of a manganese oxide, *i.e.* birnessite, with NH_4^+ by monitoring the solid phase transformation and the species present in solution.

Birnessite is a class of layered manganese oxide widely studied for its ion-exchange properties suitable for battery application. In addition, it has been shown that birnessite is involved in redox reactions in environmental conditions (oxidation of Fe(II) or Cr(III)). In this work we synthesised birnessite by reacting MnO_4^- and Mn^{2+} under alkaline conditions [8] and the product was characterized. The chemical reactivity of birnessite toward NH_4^+ was studied in relation to solution pH, contact time and ammonium concentration. Our results showed that birnessite is not merely a cationic exchanger toward NH_4^+ as it was previously assumed [9] but modifications to the mineral occur in the adsorption process. Depending on ammonium concentration and on the contact time, the structure of the solid and the average oxidation state of the manganese changed. The Infrared and XRD studies show that birnessite structure transformation from triclinic to hexagonal symmetry occurred even in alkaline medium. Moreover, monitoring NH_4^+ removal and total content of nitrogen in the solid showed a nitrogen defect. These observations suggest that a redox reaction took place between birnessite and NH_4^+ inducing chemical and structural solid transformations. Indeed, there was not only a change in the symmetry of the birnessite structure but also an increase in the average oxidation state of the manganese accompanied by a decrease of the measured cationic exchange capacity.

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CHARACTERISTICS AND INDUSTRIAL APPLICATION OF THE LOWER CRETACEOUS CLAY DEPOSITS (BOUHEDMA FORMATION), SOUTHEAST TUNISIA: POTENTIAL USE FOR THE MANUFACTURING OF CERAMIC TILES AND BRICKS

Slim Boussen (1,3)*, Dalel Sghaier (1), Fredj Chaabani (1), Bassem Jamoussi (2), Ali Bennour (3)

(1) Laboratoire de Ressources Minérales et Environnement, Université de Tunis El Manar, Faculté des Sciences de Tunis, Département de Géologie, Campus Universitaire, 2092 Tunis, Tunisia, (2) Laboratoire Central d'Analyses et d'Essais, 1, Avenue Mohamed El Melki, El Omrane 1005, Tunis, Tunisia, (3) Industrial Rocks and Useful Substances Direction, National Office of Mines, Charguia I 3023, Tunisia

The assessment of the possible applications of the Lower Cretaceous clays, belonging to the Bouhedma Formation, as raw materials in ceramic applications, was performed on the basis of the mineralogical, chemical, thermal and physical properties. The characterization was carried out by Atomic Emission Spectrometry (ICP-AES), X-ray diffraction (XRD) and Thermogravimetric-Differential Thermal Analysis (TG-DTA) techniques. Physical properties were determined by specific surface area, particle size distribution, dilatometry and consistency limits. The data showed that these materials were composed of illite, kaolinite, and chlorite and mixed layered clay minerals in variable amounts. Quartz, feldspars and dolomite were also detected. The plasticity presented a medium value; suggesting that these clays are plastic. The firing shrinkage and the expansion were limited. Mixtures of clays were prepared from the Bouhedma clays, and heated to the desired temperature to obtain different earthenware products. Semi-industrial processed mini-bricks revealed promising characteristics and were visibly free of defects. Ceramic tiles had a bending strength complying with the required standards. Therefore, the technological properties of the investigated deposits make the Bouhedma clays suitable for the production of high-quality common bricks.

Keywords: Zemlet El Beidha Cretaceous clays Technological properties Ceramic applications.

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THE PHYSICAL AND MECHANICAL BEHAVIOR OF MASONRY BRICKS CONTAINING CALCINED HYDROXIDE SLUDGES WASTES

Nedjima Bouzidi (1)*, Souad Kherbache (2), Salima Chebbi (1), Aissou Siham (1), Abdelkader Tahakourt (2)

(1) Materials Technology Laboratory of Process Engineering (LTMGP), Department of Technology, University of Bejaia, Targua Ouzemmour Road (06000) Bejaia, Algeria, (2) Laboratory of Construction Engineering and Architecture, Department of Technology, University of Bejaia, Algeria
*nedjima.bouzidi@univ-bejaia.dz

A promising strategy for effectively incorporating metal oxide waste materials (calcined hydroxide sludges wastes (CHS)) into a variety of building materials was examined in this study. Elemental analysis confirmed that chromium, zinc and copper were the predominant metal components in the collected hydroxide sludges. These wastes produced from the unit of cutlery were calcined at 600 °C then mixed with clay to form bricks. The bricks were manufactured using conventional processes. The influence of the amount of CHS (5, 10, 15 and 20%) was evaluated after firing the mixtures at 950 °C for 1 h. The influence of the CHS addition on the linear shrinkage, water absorption, bulk density and open porosity was investigated. Open porosity decreases from 39% with 0% of CHS to 32% with 20% of calcined waste. Moreover, the incorporation of the CHS into the clay mix clearly decreased the linear shrinkage and the water absorption. The compressive strength decreased by a maximum of 10 wt% of CHS giving a value of 33 MPa. The evaluation of the release of various chemical species (Cr^{3+}, Zn^{2+} and Cu^{2+}) contained in the fired bricks by a leaching test indicates successful stabilization of the pollutants.

Keywords: Calcined hydroxide sludges, Bricks, Mechanical properties, Environment, Benificiation.

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STUDY OF MICROSTRUCTURE AND MECHANICAL PROPERTIES OF *HALLOYSITE*-KAOLINITE/BACO$_3$ CERAMIC COMPOSITES

Nedjima Bouzidi (1)*, Djoudi Merabet (1), Raphael Oliveira Nunes (2)

(1) Materials Technology Laboratory of Process Engineering (LTMGP), Department of Technology, University of Bejaia, Targua Ouzemmour Road (06000) Bejaia, Algeria, (2) Federal Center of Technological Education of Minas Gerais, Mechanical Engineering Department, Belo Horizonte, MG, Brazil
*nedjima.bouzidi@univ-bejaia.dz, nedjmabouzidi@yahoo.fr

The objective of this work is to study the microstructure and mechanical properties of ceramic composites based on kaolin naturally rich in kaolinite and halloysite (Djebel Debbagh, northeastern Algeria) associated at various weight ratios of $BaCO_3$ (0, 30, 40 and 60 wt%). The ceramic composites where elaborated by high-energy ball milling and sintered at two different temperatures (1100 °C and 1200 °C) during 3 hours. The results show that the intensity of the (001) peak of kaolinite and halloysite diminished as the amount of $BaCO_3$ is increased. When sintered at 1200 °C without the addition of $BaCO_3$ the material is composed mainly of mullite, whereas this phase disappears when $BaCO_3$ is added. XRD of the samples shows that they were mainly composed by hexacelsian ($BaAl_2SiO_6$ and $BaAl_2Si_2O_8$) when sintered at 1100 and 1200 °C, however, when the amount of $BaCO_3$ exceeds 50 wt% these two phases disappear in favor of apparition of barium aluminum and barium silicate phases. Porosity of the sintered samples increases with $BaCO_3$ contents. The microhardness was found to be affected when porosity of the samples is enhanced. However, when the amount of $BaCO_3$ is 30 wt%, porosity of composites decreases from 0,7 to 0.1% and the microhardness increases from 7 to 8 GPa respectively at 1100 and 1200 °C. The improvement of the mechanical properties was directly related to the amorphous phase content.

Keywords: Halloysite, Kaolinite, Barium carbonate, Hexacelsian, Mechanical properties.

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AGE, DURATION AND ORIGIN OF SKARN TYPE IRON MINERALIZATION, BIZMISEN-ERZINCAN, EAST-CENTRAL TURKEY: CONSTRAINTS FROM CLAY MINERALS

Ömer Bozkaya (1)*, Gülcan Bozkaya (1), Hüseyin Yilmaz (2), Deniz Hozatlioğlu (3), David A. Banks (4), Adrian J. Boyce (5)

(1) Department of Geological Engineering, Pamukkale University, 20070 Denizli, Turkey, (2) Department of Geophysical Engineering, Cumhuriyet University, 58140 Sivas, Turkey, (3) Department of Geological Engineering, Cumhuriyet University, 58140 Sivas, Turkey, (4) School of Earth and Environment, University of Leeds, LS2 9JT Leeds, UK, (5) Scottish Universities Environmental Research Centre, East Kilbride, G75 0QF, UK

In east-central Turkey, Paleocene-Eocene (42-46 Ma) [2] plutonic rocks (diorite, quartz diorite) were intruded into Triassic-Cretaceous limestones and Upper Cretaceous ophiolitic rocks producingskarns, (garnet, diopside, epidote, scapolite and tremolite), iron mineralization and clay-bearing alteration zones (argillic alteration). The Bizmişen skarn-type iron deposit is one of the major operating mines in this region of Turkey [1]. Clay/phyllosilicate-bearing rocks and separated clay mineralswerestudied by textural (optical and electron microscopy), mineralogical (X-ray diffraction) and geochemical (major/trace elements, stable and radiogenic isotopes, ICP-MS) methods. Hydrothermally alteredrocks contain mainly quartz, calcite, dolomite, feldspar and clay/phyllosilicate minerals. Clay/phyllosilicate minerals comprise dioctahedral (smectite, kaolinite, mixed-layered illite smectite/I-S andillite) and trioctahedral (vermiculite, serpentine/chrysotile, talc and chlorite) composition. Na- and Ca-smectite and kaolinite are developed at diorite-limestone contact and within the diorite body. However, at the diorite-ophiolite contact the alteration mineralogy consists of vermiculite, serpentine/chrysotile, talc and chlorite were, indicating the distributions of clay/phyllosilicate mineral composition are influenced primarily by the host-rock composition. Kaolinite and I-S (I_{75}-S_{25}, R1 ordering) have 1*M* (one-layer monoclinic) and $1M_d$ (one-layer monoclinic, disordered) polytypes, respectively, indicating low-temperature (< 200 ºC) conditions. Optical and electron microscope dataof kaolinite, smectite and I-S indicate completely hydrothermal (neo-formation) origin without any detrital input. Major and trace element compositions of smectite, kaolinite and I-S have a composition between diorite and ophiolite, but relatively close to diorite composition. Chondrite-normalized rare earth element (*REE*) data of clays show distinct enrichments with respect to chondrite, increasing from kaolinite (5-10 times) to smectite (10-100 times), together with the decreasing temperature conditions. Stable isotope data ($\delta^{18}O_{V\text{-}SMOW}$ and $\delta D_{V\text{-}SMOW}$) of clay minerals indicate 100-200 ºC for smectite, in the supergene or low-grade argillic zone, whereas in excess of 200 ºC for I-S and kaolinite, in the hypogene or high-grade argillic zone. Fluids in isotopic equilibrium with the measured values, using the average values for fluid-inclusion homogenization temperatures [4], indicate magmatic waterdominance. This magmatic association is further reflected in calculated fluid $\delta^{18}O$ and δD data in quartz, $\delta^{13}C$ and $\delta^{18}O$ data of calcite and $\delta^{34}S_{V\text{-}CDT}$ data of pyrite and chalcopyrite, all of which reflect a strong magmatic influence which are also indicative of magmatic source. Ar/Ar total gas age data of I-S samples are consistent with argillic alteration starting in the Upper Eocene, 10 Ma after the plutonic intrusion, and continuedto the uppermost Oligocene, with duration of approximately 12 Ma. The data show that hydrothermal clays were formed from magmatic fluids in a hydrothermal system that persisted for an extended period well after the intrusion of the igneous body, thus perhaps constraining how long hydrothermal systems are required operate to produce major areas of mineralization.

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FIRST DISCOVERY OF LATE DEVONIAN-EARLY CARBONIFEROUS K-BENTONITES IN CENTRAL TAURIDES, SOUTHERN TURKEY

ÖmerBozkaya (1)*, Mehmet Cemalgöncüoğlu (2), Asuman Günal-Türkmenoğlu (2), Cengiz Okuyucu (3), ÖzgeÜnlüce-Yücel (2), Ömer Faruk Özkaya (4), İrem Alköse (4)

(1) Department of Geological Engineering, Pamukkale University, 20070 Denizli, Turkey, (2) Department of Geological Engineering, Middle East Technical University, 06531 Ankara, Turkey, (3) Department of Geological Engineering, Selçuk University, 42250 Konya, Turkey, (4) Graduate School of Sciences, Pamukkale University, 20070 Denizli, Turkey

Five thin (5-15 cm) and yellowish green tephra (K-bentonite) layers are exposed within the Late Devonian-Early Carboniferous red dolomite-dolomitic limestone succession of the Aladağ Unit (northerly allochthonous unit of Tauride Belt) in southern Turkey. K-bentonite layers are discovered in the Engilli and Harlak areas, located at 10 km southeast of Akşehir district (Konya). The aim of the study is to determine mineralogical and geochemical characteristics and to interpret the magmatic originand diagenetic history. In this context, K-bentonite and host-rock samples are studied by optical and scanning electron microscopy (SEM), X-ray diffraction (XRD) and Inductively Coupled Plasma-Mass Spectrometer (ICP-MS) methods. The host rocks are characterized by coarse-crystalline dolomite and calcite crystals with mosaic texture indicating high-grade diagenetic/very low-grade metamorphic progress. K-bentonites exhibit typical porphyritic texture with euhedral plagioclase phenocrystals (pseudomorph) replaced by fine-grained white K-micas (i.e., sericite) and sparrydolomite crystals. Volcanic matrix has vitrophyric texture and contains hydroxidized (limonitized) euhedral pyrite crystals.

Illite is the single clay mineral in all K-bentonite samples, as non-clay minerals; dolomite, calcite, quartz, pyrite and zircon are found. Illites have leaf-like flakes (1-4 µm sizes) showing well-developed orientations and slaty cleavage. Kübler index [1] values (KI, $\Delta°2\theta$) of illites reflect high-grade diagenesis for Engilli area, whereas anchizoneconditions indicative for temperatures up to 200 °C [2] are identified for Harlak area. The swelling (or smectite) component (<3%) and crystallite size (N = 10-90 nm) values of illites in K-bentonites from both areas are also compatible with KI data. Illite d_{060} values (1.4990-1.5007 Å) correspond to a range of octahedral Mg+Fe values of 0.27-0.35 atoms per formula unit (the composition between muscovite and phengite end-members). Illitepolytypes are characterized by the association of $2M_1$ (30-45%), $1M$ (13-53) and $1M_d$ (17-55%). The dominance of $1M$illites despite anchi-epizonal conditions is also indicative for volcanic origin [3].

Immobile element compositions of K-bentonites suggest that tephras have been derived from trachyandesitic volcanism for Engilli area, from rhyodacite/dacite composition for Harlak area. Both occurrencesare completely different fromLate Devonian-Early Carboniferous K-Bentonites from Northwestern Turkey [4,5]. Chondrite-normalized rare earth element (*REE*) distributions of K-bentonites have negatively sloping curves and exhibit an enrichment of light rare earth elements. However, the tephras of the Harlak area are relatively more enriched than tephras of the Engilli area. The negative Eu anomaly, related to the removal of Eu by plagioclase fractionation in the source melt, is observed in both areas. Mineralogical-chemical data point out that K-bentonites evolved in anchizonal conditions (approximately 200 °C) from the products of volcanic eruptions of disputed sources and distances during the Late Devonian time, possibly related to Variscan orogeny in Europe.

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ORGANIC MATTER REFLECTANCE AND CLAY MINERALOGICAL EVIDENCES FOR OROGENIC EVENTS: EXAMPLES FROM VERY LOW-GRADE METAMORPHIC SEQUENCES IN SOUTHERN AND NORTHWESTERN TURKEY

Ömer Bozkaya (1)*, Rafael Ferreiro Mählmann (2), Hüseyin Yalçin (3), Mehmet Cemal Göncüoğlu (4)

(1) Department of Geological Engineering, Pamukkale University, 20070 Denizli, Turkey, (2) Technische Universität Darmstadt, Technical and Low Temperature Petrology, Institut für Angewandte Geowissenschaften, 64287 Darmstadt, Germany, (3) Department of Geological Engineering, Cumhuriyet University, 58140 Sivas, Turkey, (4) Department of Geological Engineering, Middle East Technical University, 06531 Ankara, Turkey

Diagenetic to very low-grade metamorphic characteristics of the Palaeozoic sedimentary rocks of tectonostratigraphic units from northern (Istanbul-Zonguldak Terrane, IZT) and southern (Geyikdağı Unit, GDU of the Taurides) Turkey were investigated by textural-mineralogical and organic petrographic methods. In this context, textural (fabric), mineralogical (clay mineral associations, illite Kübler Index (KI), polytype, b-cell dimension) and organic matter (vitrinite, vitrinite like solid bitumen, bitumen and graptolite) reflectance (OMR) studies were performed on the organic matter-rich samples and correlated with each other. OMR values indicate bituminous coal to anthracite ($\%R_{max}$ = 0.67 to 3.61) for Silurian-Carboniferous sequence from IZT. Mean bireflectance ($\Delta\%R_{max}/R_{min}$) values of Silurian units (0.62-1.37) are anomalously higher than those of Devonian units (0.067-0.11), indicating higher tectonic impact for pre-Devonian units and therefore diagenetic/metamorphic hiatus between Silurian and Devonian rocks. The same was previously confirmed by KI and b-cell dimension data of illites [1]. In the GDU, OMR values ($\%R_{max}$) from Permian samples of the high volatile bituminous coal stage increase from 1.02%, (according to KI = low-grade diagenesis) to 6.05$\%R_{max}$ of the anthracite/meta-anthracite stage in Ordovician samples (according to KI = anchizone/epizone). $\Delta\%R_{max}/R_{min}$ values increase with increasing OMR values from 0.066 (Permian) to 4.33 (Ordovician), reflecting higher strain and probably pressure conditions towards older units. The temperature conditions, roughly estimated through vitrinite reflection data with a simple model [2] critical discussed [4,5], correspond to 150 ºC for Permian and 335 ºC for Ordovician rocks. OMR values increase together with increasing temperature and pressure toward older units, in accordance with textural (fabric) and mineralogical (KI, polytype, b-cell dimension) data. According to KI and OMR$\%R_{max}$ values of 3.7 and 5.6 grade of metamorphism corresponds to the diagenesis-anchizone and anchizone-epizone boundaries, respectively. These values are close to values of 3.0 and 6.0 as proposed by [4,5]. OM bireflectance values increase in the samples with anthracitic stage, and reach their maximum in samples with slaty cleavages. The temperature difference determined for Permian and Ordovician units points to high geothermal gradients of 50-55 ºCkm^{-1} for a 3500 m thick succession. Contrary discontinuous maturity detected by OM studies (sudden changes in OMR) along the sedimentary sequence indicates older orogenic events in the stratiform older sedimentary section and a diagenetic/metamorphic jump reflecting a sedimentary hiatus [1,3]. The obtained data show that the new organic petrographic study corroborates clay mineral and facies critical mineral results to elucidate the thermo-tectonic history. Both, organic and inorganic data are important for a better determination of the geological evolution of old and thick sedimentary sequences and increasing the probability of the thermal model adapted [4].

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BEHAVIOR OF TALC AND MICA IN COPPER FLOTATION

Saeed Farrokhpay, Bulelwa Ndlovu, Dee Bradshaw

The University of Queensland, Brisbane, QLD 4068, AUSTRALIA

Talc and mica are major gangue minerals. Talc is naturally hydrophobic and therefore it is easily floatable. There have been many studies to overcome this problem and depress talc with various reagents. However very little know about the source of its deleterious effect in flotation. In this work, the effect of talc on the flotation of a copper ore was studied and the mechanisms and critical concentration is discussed. It was found that talc affect the copper flotation mainly via froth phase. The copper grade and recovery are both affected in the presence of only 7% talc. On the other hand, muscovite (a mica type clay) affects the pulp phase via affecting the pulp rheology. The copper flotation grade is reduced in the presence of relatively high amount (i.e. 30%) of muscovite due to the entrainment, but its effect on the copper recovery is negligible.

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CLAY POLYMER COMPOSITES FOR SUSTAINED RELEASE, ANTIMICROBIAL WOUND DRESSINGS

Chris Breen (1)*, Francis Clegg (1), Neil Bricklebank (2), Louise Freeman-Parry (2), Keith Miller (2), Lukas Petra (3)

(1) Materials and Engineering Research Institute, Sheffield Hallam University, Sheffield, S1 1WB, UK, (2) Biomolecular Sciences Research Centre, Sheffield Hallam University, Sheffield, S1 1WB, UK, (3) Institute of Inorganic Chemistry, Slovak Academy of Sciences, Bratislava, Slovakia

Wound infections are a very common healthcare problem and can lead to significant morbidity and mortality. Historically, antimicrobial agents such antiseptics, disinfectants, topical and systemic antibiotics have been used to treat wounds. The use of many of these agents has declined due to concerns about antimicrobial efficacy and potential toxicity to wound tissue. Routine use of topical and systemic antibiotics to treat wound infection is not usually recommended because of the risk of developing bacterial resistance.

The novel wound dressing material described here is based on a polymer-clay composite, which exhibits a significant advantage in that it shows a gradual and sustained release of the antimicrobial agent over 5-7 days, whereas its release from comparative dressings is complete within 24 hours [1]. The material has demonstrated *in vitro* activity against a range of common bacteria including Staphylococcus Aureus (*S. aureus*), Escherichia Coli (*E. Coli*), and Pseudomonas Aeruginosa (*Pseudo A.*), extending for up to 7 days. The clay composite dressing was most effective against Staphylococcus Aureus so it was tested against Methicillin Resistant Staphylococcus Aureus (MRSA), an ongoing challenge to the UK's National Health Service (NHS). The dressing were shown to be active *in vitro* against two strains of hospital acquired MRSA and a strain of community acquired MRSA. The dressing continues to kill MRSA for at least 5 days, which is an extremely useful result. The longer lived activity offers the potential to reduce costs to the NHS and to provide immediate and longer-lived treatment, to those injured as a result of disasters in remote locations.

The longer term kill data was obtained by transferring a given dressing to a new microbe-laden agar after each 24 hour period - known as a passage test. A particularly common feature of the activity observed, against all the pathogens tested, was that the maximum effectiveness was not immediate but peaked at 48 hours.

In this contribution, the influence of different amounts (≤ 20 wt%) of a commercially available bentonite of high purity, selected exchange cations (Na^+- or Ca^{2+}-) and a synthetic hectorite, Laponite® (Registered trademark of BYK Additives) on the nature of the time/kill studies will be presented and discussed.

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OPTICALLY ANISOTROPIC COATINGS MADE BY ENCAPSULATING DYES IN CLAY DOUBLE STACKS

Kevin Ament (1), Matthias Stöter (1), Bernhard Biersack (2), Sabine Rosenfeldt (3), Markus J. Leitl (4), Hussein Kalo (1), Rainer Schobert (2), Hartmut Yersin (4), Geoffrey A. Ozin (5), Stephan Förster (3), Josef Breu (1)*

(1) Bavarian Polymer Institute and Inorganic Chemistry I, University of Bayreuth, 95440 Bayreuth, Germany, (2) Organic Chemistry I, University of Bayreuth, 95440 Bayreuth, Germany, (3) Physical Chemistry I, University of Bayreuth, 95440 Bayreuth, Germany, (4) Physical Chemistry, University of Regensburg, 93053 Regensburg, Germany, (5) Department of Chemistry, University of Toronto, M5S 3H6 Canada
*josef.breu@uni-bayreuth.de

The strict alternation of two different types of interlayer cations in layered materials, e.g. layered silicates, is called ordered interstratification and represents an ordered one dimensional (1D) heterostructure. These can be utilized as a system with two separated nanoreactors [1] or can be further processed to giant Janus platelets [2] or double stacks for the oriented encapsulation of organic molecules.[3]

For synthetic Na-hectorites with superb homogeneity of the charge density,[4] the 1D heterostructures represent the thermodynamic product of a partial cation exchange e.g. of a cationic dye, and can thus be made quantitatively with high precision: Due to the pronounced differences in basal spacings of hydrated Na^+- and dye-interlayers, the dominant Coulomb attraction between positive interlayer and negative silicate layer strongly favours segregation of the organic cations into separate, highly hydrophobic interlayers. The segregated densely packed dye interlayers will, however, have a charge density deviating from the charge density of the clay host. According to Pauling's rules, in ionic crystals (and an intercalation compound represents a one-dimensional ionic crystal) electroneutrality has to be achieved by local charge compensation. Thus, once nucleation has started with the first densely packing dye-interlayer, a local charge balance can only be realized by arranging a higher Na^+-cation density in both adjacent interlayers. This way a single exchanged interlayer can act as a nucleus for an 1D ordered domain eventually stretching over the complete stack [1,5,6].

Here we present a 1D heterostructure of a fluorescent stilbazolium dye and Na^+ made according to the sketched route. Addition of water selectively delaminates the heterostructure along the Na^+ interlayers by osmotic swelling [7] while the dye interlayers remain unaffected. As a result, an aqueous suspension of well dispersed clay double stacks is obtained with highly hydrophobic organic molecules sandwiched in between two, one nanometer thick, silicate layers. This approach not only allows for dispersion of hydrophobic molecules in water, but also improves the chemical, photochemical and thermal stability of organic dyes. Surprisingly, encapsulation of the dye increases the quantum yield compared to the bromide salt of the dye. Moreover, the confined space of the interlayer, forces fluorescent molecules into an ordered orientation between the layers leading to the polarized emission of light [8]. Due to their huge aspect ratio (>1000), the double stacks can be compounded into polymer matrices and assembled into textured films on planar substrates. Polarized UV/Vis spectra indicate that the optical anisotropy and thus the orientation of the dye are preserved in the films. This might be applicable in organic solar cells, where the controlled arrangement of molecules is of great importance.

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FROM CLAY POWDERS TO LIQUID CRYSTALLINE PHASES

ANDREAS EDENHARTER (1), SABINE ROSENFELDT (2), MATTHIAS STÖTER (1), MATHIAS SCHLENK (2), THOMAS MARTIN (1), RODRIGO QUEIROZ ALBUQUERQUE (3), STEPHAN FÖRSTER (2), JOSEF BREU (1)*

(1) Bavarian Polymer Institute and Inorganic Chemistry I, University of Bayreuth, 95440 Bayreuth, Germany, (2) Physical Chemistry I, University of Bayreuth, 95440 Bayreuth, Germany, (3) São Carlos Institute of Chemistry, University of São Paulo, 13560-970 São Carlos, Brazil
*josef.breu@uni-bayreuth.de

Delamination is a key step to obtain individual layers from inorganic layered materials needed for fundamental studies and applications [1,2,3]. For layered van der Waals materials such as graphene, the adhesion forces are small, allowing for mechanical exfoliation, whereas for ionic layered materials such as layered silicates, the energy to separate adjacent layers is considerably higher. Quite counter intuitively, we show for a synthetic layered silicate ($Na_{0.5}$-hectorite) that a scalable and quantitative delamination in water by simple hydration is possible for high and homogeneous charge density, even for aspect ratios as large as 20000 [4,5,6]. The superb and homogeneous intracrystalline reactivity of this hectorite allows for subsequent step-wise hydration by simply adding increasing amounts of water to the as synthesized powder.

In conclusion we show that the delamination of charged layers requires that the layer separation exceeds the Gouy-Chapman length ($h>2l_{GC}$) such that interactions between adjacent layers become repulsive, leading to osmotic swelling. In the electrostatically attractive regime ($h \sim l_{GC}$) layer separation occurs by discrete hydration steps. During initial steps of osmotic swelling the classical double layer structure consisting of an inner and outer Helmholtz plane followed by a diffuse double layer is established. Upon further hydration up to 34 nm there is a regime of strong osmotic-repulsion (Gouy-Chapman regime), where the layers form a highly ordered one-dimensional Wigner crystal. Up to eight higher-order reflections indicate excellent positional order of individual layers. When the interlayer distance reaches the Debye-length, a new regime with screened osmotic repulsion is entered, accompanied by a melting of the Wigner crystal and formation of a first microscopically phase separated system. The layers become weakly charge-correlated, which is indicated by fulfilling the classical Hansen-Verlet and Lindeman criteria for melting. Furthermore, this diluted liquid crystalline phase has peculiar flow behaviour. Dependent on the layer separation, flow through a narrow microfluidic channel will lead to reorientation of the platelets perpendicular to the flow direction. Macroscopic phase separation by gravitation does not set in until much lower concentrations ($\phi <0.0015$). At very low concentrations ($\phi <\sim 0.0001$) finally a dilute isotropic phase is reached.

Expanding swelling experiments to water/solvent mixtures allows for fine-tuning of solvent properties simply by varying its composition. Surprisingly, we observed discrete crystalline swelling steps extending all the way up to 3.5 nm, while in water osmotic swelling sets in at basal spacings >1.5 nm. Typically, at water contents >30 vol% osmotic swelling to a gel sets in for these water/solvent mixtures. We provide insight into the requirements for layer separation and controlling the layer distances and outline an important pathway for the integration of layers into devices for advanced applications [7,8,9].

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SPRAY COATING OF LARGE AREA SMECTIC LIQUID CRYSTALS FOR ULTRA HIGH GAS BARRIERS

Christoph Habel (1), Michael Möller (1), Patrick Feicht (1), Daniel Kunz, Jasmin Schmid (1), Evgeny Tsurko (1), Matthias Stöter (1), Kalo Hussein (1), Elena Doblhofer (2), Sabine Rosenfeldt (3), Thomas Scheibel (2), Josef Breu (1)*

(1) Bavarian Polymer Institute and Inorganic Chemistry I, University of Bayreuth, 95440 Bayreuth, Germany, (2) Biomaterials, University of Bayreuth, 95440 Bayreuth, Germany, (3) Physical Chemistry I, University of Bayreuth, 95440 Bayreuth, Germany
*josef.breu@uni-bayreuth.de

Ultrahigh gas barrier systems for packaging of flexible optoelectronic devices like organic photovoltaics and organic light-emitting diodes require transmission rates for oxygen (OTR) and water vapor (WVTR) of less than 10^{-5} $cm^3/(m^2$ day bar) and 10^{-6} $g/(m^2$ day), respectively [1]. The Cussler model describes the dependence of the transmission rate on the filler content and the aspect ratio of the filler [2].

An expeditious melt synthesis of a phase pure sodium hectorite $[Na_{0.5}]^{inter}[Mg_{2.5}Li_{0.5}]^{oct}[Si_4]^{tet}O_{10}F_2$ yields large tactoids of up to 20 µm in diameter [3,4]. The superior charge homogeneity of this material allows for swelling and quantitative delamination into individual platelets with aspect ratios of up to 20 000 [5,6,7].

For ultra high gas barrier systems perfect alignment of the filler platelets into a textured nanocomposite film is indispensable as it increases the tortuous path length according to Cussler. If on top of the alignment, the filler platelets can be arranged equidistant into a one-dimensional (1D) crystalline, smectic liquid crystalline film it is expected that the Coulomb interactions are amplified by 39% (Madelung factor) which will help to reduce the free volume and thus reduce permeability further.

We first observed such a 1D-crystallinity in a waterborne spider silk/clay nanocomposite made by sedimentation. Although this film still swells to some degree at elevated relative humidity (rh), it surprisingly shows a small water vapour permeability indicating severely restricted water diffusivity [8].

The crystallinity of such composite films can be improved a great deal by spray coating. This processing yields large area liquid crystalline, smectite composite films. Up to four higher-order reflections indicate excellent positional order of individual layers separated by the polymer matrix.

For such liquid crystalline nanocomposite films of a water soluble ethoxylated polyethylenimine/polyacrylic acid polymer, transmission rates of 10^{-4} $cm^3/(m^2$ day bar) and 10^{-4} $g/(m^2$ day) were observed for OTR and WVTR at 23 °C and 50% rh, respectively [9]. Clearly, the quality of the liquid crystallinity is responsible for the superb barrier performance as less ordered films made by doctor blading show transmission rates inferior by 2 orders of magnitude.

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CO_2 SELECTIVE GATE-OPENING BY FREEZING ROTATIONAL DYNAMICS IN MICROPOROUS ORGANICALLY PILLARED LAYERED SILICATES (MOPS)

Martin Riess (1), Kilian Bärwinkel (2), Markus M. Herling (1), Hiroshi Sato (3), Liangchun Li (4), Yamini S. Avadhut (2), Tobias W. Kemnitzer (2), Hussein Kalo (1), Jürgen Senker (2), Ryotaro Matsuda (4,5), Susumu Kitagawa (4), Josef Breu (1)*

(1) Bavarian Polymer Institute and Inorganic Chemistry I, University of Bayreuth, 95440 Bayreuth, Germany, (2) Inorganic Chemistry III, University of Bayreuth, 95440 Bayreuth, Germany, (3) Department of Chemistry and Biotechnology, School of Engineering, The University of Tokyo, 113-8656 Tokyo, Japan, (4) Institute for Integrated Cell-Material Sciences (WPI-iCeMS), Kyoto University, 615-8510 Kyoto, Japan, (5) Department of Applied Chemistry, Graduate School of Engineering, Nagoya University, 464-8603, Nagoya, Japan
*josef.breu@uni-bayreuth.de

Gas capture, separation and storage are key processes for both, an energy efficient and sustainable manufacturing of bulk chemicals and for carbon-neutral energy cycles. In this context, selective gate-opening in flexible microporous frameworks represents one of the most attractive mechanisms for CO_2 capture applying pressure swing cycles. In conventional gate-opening in metal-organic frameworks (MOFs), the additional adsorption capacity is realized by macroscopic volume changes and thus creates mechanical stress on the framework which is a serious limitation.
While pillaring of natural clays [1] yields porous materials with wide pore size distributions [2], with synthetic, charge homogenous clays narrow, zeolite-type pore size distributions are obtained.[3-6] The intercalation of cationic molecules, such as organocations or metal complexes, in synthetic layered silicates provides access to a largely unnoticed class of microporous hybrid materials. These so called Microporous Organically Pillared Layered Silicates (MOPS) integrate the concepts of functional porosity and component modularity with a continuous porosity tuning in the sub-Ångström range [7,8]. Tuning the pillar density of MOPS allows for optimization of guest recognition without the need of exploring different framework topologies [6,8]. It was found, that MOPS are capable of discriminating very similar gases (CO_2/C_2H_2 or CO/N_2) by a new selective gate-opening mechanism [9,10]. The additional adsorption capacity is, contrary to conventional gate-opening in MOFs, realized without macroscopic volume changes solely through quenching pillar dynamics, thus avoiding mechanical stress on the framework. The mechanism is restricted to CO_2 and CO and is not observed for C_2H_2 or N_2. Moreover, we found that the mechanism underlying the additional CO_2 adsorption and the total adsorption capacity beyond gate-opening pressure can be altered by tuning the charge density of the host layers. A decrease of the pillar density entails, that simultaneously the Coulomb attraction of cationic interlayer space and anionic host layers is reduced, which modifies the gate-opening mechanism to a conventional structural gate-opening involving an increase in volume.
Systematic variation of charge density of the host, equivalent area of the molecular pillar and their chemical functionality are the building blocks for a straightforward rational design of microporous materials optimized for CO_2 capture or tailored for separation of various industrially relevant gas mixtures.

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NATURE AND ORIGIN OF NATURAL Zn CLAY MINERALS FROM THE BOU ARHOUS ZN ORE DEPOSIT

Buatier Martine (1), Choulet Flavien (1), Petit Sabine (2), Chassagnon Rémi (3), Vennemann Torsten (4)

(1) Chrono Environnement UMR CNRS 6249, Université Bourgogne-Franche Comté, 16 Route de Gray Besançon, France, (2) Institut de Chimie des Milieux et Matériaux de Poitiers (IC2MP) UMR 7285 CNRS - Université de Poitiers - 4, rue Michel Brunet, 86073 Poitiers cedex 9, France, (3) Laboratoire Interdisciplinaire Carnot de Bourgogne, UMR 6303 CNRS-Université de Bourgogne Franche-Comté, 9 Av. A. Savary, BP 47870, F-21078 Dijon Cedex, France, (4) Institut des dynamiques de la surface terrestre, Université de Lausanne, Bâtiment Géopolis, Lausanne, Suisse

Zn-clay minerals have been found in the non-sulfide deposit of Bou Arhous (High Atlas, Morocco). They occur as white or ochre clays embedding willemite (Zn_2SiO_4) and are commonly associated to red detrital clays in karstic cavities. Scanning Electron Microscopy (SEM), X-Ray Diffraction (XRD) and Transmission Electron Microscopy (TEM) with Energy Dispersive X-ray (EDX) analyses were combined in order to characterize the clay minerals and to determine the mechanism of their formation.

XRD patterns on oriented and powdered clays and Fourier Transform InfraRed (FTIR) spectroscopic analyses suggest that fraipontite is the major Zn clay phase (with some smectite interstratifications). SEM observation (back-scattered electron mode) shows that Zn clays are closely associated to willemite; euhedral willemite crystals show partial dissolution that preferably affects edges adjacent to newly formed fraipontite. Zn clays are also present as aggregates of about 50 microns, filling the porosity or pervading the detrital clays. Intimate mixtures of Zn clays with detrital micas can also be observed. TEM-EDX analyses were carried out on clay separates but also on TEM foils prepared by Focused Ion Beam (FIB) milling directly on the thin section. Low- and high-resolution transmission electron microscopy images were acquired on selected areas preserving the texture of the sample. Two types of textural sites were selected: the Zn clay aggregates filling the porosity and the detrital clays partially replaced by Zn clay minerals. STEM-EDX map and point analyses confirm the occurrence of fraipontite. Individual particles of clay minerals with about 10% of Zn were analyzed. Structural formulae support the presence of a trioctahedral TO clay mineral like fraipontite. In the analyzed aggregates, the clays are composed of crystals of about 0.5-1 µm in diameter and 10 to 100 nm in thickness. At high magnification, the 0.7 nm layer periodicity was clearly imaged. Double layer periodicity is also common. In some fraipontite crystals, some intercalations with 1 nm layer were imaged. Stable isotope measurements suggest that this Zn clay mineral formed by direct precipitation of fluids which could be meteoritic and/or hydrothermal.

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THE EFFECT OF DYE SURFACE CONCENTRATION ON ENERGY TRANSFER IN HYBRID COLLOIDS WITH SAPONITE

Juraj Bujdák (1,2), Silvia Belušáková (1), Virginia Martinez-Martinez (3), Inigo Lopez Arbeloa (3)

(1) Comenius University in Bratislava, Department of Physical and Theoretical Chemistry, Faculty of Natural Sciences, 842 15 Bratislava, Slovakia, (2) Institute of Inorganic Chemistry, Slovak Academy of Sciences, 845 36 Bratislava, Slovakia, (3) Molecular Spectroscopy Laboratory, Departamento Química Física, University of the Basque Country UPV/EHU, P.O. Box 644, 48080, Bilbao, Spain

The photophysical interaction between cationic dyes, rhodamine 6G (R6G) and oxazine 4 (Ox4), was investigated in colloidal dispersions of a synthetic saponite (Sumecton from Kunimine Ind., Japan). Although R6G molecules were preferentially excited, emission from Ox4 was detected proving occurrence of Förster resonance energy transfer (FRET) between the dye molecules. Highly efficient FRET took place even at relatively low dye concentrations. FRET efficiency was investigated using steady-state and time-resolved fluorescence (TRF) spectroscopies. FRET yields from R6G to Ox4 increased with the dye surface concentration, which could be controlled by an appropriate selection of dyes/Sap loading. The FRET yields determined from the spectral data were best predicted using a model based on probability density functions describing the distances between the energy donor and energy acceptor molecules. The theoretical model and experimental results were in excellent agreement for medium and higher dye concentrations and FRET yields >50%. For lower dye surface concentrations, the theoretical values were underestimated. Diffusion of the molecules might have contributed to the increase of FRET efficiency, especially at lower dye concentrations, thus enhancing the yields with respect to the theoretical predictions. The influence of anisotropy factors was most likely negligible.

Knowledge gained by this study could be useful for the application of FRET in characterizing the properties of colloids based on clay minerals or other types of nanomaterials. Besides that, the results can be applied the development of complex systems or materials derived from the precursors in colloidal state. The applications of such systems include the construction of light-harvesting systems, optical devices, probes and sensors, photo-sensitizers and photo-disinfection agents.

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ANTIMICROBIAL PROPERTIES OF HYBRID MATERIALS BASED ON CLAY MINERALS WITH QUATERNARY ALKYLAMMONIUM AND PHOSPHONIUM CATIONS

Bujdáková Helena (1)*, Bujdáková Veronika (1,2), Májeková Hyacinta (2), Bujdák Juraj (3,4), Bizovská Valéria (4), Boháč Peter (4)

(1) Comenius University in Bratislava, Faculty of Natural Sciences, Department of Microbiology and Virology, 842 15 Bratislava, Slovakia, (2) Comenius University in Bratislava, Faculty of Pharmacy, Department of Cell and Molecular Biology of Drugs, 832 32 Bratislava, Slovakia, (3) Comenius University in Bratislava, Faculty of Natural Sciences, Department of Physical and Theoretical Chemistry, 842 15 Bratislava, Slovakia, (4) Institute of Inorganic Chemistry, Slovak Academy of Sciences, 846 35 Bratislava, Slovakia
*bujdakova@fns.uniba.sk

Organoclays mostly represent the materials composed of clay minerals modified with organic surfactants, predominantly of an alkylamonnium type. Such hybrid materials often exhibit the properties which are superior to those of their components. The main objective of this study was to characterize antimicrobial activity of tetrabutylammonium (TBA), dodecyltrimethylammonium (DDA), and tetrabutylphosphonium (TBP) cations, and effectiveness of the organoclays composed from montmorillonit SWy-2 (Mmt) and those cations. The activity was tested on gram-positive bacteria *Staphylococcus aureus* and gramnegative bacteria *Escherichia coli*. Prior to the determination of the antimicrobial activity, organoclays were characterized using X-ray diffraction and infrared spectroscopy. The results confirmed irreversible adsorption of organic cations on the surface of Mmt and the stability of the complexes in the medium used for biological experiments. The cytotoxicity of the organic cations on HeLa cell line determined by MTT (3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide) reduction assay [1] showed to be dependent mainly on the type of surfactant. While DDA with long alkyl chains fully inhibited surviving HeLa cells in the concentrations of 1 and 0.5 mmol/L, lower concentrations (0.1 and 0.05 mmol/L) were not toxic. On the other hand, TBA and TBP proved very low toxicity also at the higher concentrations. Antimicrobial activities of the organic cations, Mmt, and organoclays were measured at various concentrations of active components. Results were evaluated by the MTT reduction assay and calculation of colony forming units [2]. DDA inhibited surviving *S. aureus* and *E. coli* in the concentration of 1 mmol/L. Both TBA and TPB were efficient only in the concentration of 10 mmol/L. All organoclays were prepared with the ratio of organic cation/Mmt, 10^{-3} mol/g at the concentration ≤ 1 mmol/L. Antimicrobial effect of pure Mmt suspension was negligible and did not interfere with the effect of the organic cations. At this concentration, the most effective complex was DDA/Mmt that inhibited surviving both *S. aureus* and *E. coli* by over 93%. The organoclays based on TBA and TBP exhibited much lower antimicrobial effectiveness at the same concentration. The effectiveness of organic cations bound to the surface of Mmt particles was similar, only partially lower to that of the respective surfactant solutions. Results of this work brought new knowledge on the biological activities of the selected quarternary ammonium and phosphonium cations, which are often used in organoclays. The antimicrobial activity of the organoclays should be considered when they are applied as carriers of bioactive substances or in other applications dealing with biological systems.

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SURFACE ALTERATION MINERALS AS FLUID FLOW INDICATORS IN A GEOTHERMAL SYSTEM: THE CASE OF LICANCURA, NORTHERN CHILE

Estefanía Camus (1-2)*, Santiago Maza (1-2), Diego Morata (1-2)

(1) Department of Geology, Faculty of Physical and MathematicsSciences, University of Chile, Santiago, Chile, (2) Andean Geothermal Center of Excellence (CEGA), Santiago, Chile
*estefaniacamus@gmail.com

Geothermal activity can be evidenced on surface by the study of alteration minerals [1,2] formed as the result of the interaction between geothermal fluids and the surrounding host rocks. These minerals provide information about different features of the geothermal fluid (temperature, pH) [3,4] allowing the tracking of changes on its composition and thermodynamic properties. Within this group of minerals, it is important to highlight clay minerals, due to their susceptibility to small changes, reflecting the ongoing processes in the system [5,6] and allowing to identify zones of geothermal fluid flow. In this work, we present preliminary results regarding the study of surface alteration minerals belonging to Licancura geothermal system. The case of study corresponds to Licancura, located 220 km NE of Iquique, in the Andes mountain range. The outcrops of Licancura corresponds to Miocene andesitic to dacitic lava and tuff rocks, showing evidence of tectonic activity as faults and fractures. In this zone, large extensions of alteration minerals can be seen on surface, where samples were taken to analyze by X-ray diffraction, using the powder method for total rock samples and oriented clay mineral aggregates for the fraction $<2\ \mu$ [7]. The analyses showed three main mineral association: kaolinite-alunite, smectite-zeolites and ulexite-teruggite-nobleite, suggesting different kind of fluids circulating near the surface. First and second mineral associations corresponding to acid sulfate and bicarbonate paleofluids, respectively [2], and the third one corresponding to actual boron rich fluids. The mineral associations corresponding to paleofluids also showed the presence of minerals formed at higher temperature than the surface conditions, suggesting a field exhumation, which would lead to mineral instability and thus the transformation from one phase to another. These changes are the key to understand the evolution of geothermal systems. Furthermore, additional studies, especially in clay minerals, will lead to determine the evolution of the Licancura system.

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DIELECTRIC RESPONSE OF POLYPROPYLENECARBONATE-PRISTINE BENTONITE COMPOSITES

Emi̇ne Can (1)*, Ahmet Ugur Kaya (2), Selahaddi̇n Guner (3), Fatma Gozuak (1)

(1) Istanbul Medeniyet University, Department of Physics Engineering, İstanbul, Turkey, (2) Kocaeli University Faculty of Art&Science, Department of Physic, Kocaeli, Turkey, (3) Kocaeli, Turkey Kocaeli University Faculty of Art&Science, Department of Chemistry, Kocaeli, Turkey
*emine.can@medeniyet.edu.tr

In this study, dielectric behaviour of polypropylenecarbonate (PPC)-Pristine Bentonite composites were investigated. First PPC was dissolved in 20 mL Chloroform then this solution was added to suspension of 1 g bentonite in 30 mL of chloroform. The resulting PPC-Pristine Bentonite mixture was filtered then the solid portion was dried at room temperature under vacuum condition. Dielectric measurements were carried out 1Hz-1MHz. The measurements show that reel permittivities (ε´) of samples were increased with increase of loading up to 100 mg PPC loading. Loss factor (tanδ) was shifted to the low frequencies according to Pristine Bentonite. Infrared spectra of samples were measured and results were supported by infrared spectroscopy. As a result, at low PPC loading, clay-PC interaction increased and dielectric permittivities of composites decreased relative to pure bentonite.

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RITUAL CERAMICS FROM ARGARIC CONTEXTS: CHARACTERIZATION FROM THE ARCHAEOMETRY

J. Capel (1), J. M. Martín-García (2), M. V. Fernández-González (2), A. Molinero (2), R. Delgado (2)

(1) Dpto. Prehistoria y Arqueología. Facultad de Filosofía y Letras. Universidad de Granada, Granada, Spain, (2) Dpto. Edafología y Química Agrícola, Facultad de Farmacia. Universidad de Granada, Granada, Spain

Characterization of clays catchment area and the identification of the technological process of manufacturing are main lines of research in ceramic archaeometry [1,2]. The 3D microarchitecture of the ceramic pieces, especially its clay matrix, by scanning electron microscopy and microanalysis (SEM-EDX) is a topic that has received little attention to date. The settlement of the Cerro de la Encina (Monachil, Granada, Spain) is important for the systematization of the Bronze Age in the southeast of the Iberian Peninsula [3].

We studied ten ceramics vessels used in rituals practices from four graves. The mineralogical composition was determined by X-ray diffraction (XRD) with a Bruker D8 Advance diffractometer (Cu Kα, 40 kV, 40 mA) and mineral percentages by intensity factor method. Ceramic fragments were fractured to obtain freshly-cut surfaces, metalized with gold and studied with SEM (Hitachi S-510, at 25 kV) and EDX (Röntec, 288, M-Serie, Edwin).

Illite, paragonite, chlorite and quartz were identified in all samples. In some cases there exist K-feldspar, plagioclases, calcite, dolomite and hematite. Phyllosilicates was in 55-70% and quartz, 20-30%. The width at half height of the 1.0 nm peak of illite exhibits a range from 0.075 to 0.267 (°2θ). The predominate SEM microfabric was laminar matrix (composed by stack of laminar clusters, originated by the union of small plates -domains- of 10-5 μm width and low thickness, and composed by phyllosilicates) with skeleton grains (50-1000 μm) of different mineralogy. The stage of vitrification of the matrix was inexistent or very low; only in one sample filaments of glass had been described. The SEM images of several samples reveal the existence of fine-added layers that rework the previous surface. In other cases, a system of cracks -covered internally by phyllosilicates- was noticed. The quartz skeleton grains (composition confirmed by EDX) show angular shape.

The presence of paragonite indicates a Betic provenance of raw-clays, because this kind of mica is abundant in Nevado-Filabride Complex. Similar could be said about the presence of dolomite, since it is frequent in the Alpujarride Complex. Illites of low crystallinity could indicate a soil origin of the clay whereas those of high crystallinity have a sedimentary provenance. High phyllosilicates percentage, absence of high-temperature mineral phases, and lack (or very low) of matrix vitrification, tell us about fired temperatures not exceeded than 700-750 °C. Molding processes are recognized by the perfect adaptation of the clusters laminar matrix to the surface of the skeleton, adopting its forms and recesses. The presence of fissures covered by phyllosilicates and oblique to the surface of the piece is considered a fact with valuable technological information, indicating a second molding process -a retouching- when the piece was drier. High quartz percentages, improper of soil clays, and its angular forms, could talk about technological process of addition as a tempered.

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CLAY MINERAL ANALYSIS OF THE VACA MUERTA-QUINTUCO SHALE SYSTEM, NORTHERNNEUQUÉN BASIN, ARGENTINA

Ignacio A. Capelli (1)*, Fernanda Cravero (2), Diego A. Kietzmann (1), Roberto A. Scasso (1)

(1) Conicet-IGeBA-FCEN-UBA, Buenos Aires, PC: 1428 Argentina, (2) Conicet-CETMIC, Buenos Aires, PC: 1897, Argentina

Neuquén basin represents the most productive gas basin in Argentina, while the VacaMuerta-Quintuco system (Tithonian-Valanginian) is considered as one of the most important unconventional plays in the world. In order to increase productivity and predict their rheological behavior, detailed mineralogical analysis is essential on these plays. This contributionallowed us to make a detailed characterization of the transition from a carbonate ramp (VacaMuerta Fm) to a mixed siliciclastic-carbonate shelf (Quintuco Fm). The analysis of clay minerals revealed a high-ordered illitic material dominated shale, with variable contribution of Fe-rich chlorite. The smectite-illite interlayers (I/S) of marlstones revealed a high ordering (R3), while the I/S of other lithologies showed a subtle increase in expandibility, suggesting a different diagenetic process.

In the outcrops of PuertaCuraco (NorthernNeuquén Province), the VacaMuerta Fm is ~400 m thick and consists of rhythmic alternations of marlstones and limestones, with interbedded0.5-50 cm thick volcaniclastic layers (tuffs). Overlaying VacaMuerta Fm, Quintuco Fm (~300 m) consists of limestones, shales and fine-grainedsandstones, indicating a shallowing upward sedimentary cycle. The amount of clay minerals increases upward along the entire system while the carbonate content (calcite and dolomite) decreases (Kietzmann*et al*., 2016).

Systematic sampling and mineralogical analysis (XRD) were performed on the entire sequence (~700 m) in order to study the paleoenvironmental transition through the carbonate ramp to the mixed siliciclastic-carbonate shelf, and also to increase the knowledge about the diagenetic process.

Considering the marlstones:limestones ratio, five composite third-order sequences were recognized, each one subdivided into a transgressive system track and a regressive system track. No relation was observed between sequence stratigraphy and clay mineralogy, except for the regressive system track of Quintuco Fm, that is characterized by an important increase in clay mineral content, specially illite/mica.

Marlstones represent the main lithology in the VacaMuerta Fm and XRD analysis revealed that clay mineralogy is dominated by illitic material, with subordinated rich Fe-chlorite. Illitic material is characterized by very little amount ofexpandable layers. Limestones also present Fe-rich chlorite and illitic material with a subtle increase in expandable layers. Tuffs may show either alteration to argillaceous minerals (80%) or replacement by carbonate material (20%) (calcite and dolomite), the clay fraction revealed an important amount of Fe-rich chlorite and also interstratified illite/smectite (I/S), and, when compared to marlstones, the I/S of the tuffs presents an increase in the amount of expandable layers. The high amount of Fe-rich chlorite on tuffs deposits is expected considering the high amount of Fe-rich minerals in tuffs sediments. On the other hand, Quintuco Formation shales are characterized by illite/mica, chlorite and small amounts of I/S. The great abundance of illite/mica evidences the progressive shallowing upward system, reflecting an important increase of detrital input.

Illitic material represents the main clay mineral in VacaMuerta Fm. This fact may support the idea proposed by Wilson *et al*. (2016) who mentioned that I/S (R3) may, under particular conditions, crystallize from pore waters. The high-ordered I/S is consistent with other indicators such as pyrolysis analysis, that revealed Tmax~520ºC, characterizing this system as an overmature formation in PuertaCuraco. The difference observed on expandable layers in tuffs (carbonated or argillaceous replaced)suggestsdifferent initial material for marlstones and for tuffs, conditioning the formation of different clay mineral associations during diagenesis.

Preliminary interpretations indicate that clay minerals in VacaMuerta Fm mainly respond to diagenesis processes, while Quintuco Fm clay mineralogy may be dominated by detrital input. Finally, the advanced stage of the illitization process observed in PuertaCuraco section, is compatible with other indicators like pyrolysis analysis, characterizing the system in this part of the basin as an overmature formation.

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ISONIAZID/PALYGORSKITE NANOHYBRIDS AS A PROMISING APPROACH FOR THE TUBERCULOSIS TREATMENT: I) EQUILIBRIUM AND THERMODYNAMICS

Esperanza Carazo (1)*, Ana Borrego-Sánchez (1,3), Fátima García-Villén (1), Carola Aguzzi (1), Pilar Cerezo (1), César Viseras (1,2)

(1) Department of Pharmacy and Pharmaceutical Technology, School of Pharmacy, University of Granada, Campus of Cartuja, 18071 s/n, Granada, Spain, (2) Andalusian Institute of Earth Sciences, CSIC-University of Granada, Avda. de Las Palmeras 4, 18100, Armilla (Granada), Spain
*ecarazogil@ugr.es

Tuberculosis (TB) is the second cause of death from an infectious disease worldwide, only surpassed by the human immunodeficiency virus. It is curable but its treatment shows many problems to overcome as it long duration, the emergence of multidrug-resistant TB and its intimate link with poverty. TB treatment consists of a two month "intensive" phase (daily administration of the first-line antituberculostatic drugs: isoniazid, rifampicin, pyrazinamide and ethambutol) followed by a four month "continuation" phase (isoniazid and rifampicin) [1]. Currently, the use of nanoparticles within the field of infectious diseases arouses growing interest due to the evident failure of conventional treatments [2]. Among the wide range of nanomaterials available as support for these nanosystems, clay minerals provide spontaneous submicron dispersions in aqueous media, resulting in low cost and biocompatible systems [3,4]. Palygorskite is a fibrous clay considered a suitable candidate to vehicle bioactive molecules due to its large surface area [5]. Pharmasorb® Colloidal (PC) is an activated palygorskite clay designed for use in pharmaceutical and cosmetic application [6]. Furthermore, thermodynamics and equilibrium aspects of the interaction between the clay surface and the drug molecules must be investigated to elucidate the nature and degree of the processes involved [7]. With these backgrounds, the aim of this work was the study of the thermodynamics and equilibrium features of the adsorption of the first-line antituberculostatic drug isoniazid (INH) onto PC as a prior step in the development of a modified release system based on the INH-PC chemical interaction.

Adsorption equilibrium experiments were done as follows: a fix amount (0.1g) of PC and 20 ml of INH aqueous solutions (initial concentration C_0 ranging from 0.05 to 0.5 M) were placed in Pyrex™ glass 25 ml flasks and stirred in a thermostated bath (150 rpm) at different temperatures (20, 30, 40 ± 0.1 °C) for 24 h, 48 h and one week. After stirring, the suspensions were centrifuged and the equilibrium concentration of the drug in the supernatant liquid was determined by UV spectroscopy (UV-Vis spectrophotometer Lambda 25, Perkin Elmer, S) at 262 nm. The difference between initial (C_0) and equilibrium (C_{eq}) concentration was assumed to be due to adsorption and the amount of INH retained per gram of adsorbent was calculated. Mathematical treatment of the data was performed following [8] and thermodynamic parameters were then calculated. Adsorption experiments showed that promising delivery systems may be designed by supporting INH onto PC.

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ISONIAZID/PALYGORSKITE NANOHYBRIDS AS A PROMISING APPROACH FOR THE TUBERCULOSIS TREATMENT: II) SOLID STATE CHARACTERIZATION

Esperanza Carazo (1)*, Ana Borrego-Sánchez (1,3), Fátima García-Villén (1), Carola Aguzzi (1), Pilar Cerezo (1), César Viseras (1,2)

(1) Department of Pharmacy and Pharmaceutical Technology, School of Pharmacy, University of Granada, Campus of Cartuja, 18071 s/n, Granada, Spain, (2) Andalusian Institute of Earth Sciences, CSIC-University of Granada, Avda. de Las Palmeras 4, 18100, Armilla (Granada), Spain
*ecarazogil@ugr.es

Tuberculosis (TB) is the leading cause of death from a curable infectious disease [1]. Despite being subject to cure, TB chemotherapy is long and needs polymedication; 6 months of adherence to four first-line drugs with suboptimum toxicity profiles [2]. The potential of nanoparticulate drug delivery for the treatment of TB attracts considerable current interest on account of the substantial benefits provided, like the protection of drugs from degradation and/or the controlled release of the loaded drug, reducing dose and frequency of drug administration [3,4]. These findings raise the possibility of taking advantage of the innumerably possibilities that nanoclays offer in terms of drug delivery to contribute greatly to the improvement of patient compliance with the ultimate aim of increasing the survival rate of TB patients [5]. The aim of this work was to use a pharmaceutical-grade palygorskite (Pharmasorb Colloidal®, PC) (Basf, Spain) and the first-line antituberculostatic drug isoniazid (INH) (Sigma Aldrich, Spain) as a cheap and viable option to confront the serious challenge of the TB treatment.

The INH/PC nanohybrids were prepared at the drug/clay ratios corresponding with the monolayer adsorption capacity at the optimal contact time and temperature conditions. INH/PC hybrids systems were recovered by filtration and oven dried before characterizing. Solid state characterization was carried out in order to confirm the effectively loading of the drug, to assess qualitative and quantitatively the different interactions involved and to correctly resolve the structure of the nanohybrids as well as the localization of the drug.

a) X-Ray Powder Diffraction (XRPD) was done by using a Philips® X-Pert diffractometer with Cu Kα radiation. Data were analysed using the XPOWDER® software52. Experiments were run in triplicate (experimental error ± 5%).

b) Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were carried out by using a METTLER TOLEDO mod. TGA/DSC1 with FRS5 sensor and a microbalance (precision 0.1 µg) (Mettler-Toledo GMBH). Samples were heated in air atmosphere at 10 °C/min. Experiments were run in triplicate and standard deviations of temperature and mass loss were calculated.

c) Fourier Transform Infrared Spectroscopy (FTIR) spectra were recorded on a FTIR spectrophotometer (JASCO 6200, with software SPECTRA MANAGER v2 and with an attenuated total reflectance (ATR) accessory) from 600 to 4000 cm^{-1} at 0.25 cm^{-1} resolution. Experiments were run in triplicate (experimental error ± 0.2%).

d) Electron microscopy coupled with Energy-dispersive X-ray spectroscopy (XEDS) were performed using a Carl Zeiss SMT LIBRA 120 PLUS transmission electron microscope and a FEI Titan G2 60-300 ultra-high resolution transmission electron microscope coupled with a X-ray spectroscopy (EDX) detector.

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CLAY MINERALS AS NANOCARRIERS OF THE ANTITUBERCULOSTATIC DRUG ISONIAZID: CYTOTOCOMPATIBILITY AND INTESTINAL PERMEABILITY

Esperanza Carazo (1)*, Giuseppina Sandri (2), Marika Tenci (2), Ana Borrego-Sánchez (1,3), Fátima García-Villén (1), Pilar Cerezo (1), Carola Aguzzi (1), César Viseras (1,2)

(1) Department of Pharmacy and Pharmaceutical Technology, School of Pharmacy, University of Granada, Campus of Cartuja, 18071 s/n, Granada, Spain, (2) Department of Pharmaceutical Sciences, School of Pharmacy, University of Pavia, viale Taramelli 12, 27100, Pavia, Italy, (3) Andalusian Institute of Earth Sciences, CSIC-University of Granada, Avda. de Las Palmeras 4, 18100, Armilla (Granada), Spain
*ecarazogil@ugr.es

Tuberculosis (TB) is the leading cause of death from a curable infectious disease due to its long treatment duration, multidrug-resistant strains and deadly association with the human immunodeficiency *virus* [1]. *Isoniazid (INH) is the most widely used antituberculostatic drug. It shows high early bactericidal activity* [2], high aqueous solubility [3] but low permeability [4]. *The aim of this work was to take advantage of the innumerable advantages offered by clays in the design of novel drug delivery systems* [5,6] *directed towards the increase of INH oral bioavailability in terms of the enhancement of INH intestinal permeability, what would lead to a reduction of its toxic effects caused by the high dose required.*

Materials: halloysite nanotubes (HLNTs) (Sigma Aldrich, Spain), montmorillonite (Veegum HS®; VHS) (Vanderbilt ltd, USA), and palygorskite (Pharmasorb Colloidal®; PC) (Basf, Spain), all of pharmaceutical grade. Isoniazid (INH) (Sigma Aldrich, Spain).

A known amount of VHS, HLNTs and PC were dispersed in INH ethanol solutions with a drug to clay ratio 1:1 w/w and stirred for 24 hours. Then, the solvent was evaporated (Rotavapor®, Buchi model RII) and the residue was dried in oven at 40ºC. The resulting samples were referred to VHS-INH; HLNTs-INH; PC-INH.

Cytocompatibility and permeability of all the samples and corresponding raw materials were assessed in human colorectal adenocarcinoma cell line (Caco-2). Transepithelial electrical resistance (TEER) was measured during the experiments to monitor the integrity of the cells monolayer [7]. Results showed both the innocuousness of the resulting nanosystems as well as the great enhancement of INH permeability when loaded onto the nanoclays.

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SPECIFIC HEAT OF PELOIDS MADE WITH CLAYS. INFLUENCE OF THE MICROFABRIC

M.I. Carretero (1)*, J.M. Legido (2), C.P. Gómez (2), M.L. Mourelle (2), M.V. Fernández-González (3), J.M. Martín-García (3), F. Maraver (4), R. Delgado (3)

(1) Dpto. de Cristalografía, Mineralogía y Química Agrícola, Facultad de Química, Universidad de Sevilla, Sevilla, Spain, (2) Dpto. de Física Aplicada. Facultad de Ciencias. Universidad de Vigo, Vigo, Spain, (3) Dpto. de Edafología y Química Agrícola, Facultad de Farmacia, Universidad de Granada, Granada, Spain, (4) Escuela de Hidrología Médica, Facultad de Medicina, Universidad Complutense de Madrid, Madrid, Spain

Thermotherapy with peloids in rheumatic illness is a matter of discussion and that requires scientific answers whose resolution would aid to its optimization. The application of thermotherapy firstly depends on the specific heat (***Cp***), improving with this. One of the properties that has been little studied is the microfabric (***mfSEM***). Our goal is to determine ***Cp*** and ***mfSEM*** of clayey peloids made with industrial clays and Spanish medicinal mineral waters.

The clays used were aluminum-bentonite (B-Al), magnesium-bentonite (B-Mg) and kerolite (K). The waters came from the following Spanish thermal spas: Cuntis, Montemayor, Cofrentes, La Toja, and Talaso Atlántico. Distilled water was used as a target. Peloids were manufactured and matured for a period of 0, 3, and 6 months. ***Cp*** was determined by a CALVET microcalorimeter, equipped with a device that allows working in the absence of the vapour phase, with a calorimeter cell volume of approximately 10 cm^3. Calibration was performed electrically using a SETARAM EJP30 stabilised current source. Water percentage (***H***) was also measured. The ***mfSEM*** of peloids was studied with SEM-EDX in fresh-cut from samples prepared by cryofixation-lyophilization.

Cp data ($J \cdot kg^{-1} \cdot K^{-1}$) indicate that waters samples quadrupled clay samples (4000 *versus* 900; aprox. values). Those of low mineralization (Cuntis, Montemayor) and distilled water show a value of >4160 $J \cdot kg^{-1} \cdot K^{-1}$; followed by waters with higher mineralization, La Toja and Talaso Atlántico, near to 3990 $J \cdot kg^{-1} \cdot K^{-1}$; and finally Cofrentes, with the highest mineralization, with a value of 3346 $J \cdot kg^{-1} \cdot K^{-1}$. Clays were more homogeneous in ***Cp*** ($J \cdot kg^{-1} \cdot K^{-1}$): K, 894, B-Mg, 892; B-Al, 865. The ***Cp*** of peloids was intermediate between clays and waters (between 3300 and 2000 $J \cdot kg^{-1} \cdot K^{-1}$; aprox. values). The sequence of waters values was: Cuntis, Montemayor, distilled water > La Toja, Talaso Atlántico > Cofrentes. However, the peloids made of K, (which is the clay with highest ***Cp***), doesn't achieve the highest values and B-Mg is slightly higher than B-Al. ***H*** stands the amount of water needed to form peloids with the proper consistency to be applied. The peloids made with low-mineralization waters had the highest value of ***H***, similar to that of distilled water. However, when waters increase mineralization, La Toja and Talaso Atlántico, and especially Cofrentes (of extremely high mineralization), ***H*** decreases. ***H*** of peloids made with bentonites, resemble each other, though B-Mg had the maximum, and all of them are considerably higher than K. Peloids made with B-Al or B-Mg and the less mineralized waters had the better structured ***mfSEM***, with higher porosity and a near card-house-type microfabric.

In conclusion, the higher amount of water needed by the peloids (in order to reach the optimum for plasticity and texture) the higher ***Cp*** value. At the same time, ***H*** depends on the water mineralization in a reverse relationship, although the type of clay must be taken in account, establishing differences between ***Cp*** of B and K, in favor of the first. These differences are justified by the ***mfSEM***. House of cards, developed in B, is the most structured and porous, favoring higher ***H*** and ***Cp*** and best thermotherapy properties. By knowing the ***mfSEM*** we can deduce the quality of peloids as thermotherapy agents.

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CLAYS AND FRIENDS AT MARS: PIECING TOGETHER THEIR FORMATION PATHWAYS AT THE REGIONAL SCALE

John Carter (1), Cathy Quantin (2), Nicolas Mangold (3), Jean-Pierre Bibring (1)

(1) Institut d'Astrophysique Spatiale, Paris-Saclay University, France, (2) Laboratoire de Géologie de Lyon, France. (3) LPGN, Nantes, France
john.carter@ias.u-psud.fr

When hydrous clays and other secondary phases were first detected at Mars less than 15 years ago, there was hope that Mars would swiftly unravel its watery past. Since then, roving missions and orbital remote sensing have made much progress on the nature, geological context and chemical environment in which these clays formed at Mars. However, piecing all of this together to understand the actual formation pathways and the geological environments (e.g. supergene vs hypogene) has proven challenging.

Global analyses of Mars have been carried out from orbit, making extensive use of data fusion at the meters scale, but they are both limited and coarse geological tools. This paucity of analytical tools is solved by roving missions, but these only provide a clear cut view of clay-forming alteration that is highly localized both in space and in the timeline of Mars. Both approaches are further hampered by the degraded nature of the geological context for these >3.5 Gyrs old mineral deposits.

We report on a new analysis of clays at the coarse orbital scale that attempts to partly overcome the latter limitation. Individual mineral sites at Mars are typically overly degraded, lack erosional windows (to investigate stratigraphy), or do not possess sufficient meter-scale data coverage. If instead we treat these sites as statistical points, then it becomes possible to look for trends at the regional (1000s km) to global scale, and compare between various locales (e.g. basins, mountains, etc.). Based on this approach, we observe that Mars has undergone pervasive alteration globally, at and near its surface, but the duration and intensity of this alteration remains elusive. Regional scale variations based on context, altitude and general geography demonstrate that Mars experienced clay-forming systems that were both diverse, and in some cases likely connected over 1000s km. A by-product of this work is that it should allow better assessment of the representability and pertinence of landing site candidates for future roving missions.

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NUTRITIONAL STRATEGIES TO AVOID ENVIRONMENTAL CONTAMINATIONS EMPLOYING CUBAN NATURAL ZEOLITES

Manuel Castro*, Mayuly Martinez, Julio Ly

Instituto de Ciencia Animal, San José de las Lajas (CP: 32700), Mayabeque, Cuba

The main findings in the evaluation of Cuban natural zeolites of “Tasajeras” (Villaclara province) and “San Andrès” (Holguin province) deposits are in animal production taking into account animal behavior, health, decrease of contaminant, environmental emissions and costs in animal production. The results are in line with the demands of the country through the guidelines established for the recently approved economic program, among which food production, import substitution, environmental care and lower costs are included. The natural zeolite deposit “Tasajeras” could replace a portion of soybean meal in the feed formula for fattening pigs. The natural zeolite was able to efficiently replace part of the protein source in the protein supplement used, with savings of 180.4 kg of soybean meal per ton of concentrate for pigs, which would reduce the cost of the annual budget of the country in 20.5 million USA dollars. It was also found that when the zeolites are included in feed for pigs, ammonia nitrogen emissions to the environment are reduced by 56%. The work demonstrated once again that the mineral studied here have also ample opportunities to become a major export item or to provide elements of interest to potential investors, an aspect which also claims the Cuban economy.

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BIONANOCOMPOSITES BASED ON SEPIOLITE AS NANO-CARRIER OF NUCLEIC ACIDS AND THEIR BIOTECHNOLOGICAL APPLICATIONS

Fidel Antonio Castro-Smirnov (1,5)*, Olivier Piétrement (2), Pilar Aranda (4), Jeanne Ayache (2), Eric Le Cam (2), Jean-Remy Bertrand (3), Bernard S. Lopez (1), Eduardo Ruiz-Hitzky (4)

(1) CNRS UMR 8200, Institut de Cancérologie Gustave-Roussy, Université Paris Sud, Team Labeled “Ligue 2014”, 94805 Villejuif, France, (2) Maintenance des Génomes, Microscopies Moléculaires, CNRS UMR 8126 and University of Paris Sud, Institut de Cancérologie Gustave-Roussy, 94805 Villejuif, France, (3) CNRS UMR 8121, Laboratoire de Vectorologie et Thérapeutiques Anticancéreuses, IGR, (4) Materials Science Institute of Madrid, CSIC, 28049 Madrid, Spain, (5) Universidad de las Ciencias Informáticas, 19370 Havana, Cuba
*fsmirnov@yahoo.com

The present work focuses on a new field of multidisciplinary research located in the state of the art of Nanobiotechnology and Nanomedicine. In this way, it will be shown how nanofibers of sepiolite might constitute a potential promising non-viral nanocarrier for the intracellular transfer of biomolecules [1]. Specifically, it focused on the synthesis, physical-chemical characterization, and evaluation of biotechnological applications of new sepiolite-based bionanocomposites, as part of therapeutic strategies for the treatment of diseases of genetic origin. Firstly, insights on the adsorption of nucleic acids (DNA and RNA) on sepiolite from Vallecas-Vicálvaro region (Madrid, Spain) will be introduced to confirm the formation of the corresponding bionanocomposites. The resulting biohybrid materials were subjected to a deep characterization using novel techniques and methodologies, identifying that DNA is adsorbed in a reversible and efficient way in sepiolite nanofibers mainly via interactions with the sepiolite silanol groups located along the external surface of the silicate fibres. Moreover, it was observed that sepiolite can be internalized spontaneously by eukaryotic cells, and the predominant action of endocytic and non-endocytic mechanisms of cellular internalization were identified. These bionanocomposites have been also tested as a novel non-viral gene vector to stably transfer nucleic acids into cancer cell lines. Furthermore, additional strategies were designed in view to significantly increase transfection efficiency. In conclusion, the obtained results open the way to the use of sepiolite as a novel class of nano-platform to produce DNA-based bionanocomposites useful for gene transfer with potential clinical applications, as well as for the development of novel biological models of interest for both, Academia and biotechnological applications.

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HIGH CHARGE DENSITY SMECTITE CLAYS FOR CO_2 CAPTURE

Leide P. Cavalcanti (1)*, Georgios Kalantzopoulos (2), Pawel Sobas (2), Heloisa N. Bordallo (3,4), Geir Helgesen (1,2), Kenneth D. Knudsen (1,4), Jon Otto Fossum (5)

(1) Institute for Energy Technology (IFE), Kjeller, Norway, (2) Univ. of Oslo, Norway, (3) Univ. of Copenhagen, Denmark, (4) European Spallation Source, Sweden, (5) Norwegian Univ. of Science and Technology (NTNU), Trondheim, Norway
*leide.cavalcanti@gmail.com, jon.fossum@ntnu.no

This workpresents a structural study on the intercalation of carbon dioxide (CO_2) into fluorohectorite clays with different interlayer cations. We have recently demonstrated [1] that under certain conditions of pressure and temperature, fluorohectorite clays are able to capture a large amount of CO_2, depending on the type of interlayer cation. Intercalation of water in smectite clays occurs naturally and has been extensively studied with a wide range of techniques, among them neutron [2,3] and X-ray scattering [4,5]. Recent experiments and simulations have shown that also CO_2can intercalate in smectite clays, both in supercritical [6], and in gaseous/liquid form [7]. We have previously demonstrated that CO_2 intercalates into synthetic Na-Fluorohectorite (NaFh) clay at conditions close to ambient [8], at minus 20 °C and 15 bar. These are not the conditions found in the geological storage sites, but can be conditions relevant when clays are considered as an alternative to for example zeolites as a material for capture of CO_2. In a recent paper [9] we investigated this further, looking at fluorohectorite clays with three different cations (Na, Ni and Li), showing that Li-fluorohectorite clay is able to retain CO_2 up to a temperature of 35 °C, at ambient pressure, and that the captured CO_2 can be released by heating above this temperature. These conditions are highly relevant for mapping out, and understanding, the mechanisms involved in CO_2 capture and retention by smectite clays, either in geological formations, or in CO_2 capturing elements. Fluorohectorite is a synthetic 2:1 clay that has been demonstrated by us to be a representative and clean model system of natural smectite clays. Synthetic clays have more homogenous charge distribution than their natural counterparts, which leads to well-defined intercalation states. Synthetic clays also contain significantly fewer impurities (e.g. carbonates, (hydr)oxides, silica, and organic matter) than natural clays. Here we present results on the study ofCO_2 intercalation into a series of synthetic fluorohectorite clays using a Pressure Composition Temperatureapparatusto follow the capture of CO_2 inside the clay interlayer varying the pressure from 0 to 50 Bar for the three studied cations; X ray diffraction was used to determine the interlayer distances at ambient conditions; andSmall Angle Neutron Scattering fromJeep II reactor at IFEwas used for an in situ high pressure study.

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STRUCTURAL INVESTIGATIONS OF BIOPOLYMER/HALLOYSITE MIXTURES

Giuseppe Cavallaro (1,3)*, Leonardo Chiappisi (1,2), Giuseppe Lazzara (3), Micheal Gradzielski (1)

(1) Technische Universität Berlin - Institut für Chemie, 10623 Berlin, Germany, (2) Institut Laue-Langevin, F-38042 Grenoble, France, (3) University of Palermo - Dept. Physics and Chemistry, 90128 Palermo, Italy
*giuseppe.cavallaro@unipa.it

The selective adsorption of biopolyelectrolytes onto or into hallosyite (HNT) surfaces is a way to control the aqueous colloidal stability of the nanotubes, which is crucial for several applications within pharmaceutics and materials science. This study was aimed to investigate the structure of the complexes formed by polymer adsorption and its dependence on the polymer type. To this purpose, nonionic (hydroxylpropylcellulose), anionic (pectins and alginate) and cationic (chitosan) polymers were selected. On the other hand, HNTs provided from different geological deposits were studied in order to evaluate the influence of the their morphological characteristics (aspect ratio, polydispersity in length and inner/outer diameters, specific surface area) on the structural properties of the hybrid nanostructures. The SANS curve for HNT from Australia showed interesting scattering features, which are not observed for the nanotubes provided from different sources. This peculiarity agrees with the lower size polydispersity and a thinner shell. The absence of oscillations for the other HNT samples can be attributed to a larger polydispersity of their radii that smears out the scattering features expected for a hollow cylinder. SANS curves were performed on the biopolymer/HNT mixture in full contrast as well as HNT contrast matching conditions. The quantity of polymer adsorbed onto the HNT surfaces was estimated from the SANS data by considering the scattering intensity values at $q \to 0$ (Guinier fit). We observed that the anionic alginate is the biopolymer with the largest affinity. The SANS experiments performed in D_2O/H_2O mixtures highlighted that the oscillations for the HNT from Australia are preserved in the presence of all the investigated biopolymers. Therefore, SANS curves can be fitted by using a hollow cylinder as model providing insights on the specific interactions between the polymers and HNT. Additional insights on the structural properties of biopolymer/HNT nanostructures were obtained from Electric Birefringence (EBR) experiments, which allow to study the rotational mobility of the nanotubes. As a general result, the presence of the biopolymer induced an enhancement of the relaxation time indicating that the rotational mobility of the nanotubes is reduced. The strongest effect was observed for chitosan/HNT mixtures. The peculiar effect of the biopolymers on the HNTs rotational mobility could be explained by taking into account the electrostatic characteristics of both components. The cationic chitosan preferentially interacts with the negative HNT outer surface favoring the polymer wrapping of the nanotubes, while the anionic alginate should be mostly adsorbed onto the positively charged clay's lumen. No electrostatic interactions are expected between the non ionic HPC and the clay nanotubes (the polymer adsorption could be driven by hydrogen bonds and Van der Waals forces).

The obtained results represent a physico-chemical basis for further applications of the biopolymer hybrids as modern functional materials.

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ROMAN CERAMIC PRODUCTION: GEOSOURCES AND TECHNOLOGY FOR MANUFACTURING WINE AMPHORAE IN UMBRIA, ITALY

Letizia Ceccarelli (1), Maurizio Bellotto (2), Marco Caruso (3), Cinzia Cristiani (4), Giovanni Dotelli (5), Paola Gallo Stampino (6), Luca Primavesi (7), Ilenia Rossetti (7)

(1) University of Cambridge, McDonald Institute for Archaeological Research, Downing Street, Cambridge CB2 3ER, UK, (2) Politecnico di Milano, Department of Chemistry, Materials and Chemical Engineering "Giulio Natta", Piazza Leonardo da Vinci 32, 20133 Milan, Italy, (3) Politecnico di Milano, Materials Testing Laboratory, via Celoria 3, 20133 Milan, Italy, (4-6) Politecnico di Milano, Department of Chemistry, Materials and Chemical Engineering "Giulio Natta", Piazza Leonardo da Vinci 32, 20133 Milan, Italy, (7) Department of Chemistry, Università degli Studi di Milano, via C. Golgi 19, 20133 Milan, Italy, (8) Department of Chemistry, Università degli Studi di Milano, via C. Golgi 19, 20133 Milan, Italy

In 2016 a second season of archaeological excavation took place at the Roman site of Montelabate (Perugia, Italy) where three kilns had been excavated following their discovery in 2012. The new excavation focused on two further kilns revealed by geophysical prospection:a rectangular kiln, oriented North-South, that was initially used for the production of wine amphorae, before later being used to make tiles;a round kiln, oriented east-west, which was used to produce courseware. The pottery production site was located within walking distance of a rich Plio-Pleistocene clay deposit and in close proximity to several streams including the River Ventia, a tributary of the River Tiber. During the excavation several ancient clays were sampled in particular below the foundations of the structures. Furthermore, visible clays beds in the proximity of the site were also sampled.

The pottery workshop, in use from the 1st century AD, is an important discovery in the Upper Tiber valley and is the only amphorae production site in the area to be fully excavated and subject to scientific analysis. The site therefore offers a unique opportunity to study the *chaîneopératoire* and the Roman technology of production in Central Italy. The kilns were also used to produce courseware, providing evidence for a local production system that continued until the late 4th to the 5th century AD[1].

Ancient and modern clays were sampled and analysed: they do not significantlydiffer supporting the hypothesis of a rich local clay source that allowed a continuity of production. In some areas of the excavation, around the kilns, clays have been identified that had already been prepared for pottery production.

Characterization of the clays was performed using geotechnical methods (Atterberg limits and size distribution), by XRF[2] and XRD analysis, SEM, TG and FTIR. The material proved to be nearly suitable for pottery making, requiring only the addition of calcite and quartz sand. Production waste and discarded materials were also analysed: both amphorae and courseware pottery show differences in the preparation of the recipe and firing temperature, determined by the decomposition of clay materials and the presence of neoformed minerals.

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BLENDED FORMULATIONS OF VOLCANIC MUDS AND SEDIMENTARY CLAYS FROM AZORES (PORTUGAL): ASSESSMENT AND BENEFICIATION OF THEIR PROPERTIES AS HEALING MATERIALS

Angela Cerqueira*, Cristiana Costa, Denise Terroso, Cristina Sequeira, Fernando Rocha

GeoBioTec, Department of Geosciences, University of Aveiro, Portugal

The empirical application of muds for therapeutic purposes is known all over the world. This is called pelotherapy and consists in the local or generalized application of a mixture of a solid phase and a liquid phase (peloid) for recovering artro-rheumatic, bone- muscle traumatic damages and dermatologic affections. Volcanic thermal muds have been applied "in situ" or in Spa Centres for therapeutic purposes since a long time. Some maturation surveys have also been performed in the last years.

São Miguel island (Azores archipelago) exhibit hydrothermal manifestations such as mineral and thermal waters and also fumarolic fields as a result of their geological settings. Several samples from São Miguel island were obtained from the surface bubbling mud inside the springs. Water/mud temperature and pH were measured with a portable instrument (HI 9025 pH meter), calibrated in the field. In Santa Maria island (also in Azores) recent sedimentary clayey formations outcrop, showing a multicolor facies, reflecting, generally, changes in the mineralogical composition. 5 samples were collected in Santa Maria Island known to be used for empirical therapeutic uses.

All samples were submitted to chemical, mineralogical and technological characterizations, with particular emphasis on those allowing the assessment of the potentialities but also the risks for application as healing clays. Several analyses were carried out: grain size distribution (wet sewing and sedigraph), mineralogical composition (X-ray diffraction), geochemical (major and minor elements) analyses (X-ray fluorescence), abrasiveness, plasticity (consistency limits), cation exchange capacity and exchangeable cations, specific surface area, expandability, oil absorption and cooling rate. All the analyses had been carried in accordance with the protocols and norms followed in the Departments of Geosciences of the University of Aveiro and in the Pharmacy College of the University of Porto. The results obtained so far point to very fine materials and presenting mineralogical and chemical composition compatible with the desired applications. The same can be concluded from almost all of the technological tests, but volcanic muds showed abrasiveness and pH values needing beneficiation. On the other hand, the availability of these muds are limited. Therefore, we considered the design of blends of both geomaterials. Blends of volcanic muds from São Miguel and clays from Santa Maria were submitted to maturation procedures with mineral water. Samples were matured in tanks covered permanently by a layer of mineral water during 120 days at constant room temperature (20 ºC). The same set of analyses and test were carried out after blending/before maturation and after maturation. Abrasiveness decreased and pH became less acidic; slightly enrichment on Na and Ca was detected on samples after maturation and exchangeable cations content were improved by the process. The bicarbonated-sodium type of mineral water used for maturation seems to play a major role on features of the final peloids.

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SEPIOLITE AND PALYGORSKITE REGULATE GENE EXPRESSION OF PRO-INFLAMMATORY CYTOKINES AS DETERMINED BY A MURINE INFLAMMATION MODEL

Cynthia Paola Lopez-Pacheco (1,2), Antonio Nieto-Camacho (3), Luis Zarate-Reyes (2), Emilia Garcia-Romero (4,5), Mercedes Suarez (6), Stephan Kaufhold (7), Eduardo Garcia-Zepeda (1,2), Javiera Cervini-Silva (8,9)*

(1) Posgrado de Bioquímica, Facultad de Química, Universidad Nacional Autónoma de México, Mexico City, Mexico, (2) Instituto de Investigaciones Biomédicas, Universidad Nacional Autónoma de México, Mexico City, Mexico, (3) Instituto de Química, Universidad Nacional Autónoma de México, Mexico City, Mexico, (4) Departamento de Cristalografía y Mineralogía, Universidad Complutense de Madrid, Spain, (5) Instituto de Geociencias, Universidad Complutense de Madrid - Consejo Superior de Investigaciones Científicas, Spain, (6) Departamento de Geología, Universidad de Salamanca, Spain, (7) BGR Bundesansaltfür Geowissenschaftenund Rohstoffe, Stilleweg 2, D-30655 Hannover, Germany, (8) Departamento de Procesos y Tecnología, Universidad Autónoma Metropolitana Unidad Cuajimalpa, Mexico City, Mexico, (9) NASA Astrobiology Institute, United States

This presentation shows that sepiolite and palygorskite collected from Torrejón El Rubio and Vallecas, Spain modulate the inflammatory environment at its initial phase, consequently modify the initial and late phases of inflammation as well as edema in skin. At the same time, both clay minerals exert an effect on the recruitment of neutrophils to inflamed skin. These clay minerals, particularly sepiolite, cause a down-regulation of pro-inflammatory cytokine expressions, particularly those intrinsic of interleukin (*IL-1*) and tumor necrosis factor (*TNF-α*). The result is the modification of the local microenvironment at both stages of inflammation. We explain the effects of clay minerals on gene expression of pro-inflammatory cytokines because interactions between surface hydroxyl groups (≡Si-OH) and cytokines to form aggregates (e.g., ≡Si-O×××CO-NH-R), and subsequent stable organomineral derivatives (e.g., ≡Si-O-CO-NH-R); [1]]. Specifically, we propose binding of cytokine-gene promoter moieties at surface sites (type *N* or *P*) [2]. Taken together, results presented herein serve as the basis to support the potential use of these clay minerals as a therapeutic tool against inflammatory diseases.

First, as determined by the 12-*O*-tetradecanoylphorbol-13-acetate model for inflammation [3], sepiolite and palygorskite altered the expression of four pro-inflammatory cytokines, namely, interleukins *IL-1* and*IL-6*, *TNF-α*, and interferon gamma (*IFN-γ*).

Second, Reverse Transcription Polymerase Chain Reaction (RT-PCR) analyses after 4 and 24 h inflammatory stimuli showed that either clay mineral brought about a reduction in mRNA expression. Sepiolite provoked the highest mRNA expression inhibition for all cytokines, except for *TNF-α*, and primarily after 4 h. Conversely, the anti-inflammatory effect for cytokine *TNF-α* was found to be true in the presence of palygorskite. Most notably was the significant reduction in mRNA expression of *IL-1*, registered just shortly after exposure, in keeping with the notion that the anti-inflammatory effect may be important for modulation of the late inflammatory response. Furthermore, sepiolite and palygorskite caused modifications in the mRNA expression of *IL-1* and its receptor in endothelial cells and downstreaming inflammatory cascades resulting in the recruitment of neutrophils. Most remarkably, the activity of polymorphonuclear peroxidase was severely reduced just after short exposure to either clay mineral.

In summary, sepiolite and palygorskite impaired neutrophils infiltration to inflamed skin [4], notwithstanding ear edema and deficient cell localization to skin coupled with such impairment may affect the later stages of inflammation [2,5].

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HUMAN CANCER CELL GROWTH UNDERPINNED BY BENTONITES AND SEPIOLITES. I. STRUCTURAL CONSIDERATIONS

Javiera Cervini-Silva (1,2)*, Maria Teresa Ramirez-Apan (3), Stephan Kaufhold (4), Kristian Ufer (4), Eduardo Palacios (5), Virginia Gomez-Vidales (3), Paz Del Angel (5), Ascencion Montoya (5)

(1) Departamento de Procesos y Tecnología, Universidad Autónoma Metropolitana, Mexico City, Mexico, (2) NASA Astrobiology Institute, United States, (3) Instituto de Química, Universidad Nacional Autónoma de México, Mexico City, Mexico, (4) BGR Bundesansaltfür Geowissenschaftenund Rohstoffe, Stilleweg 2, D-30655 Hannover, Germany, (5) Instituto Mexicano de Petroleo, Mexico City, Mexico

This paper reports the roles of bentonite and sepiolite on the proliferation behaviour of two human cancer cells lines [U251 (central nervous system, glioblastoma) and SKLU-1 (lung adenocarcinoma)] supplied by the National Cancer Institute (USA)]. Four bentonites {collected from Argentine, Hungary, Indonesia, India; [1]}, and eight sepiolites {China, Dominican Republic, Italy, Madagascar, Spain (2), Turkey (2); [2]} were screened *in-vitro* against the above human cancer cell lines. The effect of sepiolite on cellular proliferation was determined using the SRB protocol [3]. Cells were exposed to 50 $\mu g\ mL^{-1}$ clay for 48 h. All experiments were conducted by quintuplicate.

Bentonites. Bentonites studied herein were characterized elsewhere [4]. Bentonites induced growth inhibition in the presence of U251 cells, and growth increment in the presence of SKLU-1 cells, explained because interactions between bentonite and cell surfaces are highly specific. The proliferation response for U251 cells was explained because clay surfaces controlled the levels of metabolic growth components, thereby inhibiting the development of high-grade gliomas, particularly primary glioblastomas. On the other hand, the proliferation response for SKLU-1 was explained by an exacerbated growth favoured by swelling, and concomitant accumulation of solutes, and their hydration and transformation *via* clay-surface mediated reactions.

Sepiolites. Diffractograms showed characteristic patterns for sepiolite, with no evidence of significant accumulation of secondary phases. XRF data confirmed the incorporation of Al, Fe and, Ti; and Ni, and different extent of isomorphic substitution (*IS*), either because of the inclusion of Al^{3+}, $Fe^{3+,2+}$, or Ti^{4+} in Si structural sites (*IS* at the tetrahedral sheet, T) or that of Ni^{2+} in Mg structural sites (*IS* at the octahedral sheet, O).

All sepiolites induced inhibition or increment on the proliferation response of U251 or SKLU cells, depending on the sepiolite; however no correlation between proliferation against composition or microporosity properties became evident. Most notably, sepiolites owning the highest microporosity (evidenced by surface area σ_s) of the sepiolite series, 343 $m^2\ g^{-1}$, exerted the highest proliferation response for U251 and SKLU-1 cells, namely, 100% inhibition and 22.8 ± 12.1% increase, respectively.

Sepiolites owing very low contents of Al ($Al_2O_3 \leq 0.2\%$) and variable σ_s yielded the highest inhibition in U251 cells proliferation, best accounted for by growth was limited by specific-adsorption mechanisms in which structural changes associated to Al-for-Si *IS* at T favoured the adsorption of metabolic growth components [epidermal growth factor receptor (EGFR)], thereby inhibiting the development of primary glioblastomas. On the other hand, increments (%) in SKLU-1 cells proliferation did not correlate with microporosity (measured σ_s values), yet two data clusters were identified, higher and lower data values, i.e., $22.8 \leq \%$ increment $\leq 39\%$ (σ_s = 83, 220, or 343 $m^2\ g^{-1}$) and $6.9 \leq \%$ increment $\leq 14.2\%$ ($96 \leq \sigma_s \leq 266$). The second group was composed by sepiolites, owing surface sites that catalyze the over expression of active in A. So, the growth behaviour for both U251 and SKLU-1 cells was affected by Al at T *via* Al-for-Si *IS* if proceeded to a small degree. In all, however, the overall chemical composition lacked to serve as predictor for growth. In summary, structural considerations supported the idea that controlled cell growth by sepiolite was not limited by the retention of small solutes at inner surfaces.

Whether the microporosity of clays and clay minerals exerted an effect on cell proliferation was strongly dependent on structural properties, namely stacking properties and surface charge (determined as *IS* or contents of structural Al) [2].

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PARTICLE SIZE-CONTROLLED ORDERED MESOPOROUS SILICA PARTICLES BY METAL-CHELATING MICELLE TEMPLATES

Jeong-ho Chang

Center for Convergence Bioceramic Materials, Korea Institute of Ceramic Engineering and Technology, Cheongju-si, Chungbuk, Korea

In this work, we report a highly ordered mesoporous silica particles with tunable morphology and pore-size which are prepared by the use of a transition metal-chelating surfactant micelle complex using Co2+, Ni2+, Cu2+, and Zn2+ ions. These metal ions formed a metal-P123 micelle complex in an aqueous solution, while the metal ions are chelated to the hydrophilic domain such as the poly(ethylene oxide) group of a P123 surfactant. The different complexation abilities of the utilized transition metal ions play an important role in determining the formation of nano-sized ordered mesoporous silica particles (MSPs) due to the different stabilization constant of the metal-P123 complex. Consequently, from a particle length of 1,700 nm in the original mesoporous silica materials, the particle length of ordered MSPs through the metal-chelating P123 micelle templates can be reduced to a range of 180-800 nm. Furthermore, the variation of pore size shows a slight change from 8.8 to 6.6 nm. In particular, the Cu2+-chelated MSNs show only decreased particle size to 180 nm. The stability constants for the metal-P123 complex are calculated on the basis of molar conductance measurements in order to elucidate the formation mechanism of MSPs by the metal-chelating P123 complex templates. In addition, solid-state 29Si, 13C-NMR and ICP-OES measurements are used for quantitative characterization reveal that the utilized metal ions affect only the formation of a metal-P123 complex in a micelle as a template.

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ANTIBACTERIAL CLAY HYBRID FILMS FOR FOOD PACKAGING APPLICATIONS

Jeong-Ho Chang*, Hyesun Lee, Junkyu Park

Center for Convergence Bioceramic Materials, Korea Institute of Ceramic Engineering and Technology, Cheongju-si, Chungbuk, Korea
*jhchang@kicet.re.kr

In this work, we report a novel processing route to synthesize antibacterial clay-hybrid polymer films for food packaging applications such as enhancement of air-permeability and antimicrobial assessment. In this process, sub-micron sized clay ceramic particles such as vermiculite, halloysite, and porous silica are mixed with a layer of polymer matrix with high packing density. Moreover, the controlled release properties of these hybrid films was also demonstrated with natural antimicrobials. The homogeneous loading and highly controlled-release formulation of natural antimicrobials on the ceramic particles enable highly efficient and facile preparation able to reduce harmfulness. The mass fractions of each constituent can be adjusted independently. During the warm pressing stage, the submicon-sized particle fraction and the polymer are pressed into the void volume of the µm-sized particles, thus achieving a homogeneous, isotropic composite structure with high packing density of ceramic particles. The material, which can easily be produced in large quantities, combines a high modulus of elasticity, tensile strength and pronounced fracture strain with an isotropic, biocompatible, metal-free composition.

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TYRAMINE ADSORPTION ON Ca-MONTMORILLONITE

Po-Hsiang Chang (1)*, Wei-Teh Jiang (1), Zhaohui Li (2), Wan-Ru Chen (3), Jiin-Shuh Jean (1)

(1) Department of Earth Sciences, National Cheng Kung University, Tainan 70101, Taiwan, (2) Department of Geosciences, University of Wisconsin - Parkside, Kenosha, WI 53144, USA, (3) Department of Environmental Engineering, National Cheng Kung University, Tainan 70101, Taiwan
*atwtj@mail.ncku.edu.tw

Tyramine (TY) is one of the common biological amines found in fermented protein-rich foods and remains of marine animals after deterioration due to microbial enzymolysis [1]. The presence of TY in foods can cause allergic reactions such as dyspnea, rash, vomiting, and trigger high blood pressure and other illnesses [2,3]. Similar to other amines, TY can be generated in the brewing processes of a variety of alcoholic beverages as well and thus its allowable concentration level is limited in many countries [4,5]. The TY has a low deterioration rate in the environment and its removal is difficult even with high temperature treatments [6]. Hence TY can be accumulated in aquatic environments through long-term contamination processes or due to a swift release from due to a sudden increase of mass animal remains or discarded foods, posing a threat to human health and economics [7]. Searching an effective adsorbent for TY removal becomes one of the key issues to control TY in the environment.

Adsorption properties and mechanisms of TY on a Ca-montmorillonite (SAz-2) were tested with batch adsorption experiments and HPLC, IC, XRD, and FTIR analyses. The adsorption kinectics matched a pseudo-second-order rate equation with equilibrium reached in 8 hrs. The adsorption was mediocrely fitted to both the Langmuir and the Freundlich isotherm models and a maximum adsorption capacity of 257 mmol/kg, approximately one fifth of the CEC value of the mineral at pH 6−6.5 was obtained, utilizing the Langmuir equation. A removal rate of ca. 88% was obtained using an initial TY concentration of 400 mg/L. The adsorption of TY and desorption of exchangeable cations exhibited a linear relationship with a slope of 0.36, implying the adsorption largely influenced by mechanisms of cation bridging or surface comlexation apart from cation exchange. The adsorption was exothermic and the Gibbs free energy of adsorption spanned from −22 to −28 kJ/mol in the temperature range of 30 to 60 °C. X-ray diffraction results indicated no apparent changes of the basal spacing and hydrated Ca remained as the principal interlayer material of the montmorillonite before and after the adsorption of TY. The results suggested that Ca-montmorillonite may be used as an adsorbent for removal of TY from aqueous solutions and can be a host for TY in soil and sediments.

Keywords: Tyramine, Theoretical calculation, Montmorillonite, Adsorption energy.

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MINERALOGY AND FLUID CONTENT OF SEDIMENTS ENTERING THE COSTA RICA SUBDUCTION ZONE - IODP EXPEDITION 344

Delphine Charpentier*, Martine Buatier, M. Perrey

IODP Exp. 344 Science Party UMR Chrono-Environnement, Université de Bourgogne Franche-Comté, 16 route de Gray, F-25030 Besançon, France

Offshore Costa Rica, the Cocos Plate subducts under the Caribbean plate forming the southern end of the Middle America trench. A high convergence rate and almost complete subduction of incoming sediments make the Costa Rica margin an extremely dynamic environment. The Costa Rica Seismogenesis Project (CRISP) is designed to understand the processes that control nucleation and seismic rupture of large earthquakes at erosional subduction zones. Site U1414 of IODP Exp.344 was drilled to investigate the material from the incoming Cocos Plate.

A key parameter of incoming plate is mineralogy, and fluid content and release because they impact deformation within the subduction complex. We therefore decided to characterize sediment composition and quantify the different types of water at Site U1414. Mineralogical and geochemical investigations were performed using X Ray Diffraction, Cation Exchange Capacity measurements, carbon analyses and sequenced extractions in NaOH. Fluid characteristics were approached by thermal gravimetric analyses.

The sedimentary sequence can be divided into three major sedimentary units. The first one is a hemipelagic silty clay to clay with a gradual increase of calcareous nannofossils. The dominant minerals are mixed layered clay minerals (I/S and Chl/S) and kaolinite with zeolites. Other minerals like quartz, feldspar and calcite are also present. Small amounts of biogenic opal have been quantified. Unit II is composed of nannofossil-rich calcareous ooze. The proportion of biosilica is variable and can reach 10 wt.%. Unit III is a lithified carbonaceous sandstone with zeolites and opal CT.

Fluid content that can be released for $T<500$ °C varies from about 15 wt.% in Unit I to 4 wt.% in Unit III. The presence of smectite yields to fluid release by dehydration and dehydroxylation in Unit I. Realease of water by biogenic opal is also observed. It seems to be the main source of fluid in the second unit, whereas in Unit III it is zeolite water.

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PREPARATION AND SOLID STATE CHARACTERIZATION OF MONTMORILLONITE-CHITOSAN NANOCOMPOSITEAS DRUG CARRIER OF DICLOFENAC SODIUM

Dorsaf Cheickh (1,2)*, Fátima García-Villén (3), Hatem Majdoub (2), Memia Benna Zayani (1), César Viseras (3,4)

(1) Laboratory of Application of Chemistry to Natural Resources, Substances and the Environment(LACReSNE), University of Carthage, Faculty of Sciences of Bizerte, 7021 Jarzouna, Tunisia, (2) Laboratory of Interfaces and Advanced Materials (LIMA), Faculty of Sciences of Monastir, University of Monastir, Bd. Of the environment 5019, Monastir, Tunisia, (3) Department of Pharmacy and Pharmaceutical Technology, School of Pharmacy university of Granada, Campus of Cartuja, 18071 s/n, Granada, Spain, (4) Andalusian Institute of Earth Sciences, CSIC-University of Granada, Avda. de Las Palmeras 4, 18100 Armilla, Granada, Spain
*cheickhdorsaf@yahoo.fr

Diclofenac sodium (DS) is a widely used non-steroidal anti-inflammatory drug (NSAID) used in pain and inflammation with recognized gastrointestinal side effects [1]. In the present study, a nanocomposite made up from Tunisian purified montmorillonite (MMT) and chitosan (CS) was developed as a drug carrier of DS via intercalation solution technique as an attempt to increase therapeutic effectiveness and reduce side effects.

X-ray powder diffraction (XRPD), thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) and Fourier transformed infrared spectroscopy (FTIR) were employed for the characterization. XRPD were done by using a Philips® X-Pert diffractometer with Cu Kα radiation. TGA and DSC analyses were carried with a METTLER TOLEDO mod. TGA/DSC1, equipped with a FRS5 sensor and a microbalance (precision 0.1 µg) (Mettler-Toledo GMBH). TGA samples were subjected to a heat interval of 30-950 ºC, while DSC were done between 30-400 ºC. Both of them used a heat rate of 10 °C/min under aerobic conditions. FTIR was performed in atmospheric conditions by using a JASCO 6200 (resolution 0.25 cm^{-1}, 400-4000 cm^{-1}), equipped with an attenuated total reflectance accessory. FTIR data were processed with *Spectra Manager v2*.

Results obtained by TEM and XRD confirmed that the anionic drug was successfully loaded in the nanocomposite structure. TGA and DSC results were in agreement with XRD data revealing an intercalation of DS and CS in the MMT interlayer gallery. When intercalated into clay mineral structure, organic compound showed higher thermal stability. FTIR results showed peaks of diclofenac endorsing the intercalation of the drug via cation exchange in the clay-polymer interlayer.

Thus our study can be fruitful for biomedical applications by using the simple and non-toxic approach described in our study for the synthesis of clay loaded nanocomposites as carriers for different therapeutic molecules.

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CRYSTAL-BUNDLES DISSOCIATION AND APPLICATION OF PALYGORSKITE

Jing Chen*, Lingli Ni, Yelin Jin, Zhihui Wang, Jinlong Jiang

Faculty of Chemical Engineering, Key Laboratory for Palygorskite Science and Applied Technology of Jiangsu Province,
Huaiyin Institute of Technology, Huaian, 223003, P.R. China
*Jingchen@hyit.edu.cn

Palygorskite is a kind of natural clay with fibrous rod-like microstructure. It has been applied in many areas such as inorganic-organic polymer hybrids, fertilizer suspensions, drilling fluids, pharmaceutical industries, catalyst, catalyst support, etc. However, palygorskite ore is usually in a tightly aggregated state. The dispersion of palygorskite aggregates into smaller crystal bundles or even single crystals is very important and necessary for the efficient application of palygorskite.

We designed a constant pressure experiment to prove the feasibility of dispersing palygorskite by steam explosion. We achieved nanodispersion of palygorskite by regulating comprehensive force field [1]. Further more, we developed the process of modification-nanodispersion-desiccation integration for the dispersion of palygorskite. The results indicate that the dispersive medium with higher polarity, lager saturated vapor pressure, higher specific heat, and lower boiling point is benifical to disperse palygorskite crystal bundles during the stream explosion. Synergistic effect of proper water and nitrogen not only give play to the salvation effect of water but also decrease the use volume of water, which can effectively avoid palygorskite reaggregation. Water is the best dispersive medium, but the dispersed nanorod tends to reunite strongly; palygorskite dispersed by water can't avoid reaggregation even replaced by organic solvent; the organic medium might hybridize with palygorskite similar to the synthesis of Maya blue during drying process.

We also inverstigated the liquid crystalline phase behavior of dispersed palygorskite crystals in liquid phase [2]. The dispersed palygorskite can spontaneously transform into typical nematic phase according to nucleation growth mechanism; concentration is the key factor for the transformation. Dry-palygorskite hybrids can also form similar nematic phase, and the greater the density, the more obvious the dichroism of the hybrids.

The dye-palygorskite hybrid mechanism was studied and its possibility of utilization as function probe for metal ions was also inverstigated [3,4]. Dye molecules which go deep into the channels or grooves can get perfect chemical stability. In the hybrid, distortion occurred in the clay crystal lattice and the dye molecular structure. Electro-donating substituents is in favour of the hybrid, but the electro-withdraw substituents can dicrease hybrid activity. During hybridization, palygorskite always catalyzed the demethylation of $N(CH_3)_2$ of the dye. The hydrophobicity dye can spreed over palygorskite surface by hybridizing with the clay, which benefit the dye to unfold its molecular structure in aqueous phase. A novel hybrid of rhodamine-palygorskite was synthesized, to identify Cu^{2+} quickly in water solution with high selectivity and sensitivity.

Pd-B amorphous alloy was successfully supported on the surface of nano-clay palygorskite (PAL) via a simple chemical reduction method [5]. Compared with the conventional supported Pd catalyst, the Pd-B/PAL amorphous catalyst possessed an ultra-high selectivity (100%) to *o*-chloroaniline (*o*-CAN) in the hydrogenation of *o*-chloronitrobenzene (*o*-CNB) to *o*-CAN and avoided the dechlorination of *o*-CNB. XPS analysis indicated that PAL support could reduce the electron density of Pd atoms and suppressed the hydrogenolysis of C-Cl bond. Meanwhile, the Pd-B/PAL amorphous catalyst exhibited a good stability. It will be a prospective catalyst for the selective hydrogenation of chloronitrobenzene to chloroaniline.

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VISIBLE AND NEAR-INFRARED SPECTROSCOPIC COMPARISON OF PHYLLOSILICATE MINERALS

HONGFEI CHENG*, YIGAO SUN, QINFU LIU

School of Geoscience and Surveying Engineering, China University of Mining & Technology, Beijing 100083, P R China

As the most likely products of chemical weathering, hydrothermal alteration and sedimentary deposition, phyllosilicate minerals are common accessory minerals in several mineral deposits including copper porphyrys, nickel laterites, volcanic volatile-rich igneous rocks and coal deposits [1]. The phyllosilicates are an important group of minerals that includes kaolinite, montmorillonite, illite, micas, chlorite, serpentine, talc, and etc. Therefore, it is necessary to find out a facile characterization techniques to identify phyllosilicate minerals [2]. In the present study, the portable visible and near-infrared (vis/NIR) spectroscopy was used to characterize and differentiate the five phyllosilicate minerals and relate the bands to the mineral structure. The feature band at 2160-2170 nm (4600-4630 cm^{-1}) has been assigned to the high presence of Al-OH and is described as typical of dioctahedral phyllosilicate with OH groups coordinated around Al, and the feature occurred near 2322 nm is considered to be due to a combination of the OH stretch with the Mg-OH deformation mode, which is a typical of trioctahedral phyllosilicates. The presence of the bands 1400 and 1900 nm in vis/NIR spectrum indicated that some water is present in this sample. The absence of a 1900 nm band but the presence of a 1400 nm band indicates that only OH is present. Moreover, the significant differences between the five minerals were observed by the portable vis/NIR spectroscopy. The main differences between the five phyllosilicate minerals are observed by vis/NIR spectroscopy. A typical band near 2200 nm resolves into a double located at 2208 and 2166 nm in the spectrum of the mineral kaolinite, and another special band near 1400 nm resolves into two bands at 1392 and 1414 nm for the mineral kaolinite. Only two broad bands were observed the spectrum of antigorite. But several weak bands were observed in the vis/NIR spectrum of talc. The spectrum of the mineral muscovite sample showed a typical band at 2197 nm with two shoulders in the region between 2000 and 2400 nm, and it also had a broad band at 1414 nm. A typical band observed at 2172 nm with two shoulders was observed in the spectrum of the mineral pyrophyllite. Furthermore, the vis/NIR spectrum of pyrophyllite was dominated by very strong molecular water bands near 1400 and 1900 nm due to the bound water typical of pyrophyllite. The results show a potential for the application of vis/NIR spectroscopy in the identification and quantification of the minerals in the field. Further, such analysis can also provide important constraints on the nature of putative global and local-scale mineralogical transitions on Mars. Therefore, a new prospecting approach is discussed which helps to know a simple and user friendly technique to identify mineralization and field characterization can be done.

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STUDY ON CALCIUM SORPTION MECHANISMS IN CLAY-LIME SYSTEM

Chinchu Cherian*, Sandeep Bandipally, Nikhil John Kollannur, Dali Naidu Arnepalli

Department of Civil Engineering, Indian Institute of Technology Madras, Chennai 600036, India
*chinchu0401@gmail.com

The complex physico-chemical interactions occurring in a clay-lime system involves number of strongly coupled processes, such as short-term cation exchange reactions and flocculation mechanism as well as long-term pozzolanic reactions [1,2]. The adsorption of free lime significantly alters the physico-chemical and surface charge properties of clay minerals [3,4,5]; consequently, it has compounding effects on the overall kinetics of immediate and long-term reactions occurring in clay-lime system. Furthermore, each of these physico-chemical processes proceed at different rates due to the influence of various governing parameters such as inherent clay mineralogy and reactive nature of soil, as well as the pore fluid chemistry (viz., pH and ionic strength) [6,7,8,9]. In this context, aim of the present study is to improve the current understanding on the mechanisms of calcium sorption on clay minerals in a fundamental stand view of their reactive nature.

For experimental analysis, two commercial clays (white clay, WC and brown clay, BC) and a natural silty clay (SC) are selected and characterized for their physico-chemico-mineralogical properties (viz., pH buffering capacity (pHBC), cation exchange capacity (CEC), silica sesqui-oxide ratio (SSR)). The conventional batch-equilibrium sorption experiments are conducted to evaluate the characteristic sorption-desorption properties of selected soils for calcium ions, as a function of liquid-to-solid ratio, calcium concentration, temperature and pH. The equilibrium calcium concentration data of various sorption systems is procured and modelled using theoretical adsorption isotherms. From the obtained results, a considerable variation is observed in the sorption ability of the three clays owing to disparity in their reactive nature (reflected in terms of pHBC, CEC and SSR). A pH-dependent increase in calcium holding capacity is observed; this might be partly due torapid increase in the net negative surface charge, thereby enhancing affinity for calcium ions. Yet another reason can be the accelerated dissociation of weakly acidic Si-OH groups (exposed on edges of clay minerals) at high pH, and hence, providing more reactive sites for calcium sorption. The elevated temperature increases calcium sorption density, which might be attributed to the temperature dependent increase in silica dissolution from clay minerals [10]. In addition, the electrokinetic studies in terms of zeta potential variation also indicate significant alteration of surface charge properties of clay minerals owing to sorption phenomena. Further investigations on speciation of calcium in the presence of dissolved clay minerals are carried out with the aid of XRD and FTIR techniques. The obtained results show consistent lowering of silica intensities with increasing pH which illustrates incongruent dissolution of reactive silica. It is expected that at high pH condition the available free calcium can form new species with dissolved silica by surface complexation. On the whole, it can be inferred that the influence of pore fluid chemistry upon calcium sorption capacity of clay is mainly derived from the changes in its reactive nature, being manifested as variations in surface charge properties and dissolution kinetics.

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MICROBIAL TRANSFORMATION OF BENTONITE

Nicole Matschiavelli, Jennifer Steglich, Sindy Kluge, Andrea Cherkouk*

Helmholtz-Zentrum Dresden-Rossendorf, Institute of Resource Ecology, Bautzner Landstraße 400, 01328, Dresden, Germany
*a.cherkouk@hzdr.de

For the storage of highly radioactive waste in a deep geological repository a multi-barrier concept is favoured, which combines a technical barrier (canister including the highly radioactive waste), a geotechnical barrier (e.g. bentonite) and the geological barrier (host rock). Due to their properties, namely a high swelling capacity and a low hydraulic conductivity, bentonites fulfil in this system a sealing and buffering function. For the potential repository of nuclear waste the microbial mediated transformation of bentonite could influence its properties as a barrier material. To elucidate the microbial potential within selected bentonites, microcosms were set up, which contain 20g bentonite and 40ml anaerobic synthetic Opalinus-clay-pore water solution under an N_2/CO_2-gas-atmosphere. Substrates like acetate and lactate were supplemented to stimulate potential microbial activity. Microcosms were incubated in the dark, without shaking at 30 °C. Within an indefinite time scale samples were taken at different time-points of incubation and were analysed regarding geochemical parameters like pH, O_2-concentration, redox potential, iron-concentration and sulphate-concentration as well as biological parameters like the consumption and formation of metabolites. First results show that bentonites represent a source for microbial life, demonstrated by the consumption of lactate and the formation of acetate and pyruvate. Furthermore, microbial iron-reduction was determined. The results reveal the importance of the selection of the best suitable bentonite in order to avoid transformation of the mineral structure by indigenous microbes.

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SEPIOLITE CLAY PROMOTED WITH NICKEL AS AN EFFICIENT CATALYST TO PRODUCE METHANE FROM CO_2

Cristina Cerdá-Moreno*, Antonio Chica

Instituto de Tecnología Química, Universitat Politècnica de València-Consejo Superior de Investigaciones Científicas,
Avenida de los Naranjos s/n, 46022, Valencia, España

The necessity of lowering CO_2 emissions requires a noteworthy transformation of the future energy and fuel supply. A feasible approach is the utilization of this greenhouse gas as a raw material to procure useful fuels and chemicals [1]. In particular, the reaction of CO_2 with renewable hydrogen allows sustainable production of methane, which is an easily transportable and storable energy source. The reaction (1) of CO_2 with hydrogen that forms methane and water (also referred to as the Sabatier reaction) is a highly exothermic. According to Le Chatelier's principle, low temperatures and high pressure shift the equilibrium to the products side.

$$CO_2 + 4H_2 \rightleftarrows CH_4 + 2H_2O \quad \Delta H_{298K} = -\ 164{,}9\ kJ\cdot mol^{-1} \qquad (1)$$

Due to the high stability of CO_2 a catalyst is needed to overcome the significant kinetic barriers of this reaction. Transition metals catalysts, including Ni, Ru and Rh, with different supports (Al_2O_3, zeolite, SiO_2) have been demonstrated to be active in this reaction [2]. In the present work, a promising catalyst based on natural sepiolite promoted with Ni has been developed and studied in the CO_2 methanation. Sepiolite based catalyst has been characterized in order to know its most relevant physicochemical properties. The effect in the catalytic performance of different synthesis methods and reaction conditions (temperature, molar ration and partial pressure) has been also explored and a preliminary kinetic study is presented for the first time for this type of clay promoted with Ni.

Firstly, natural sepiolite containing 20 wt.% of Ni wwas prepared using three different preparation methods: precipitation (P), incipient wetness impregnation (IWI) and wet impregnation (WI). Secondly, the best method for Ni incorporation was used to prepared sepiolite based catalysts with different levels of Ni (5-35 wt.%) in order to find its optimal concentration. Finally, a kinetic study was carried out on the optimized sepiolite based catalyst.

$Ni(NO_3)_2\cdot 6H_2O$ was used as Ni precursor for the preparation of sepiolite based catalysts. After Ni incorporation the samples were calcined at 450 °C for three hours and activated in situ before reaction with H_2 at the same temperature for two hours. Catalysts were characterized by XRD, ICP-OES, BET surface area, TPR and H_2 chemisorption. Test reactions for the research of Ni incorporation methods and level of Ni were carried out in a flow fixed bed reactor at GHSV of 9000 mL/(gcat·h), H_2:CO_2 ratio of 4, atmospheric pressure and a reaction temperature between 250 and 450 °C. Kinetics study was carried at differential conditions. GHSV and reaction temperature were varied between 73440 and 116640 mL/(gcat·h) and 250 and 290 °C, respectively.

In the study of the influence of the Ni incorporation methods was found that the sample prepared by precipitation exhibited the highest CO_2 conversion values, especially at low reaction temperatures. The better activity of this catalyst is explained by its lower reduction temperature of the incorporated Ni, what allows a greater exposure of Ni metallic surface. The highest CO_2 conversion was obtained with the 30wt.% Ni incorporated sample, which also showed the highest proportion of exposed Ni metallic surface. The results of the kinetic studies carried out using the 30 wt.% of Ni samples suggest that the operating conditions (temperature, molar ratio of CO_2 and H_2 and partial pressure of products) had a significant influence on the CO_2 conversion. Power rate law expression and Langmuir-Hinshelwood mechanism have been considered for the kinetic analysis.

Our results show that the natural sepiolite prepared by precipitation of 30 wt.% of Ni is a promising catalyst for the sustainable production of methane from an atmosphere contaminant as the CO_2.

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CHLORITE GEOTHERMOMETRY APPLIED TO MASSIVE AND OSCILLATORY-ZONED RADIATED Mn-RICH CHLORITES IN THE PATRICIA POLYMETALLIC EPITHERMAL DEPOSIT (NE, CHILE)

Darío Chinchilla (1,2)*, Xabier Arroyo (3), Raúl Merinero (1), Rubén Piña (1), Fernando Nieto (4), Lorena Ortega (1), Rosario Lunar (1,2)

(1) Department of Crystallography and Mineralogy, Complutense University of Madrid, 28040, Madrid, Spain, (2) Institute of Geosciences (CSIC, UCM), Complutense University of Madrid, 28040, Madrid, Spain, (3) CAI of Geological Techniques, Complutense University of Madrid, 28040, Madrid, Spain, (4) Department of Mineralogy and Petrology, University of Granada-CSIC, 18002, Granada, Spain

The Patricia Zn-Pb-Ag deposit represents an example of polymetallic epithermal mineralization, unusual in northern Chile. The sulfide mineralization occurs as W-E oriented veins hosted in volcanic rocks, mainly andesite of Upper Cretaceous to Middle Tertiary age. Three main stages of mineralisation have been defined in the Patricia deposit: (1) pre-ore stage, (2) base-metal stage which is divided into two substages: substage 2A and substage 2B, and (3) post-ore stage. The pre-ore and post-ore stage is characterized by quartz, pyrite and arsenopyrite whereas the second stage is characterized by sphalerite, galena and minor amounts of Ag-bearing minerals. Two textural types of chlorite are identified within the mineralised veins of Patricia deposit: massive and oscillatory-zoned radiated chlorites. Both types of chlorite are classified as chamosite and occur coeval to the sphalerite precipitation during the substage 2A. Massive chlorite shows an average content of 33 wt.% FeO, 4.9 wt.% MnO, and 4 wt.% MgO. Oscillatory zoning in radiated chlorites consists of concentric bands with different contents on FeO (from 26.45 to 41.41 wt.%), MgO (from 1.7 to 5.44 wt%) and MnO (from 1.7 to 9.32 wt.%).

Temperature and pressure of mineralising fluids are essential parameters to characterise ore forming processes in hydrothermal systems. Changes in chemical and/or physical conditions during the sequence of mineralisation are reflected in banded veins and comb, crustiform and colloform textures as well as compositionally zoned minerals. Several methods are commonly used to trace thermal variations within hydrothermal systems, including fluid inclusions studies, stable isotopes and mineral geothermometry. However, careful paragenetic determinations on the mineralogical assemblage are essential for obtaining meaningful results from the geothermometric methods. The aim of this study is to calculate the temperature to both types of chlorites using four different chlorite geothermometers [1,2,3,4] based on the system SiO_2-Al_2O_3-FeO-MgO-H_2O, and contrasting the results with fluid inclusions data [5]. The temperature estimations are in agreement with temperatures data of fluid inclusions previously measured in sphalerite of the sub-stage 2A. Despite the high content in Mn of chlorites, the study confirms the applicability of the chlorite geothermometers without the knowledge of the Fe^{3+}/Fe ratio in low-pressure paragenesis and its usefulness as an important tool for characterising the thermal conditions in epithermal ore deposits.

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RECENT DEVELOPMENTS IN ELECTRON AND ION MICROSCOPY FOR CLAY RESEARCH

Wen-An Chiou

Advanced Imaging and Microscopy Laboratory (AIM Lab), NanoCenter, University of Maryland, College Park, 20742-2831, USA
wachiou@umd.edu

A plethora of advanced instrumentations and technologies are available for scientific and engineering research at the nano- and subnano-meter scale. High resolution and analytical tools are enable researchers to accurately understand and deduce the microstructure, composition, and behavior of small clay particles. Recent developments in electron microscopy (EM) and focused ion beam (FIB) technology have resulted in very powerful and indispensable tools that greatly enhance clay research. Furthermore, *in-situ* experiments at the nano-scale are crucial in understanding the natural processes (interactions and reactions) of clay materials. This paper presents unique applications of FIB in sample preparation and clay characterization. Additionally, the application of various *in-situ* experiments of clays, including microstructural examination of wet specimens, in both scanning electron microscopy (SEM) and transmission electron microscopy (TEM) using ionic liquids will be introduced.

Clay materials, both synthetic and natural samples (from different localities), were examined using different techniques. Experimental results will be presented and discussed in this paper. Conventional sample preparation of small clay particles (such as drop of clay suspension on various substrates, or grinding and polishing for ion milling and ultra-microtoming) for individual clay particles, especially at interfaces has been difficult due to the minute size and property differences. Using a combined FIB/SEM (dual-beam) technique, specimen cutting and imaging can be performed simultaneously and precisely (site specific). Microstructures and microchemistry of clay particles/assembles can thus be reconstructed and presented in 3D using modern computer software. Time of flight secondary ion mass spectroscopy (ToF-SIMS) attached on modern FIB/SEM provides depth profile of elemental distribution and concentration. An attached cathodoluminscence (CL) detector enables production of high-resolution digital cathodoluminescent (CL) images of luminescent materials. Results will be presented that demonstrated the unique, versatile application of dual beam FIB/SEM with attached analytical equipment in clay materials research.

Special EM sample holders have been developed and fabricated for *in-situ*, high-resolution, investigative experiments in EM. One long-standing challenge of clay research is specimen preparation for investigating naturally wet specimen in EM. In addition to wet-cell environmental TEM (WETEM) and cryo-TEM, a new simple technique uses the application of ionic liquid to examine wet clays in both TEM and SEM. Ionic liquid (also known as liquid electrolyte), is a salt in liquid state that has high conductivity, high affinity to biological organism that are typically solid in ambient temperature, high osmotic pressure, and zero vapor pressure. These special properties allow for investigation of natural wet clay samples in a regular, high vacuum SEM and TEM without dehydration and coating of conductive materials on the clay (specimen) surface. Electron diffraction patterns reveal that water molecules remained in clay particles despite immersion in the high vacuum environment EM column. Examples of the application of ionic solution to study wet specimen in SEM and TEM will be shown and discussed.

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IN-SITU HEATING OF SMECTITE NANOPARTICLES

Wen-An Chiou*, Sz-Chain Liou

Advanced Imaging and Microscopy Laboratory (AIM Lab), NanoCenter, University of Maryland, College Park, 20742-2831, USA
*wachiou@umd.edu

The crystallographic structure of clay minerals has been well known for decades. X-ray diffraction (XRD) has been the major and most popular method in clay minerals research. The technique is based on the identification of d-spacing obtained from (00l) prefer-oriented mounted clay samples with different treatments; and heating treatment of clay minerals at various elevated temperatures is the typical criteria for clay identification. It is known that the reduction of basal (d-) spacing is due to the collapsing of lattice structure on the c-axis by losing water molecules and organic matters at higher temperatures. While the intensity of basal plane (00l) spacing of clay minerals is variable under increased temperature, eventually all clay minerals become amorphous after exposure to higher temperatures. Problematically, research investigating heating treatment and mechanisms of amorphization are currently lacking. This research capitalizes on the unique capabilities of environmental TEM (ETEM) to examine the process of smectite amorphization under *in-situ* heating in TEM.

Smectite (Wyoming bentonite) was selected for this research. Wyoming bentonite was crushed, dispersed in deionized water, and less than 0.2 µm smectite was collected using a sedimentation method. A very small drop of smectite suspension was pipetted on a holey carbon grid and air-dried. The smectite specimen was then placed onto a TEM heating holder/stage (Gatan, Inc) that enabled heating of the sample from room temperature to different temperature settings up to 1,100 °C. Smectite was heated at 100 °C, 300 °C, 500 °C, 700 °C, 800 °C, 900 °C and 1,000 °C in the TEM for different lengths of time. Morphology and electron diffraction studies were carried out using JEOL 2100 TEM equipped with Oxford EDS system and Gatan CCD camera.

Morphology of smectite before and after various heating treatments was investigated. The majority of smectite particles (platy flakes) appeared relatively stable with very little change before 550 °C. More drastic changes of the smectite morphology were observed when smectite clays were heated between 550 °C to 700 °C. With increased temperature and the duration of heating, TEM images showed that edges of the smectite flakes appeared unclear, indistinct, and homogeneous such that it resembled to amorphous materials. High resolution TEM images also depicted some loss of lattice spacing after heating at 550 °C. After heating at 700 °C the size and volume of amorphization increased, and only a few lattices remained in several particles. The result of selected area electron diffraction (SAD) is consistent with TEM study. However, SAD patterns showed the onset of diffused diffraction rings at 550 °C. A few diffraction rings were enhanced in sharpness and intensity which indicated crystallization had occurred through temperature heating. However, diffraction patterns quickly weakened after heating at 700 °C, becoming broadly diffused except in some diffraction spots due to the presence of non-smectitie nanoparticles.

Notably, small nanoparticles particles of 5 ~10 nm in diameter were observed on thin sheets of smectite after heating at 550 °C. Those nanoparticles were identified as pure Cu. The size and amount of Cu nanoparticles increased with the increase of temperature. At 700 °C the vast majority of smectite particles were covered with Cu nanoparticles. Heating at 800 ˚C showed increased size of Cu nanoparticles on smectite, and the formation of large euhedral Cu particles (>150 nm in diameter) on the supporting carbon substrate. Cu particles grew to 500 nm in diameter after heating at 900 °C and remained visible on smectite particles. The Cu particles likely formed at as a result from heating process of the Cu grid. While heating the sample (and thus the Cu grid) to 550 °C or higher, a very small amount Cu vapor from the grid was condensed and adsorbed on the negatively charged surface of the smectite. This *in-situ* TEM heating experiment illustrated the evolution of smectite microstructure with heating treatment. The formation of Cu nanoparticles on the smectite surface also provided another means to investigate the surface chemistry of smectite at higher temperature.

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Co-CONTAINING HYDROTALCITE-LIKE MATERIALS AS PRECURSORS OF EFFECTIVE CATALYSTS FOR METHANOL COMBUSTION - ROLE OF Co CONTENT, Mg/Al RATIO AND CALCINATION CONDITIONS

Sylwia Basąg (1), František Kovanda (2), Zofia Piwowarska (1), Andrzej Kowalczyk (1), Katarzyna Pamin (3), Lucjan Chmielarz (1)*

(1) Jagiellonian University, Faculty of Chemistry, Ingardena 3, 30-060 Kraków, Poland, (2) University of Chemistry and Technology, Department of Solid State Chemistry, Technická 5, 166 28 Prague, Czech Republic, (3) Jerzy Haber Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences, Niezapominajek 8, Kraków, Poland
*chmielar@chemia.uj.edu.pl

Hydrotalcites, called also layered double hydroxides (LDHs), are minerals characterized by the brucite-like network, $Mg(OH)_2$, where octahedra of Mg^{2+} are six-coordinated to OH^-. Part of Mg^{2+} cations is substituted by trivalent aluminium cations, what results in the positive charging of the brucite-like layers compensated by anions (typically CO_3^{2-}), which together with water molecules are located in the interlayer space of hydrotalcite. It is possibly to relatively easy synthetize materials with the hydrotalcite-like structure in laboratory conditions. In such hydrotalcite-like materials Mg^{2+} as well as Al^{3+} ions can be partially or completely replaced by various di- (e.g. Cu^{2+}, Co^{2+}) and/or trivalent (e.g. Fe^{3+}, Cr^{3+}) cations, respectively. The range of various metal cations that can be incorporated into the brucite-like layers is relatively broad and is determined by their size, which should be similar to that of Mg^{2+} in the case of divalent cations and to Al^{3+} in the case of trivalent cations. Thermal decomposition of hydrotalcite-like materials results in the formation of mixed metal oxides, which due to their relatively high surface area, porosity and homogenous distribution of metal cations are very interesting for potential application in catalysis [e.g. 1-3], including also the processes of catalytic VOCs combustion [e.g. 4,5].

Hydrotalcite-like materials containing cobalt, magnesium and aluminium were synthesized by co-precipitation method. The structure of the obtained materials was characterized by XRD studies, which showed apart from hydrotalcite no other phases. Thermal decomposition of hydrotalcite-like materials was studied by combined thermogravimetric method with analysis of evolved gas products (QMS). Hydrotalcite-like materials were calcined at 600, 700 and 800 °C in air atmosphere. In diffractogram of the samples calcined at 600 and 700 °C only reflections characteristic of periclase (MgO) were identified, while calcination of the samples at 800 °C resulted also in the formation of the spinel phases. The obtained Co-Mg-Al mixed metal oxides were tested as catalysts for methanol combustion (methanol as model VOC molecule). Catalytic performance of the oxides depended on cobalt content, Mg/Al ratio and calcination temperature. The catalysts with lower cobalt content, higher Mg/Al ratio and calcined at lower temperatures were less effective in the process of methanol combustion. In a series of the studied catalysts the best results, with respect to high catalytic activity and selectivity to CO_2, were obtained for the mixed oxide with Co:Mg:Al molar ratio of 10:57:33 calcined at 800 °C. High activity of this catalyst was likely connected with the presence of a Co-Mg-Al spinel-type phase formed during high-temperature treatment of the hydrotalcite-like precursor. It seems that the Co^{3+}-containing spinel-type phase, very likely the $MgCo_xAl_{(2-x)}O_4$ mixed oxide; is more catalytically active in methanol combustion than other cobalt-containing phases formed during calcination of the hydrotalcite-like precursor. High catalytic activity of the spinel phase was ascribed to the relatively easy reducibility of Co^{3+} to Co^{2+} cations identified by cyclic voltammetry (CV) and temperature programmed reduction (H_2-TPR) measurements.

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POROUS CLAY HETEROSTRUCTURES (PCH) INTERCALATED WITH SiO_2-Al_2O_3, SiO_2-TiO_2 AND SiO_2-ZrO_2 PILLARS AS PROMISING CATALYST OF DEHYDRATION OF METHANOL IN DIMETHYL ETHER

Andrzej Kowalczyk, Małgorzata Rutkowska, Piotr Natkański, Lucjan Chmielarz*

Jagiellonian University, Faculty of Chemistry, Ingardena 3, 30-060 Kraków, Poland
*chmielar@chemia.uj.edu.pl

Clay minerals, especially those belonging to the group of smectites, attract much interest due to their possible applications in various industries. Many scientific reports presenting various methods of their modifications including surfactant-directed intercalation with silica pillars (PCHs - porous clay heterostructures) were published [e.g. 1]. This method of clay minerals modification appears to be very promising due to high surface area and porosity as well as high thermal and hydrothermal stability of the obtained PCH materials. Moreover, surface acidity and ion-exchange properties, make these materials very promising for the potential applications in catalysis. The properties of PCH materials can be designed by using various layered clay minerals characterised by different density of acid sites and ion-exchange potential [2]; surfactants and co-surfactants of various structure and size to design pore diameters in PCHs; incorporation of various components into the silica pillars to generate additional acid sites and/or ion-exchange properties [3]. PCH materials containing apart from silica also other components generating acid sites were studied in the role of catalysts for dimethyl ether synthesis from methanol.

Dimethyl ether (DME) is one of the most promising environmentally friendly and economic alternative fuel for the future applications [4,5]. DME is use among others as a source of hydrogen for fuel cells, fuel in gas turbines for power generation [4,5]. Furthermore, it has similar properties to propane and butane, the principal constituent of LPG, and therefore it can be used as a LPG substitute in domestic energy supply or for industrial uses [5]. Another advantage of DME is that it can be used as an additive for diesel fuel due to its high cetane number (about 55-60), high oxygen content (34.8% by mass) and lack of C-C bond [4,5]. The DME synthesis from alcohol is known to be acid catalysed. Commercial catalysts used for converting methanol to dimethyl ether are solid acid materials, such as γ-Al_2O_3, zeolites (HZSM-5 or HY), silica-alumina or phosphorus-alumina [5], however due to side process of carbon deposit formation the catalysts with small pores (e.g. zeolites) can be quickly deactivated due to blocking of pore system by coke [4]. The solution of this problem could be application of PCH materials, which are characterized by larger pores than zeolites, and therefore are considered to be much less susceptible for deactivation due to lower diffusion limitations in their pore systems.

A series of PCHs intercalated with SiO_2, SiO_2-Al_2O_3, SiO_2-TiO_2 and SiO_2-ZrO_2 pillars was obtained from montmorillonite by the surfactant-directed method. The obtained materials were characterized by high surface area and uniform porous structure. Their surface acidity depended on the type of parent clay mineral as well as on chemical composition of interlayer pillars. Incorporation of titanium, aluminium or zirconium into the structure of the silica pillars significantly increased their surface acidity and catalytically activated PCHs in the reaction of DME synthesis. Catalytic performance of the PCH materials was correlated with the nature and strength of acid sites, which are known to play role of active sites in the process of DME synthesis from methanol. For the selected PCH based catalysts the tests of catalytic stability were done.

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STRUCTURAL CHANGES OF Mn-SUBSTITUTED FERRIC IRON OXYHYDROXIDE (MSF) AND THEIR ADSORPTION PROPERTIES FOR ARSENIC IN AQUEOUS SOLUTION

Chul-Min Chon*, Soh-Joung Yoon, In-Hyun Nam, Jae Gon Kim

Korea Institute of Geoscience and Mineral Resources, Daejeon, South Korea

Synthetic MSF samples with different Mn/Fe molar ratios were prepared by hydrolysis of Fe(II) ions and Mn(II) ions under alkaline conditions followed by rapid oxidation with H_2O_2. In analysis of transmission electron microscope (TEM), MSF consisted of nano-sized hexagonal-like particles and was similar to hematite. Synchrotron based powder X-ray diffraction patterns were collected on the beamline 9B (HRPD) at Pohang Accelerator Laboratory (PLS-II) in Korea. The incident X-rays were monochromatized to wavelength of a 1.4970 Å using a double-crystal Si(111) monochromator. Diffraction patterns were collected in the 2θ range of 5-125.5°, with a step size of 0.02°. Rietveld structural refinement was performed with the TOPAS program (ver. 4.2; Bruker, Germany) to evaluate the changes in crystal structure with the substitution of Mn. Varying the ratio of Mn/Fe had an influence on the crystal structure of the produced MSF as shown by the X-ray diffraction (XRD) results. An interesting observation in the XRD spectra of the different MSF materials was the significant change in the unit cell parameter with different Mn/Fe ratios. Rietveld refinement analysis revealed that the crystal structures of MSF materials resemble those of feroxyhyte (δ'-FeOOH), with the unit cell volume and *a*-axis lattice parameter proportionally decreasing with increasing Mn-substitution, resulting in the formation of a δ-(Fe_{1-x}, Mn_x)OOH-like structure. Zeta potential analysis of MSF showed that the particles became negatively charged with an increasing Mn ratio. MSF with a high molar ratio of Mn showed high oxidative capacity to oxidize As(III) to As(V), while the composite had relatively low adsorption capacities for both the arsenic species. The δ-($Fe_{0.9}$, $Mn_{0.1}$)OOH removed 72.5-89.2% of total adsorbed arsenic species within the first 70 min in the range of initial concentrations of 19.4-98.0 As mg L^{-1}. The oxidative capacity of MSF increased proportionally with increasing Mn-substitution, but magnetic moment significantly decreased. The magnetic MSF, developed at the optimal Mn/Fe molar ratio, could oxidize contaminants and adsorb arsenic species in aqueous solution, and could easily be recovered by magnetic separation.

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PREPARATION AND CHARACTERIZATION OF CLAY-TITANIA NANOFILTRATION MEMBRANES

Sridhar Pandian, Arshad, Pavithiraa S, Tanushree Choudhury*

Vit University, Chennai, India

Most of NF (nanofiltration) membranes which are developed recently are composite membranes, whose support layer is covered with an active layer. Among different ceramic support materials that are currently used as support layers, γ alumina supports are integral part of membrane which is made of artificial materials like alumina and thus adds to the high price of the membrane. This draws our attention in making low cost support material of natural clay which aims to be an excellent membrane support as it possesses high mechanical strength, high permeability, narrow pore size distribution, and low manufacturing cost. Apart from these advantages, natural clay's application to membrane making is still new. Only some works deal with clay membranes in tubular form, but very few as flat disks. The aim of this work is to develop ceramic flat disk multilayer nanofiltration membranes which can be used for industrial waste water treatment.

Macroporous flat disk supports of the order of 25 mm in diameter and 2 mm in thickness are prepared from bentonite by uniaxial pressing method and sintered at 950 °C for 6 hours in a temperature controlled muffle furnace at a controlled heating and cooling rate of 2 °C/min. Two types of colloidal sol-gel derived mesoporous interlayers are considered for dip coating of the supports: TiO_2 sol and TPIC (titania pillared clay) binary sol. The active NF top layer is a very thin and fine textured polymeric TiO_2 top layer. The supported as well as the unsupported membranes are characterized by scanning electron microscopy (SEM), X-ray diffractometer (XRD), Fourier transform Infra Red Spectroscopy (FT-IR), and N_2 adsorption-desorption method to study the porosity. The polymeric top layer is defect free and very thin layer of polymeric TiO_2 of particle size of around 5 nm and layer thickness of 2.39 µm. Other parameters that are studied included the effect of pH and sintering temperature on the porosity and pore size distribution of the membranes. Results concluded that these nanofiltration membranes could be used for industrial waste water treatment.

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MICROSTRUCTURAL CHARACTERIZATIONS OF THE KAOLINITE SAMPLES UNDER SECONDARY COMPRESSION USING THE 3D PRINTING TECHNIQUE AND MICROMECHANICAL APPROACH

Jun Kang Chow (1)*, Yu-Hsing Wang (2)

(1) Research student, Department of Civil and Environmental Engineering, The Hong Kong University of Science and Technology, Clear Water Bay, Hong Kong SAR, (2) Professor, Department of Civil and Environmental Engineering, The Hong Kong University of Science and Technology, Clear Water Bay, Hong Kong SAR

The objective of this paper is to study the microstructural responses of kaolinite samples subjected to secondary compression, using high-quality and representative samples. Following the practical guide proposed by Chow and Wang [1], high-quality, load-preserved fabric 1-D consolidated kaolinite samples were prepared. In conjunction with that, a tailor-made oedometer was invented and produced using a 3D printing technique, which aiming at maintaining the applied loading during the freezing process to preserve the fabric associations for the subsequent microstructural characterizations. Then, Mercury Intrusion Porosimetry (MIP) and Scanning Electron Microscopy (SEM) were used to and obtain the information on the pore-size distribution and observe the morphological information at the observation plane (along the center of the sample), respectively. In addition to that, for each sample, about 20 ~ 30 SEM images were taken, with approximately 150 ~ 300 particles being identified in each SEM image, for providing representative results. Also, the SEM images were converted into binary images for better identification of the voids, which were then described using an equivalent ellipse. To concisely quantify the directional probability distribution of both voids and particles, second order weighted fabric tensors, as suggested by several researchers, e.g., Fu and Dafalias [2], were used. The fabric tensors obtained could be described using the major principal direction and the anisotropy intensity factor. Also, the evolution of the pore shape was examined based on the SEM images.

Two kaolinite samples (Sample ① and ②) were undergone 1-D consolidation at pressure of 100 kPa, using the 3D-printed oedometer. The consolidation period lasted for 24 hours, and Sample ② was further consolidated for an additional 4 days of secondary compression. Based on the MIP results, the upper boundary of intra-aggregate pores identified was ~ 0.14 μm. The findings showed that the large inter-aggregate pores were further compressed during secondary compression, and the intra-aggregate pores remained constant. Also, the study of fabric tensors revealed that secondary compression caused both particles and voids converged more to the major principal direction lying along the horizontal direction (perpendicular to the vertical loading). Further evidence was given based on the examination of the pore shape. During secondary compression, the inter-aggregate pores that were initially elongated vertically were compressed slightly into a rounder shape. For those pores which were aligned horizontally, they were further compressed and became slightly more elongated in the horizontal direction. The findings were consistent with results reported by several researchers, e.g., Wang and Xu [3], where the secondary compression is a continuation of the primary consolidation that takes place in the inter-aggregate pores.

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SHALE OF THE IVORY COAST AS A FILTRATION MATERIAL FOR PHOSPHATE REMOVAL FROM WASTE WATER

Kpannieu Eude (1,2), Mallet Martine (1), Abdeloula Mustapha (1), Coulibaly Lacina (2), Ruby Christian (1)*

(1) Laboratoire de Chimie Physique et Microbiologie pour les Matériaux et l'Environnement - LCPME UMR 7564 CNRS-Université de Lorraine, 405 rue de Vandoeuvre, 54600 Villers-lès-Nancy, France, (2) Laboratoire d'Environnement et de Biologie Aquatique, Université Nangui Abrogoua, 02 BP 801, Abidjan 02, Côte d'Ivoire

The annual population growth rate of African cities is on average 5%. This situation leads to increasing quantities of wastewater generated in most cities. For example, in the Ivorian capital Abidjan, the daily volume of collected wastewater is actually ~190 000 m^3. The Abidjan wastewaters only undergo a passive treatment prior to discharge into the Ebrié lagoon. Moreover, excess of orthophosphate is at the origin of eutrophication that leads to strong perturbation of the lagoon biodiversity. Therefore, there is a growing interest to identify easily available minerals for performing tertiary treatment of dephosphatisation [1].

In this study, samples of shale were collected from Toumodi region (*i.e.* Lomo North site) in the Center of Ivory Coast. The solid samples were characterized by several techniques including XRD, Mössbauer spectroscopy, SEM-EDX, XPS and ICP-MS. The major minerals of the shale are silicates and phyllosilicates, *i.e.* quartz, albite, muscovite and clinochlore. Structural Fe^{III} and Fe^{II} species are present in substitution of other cations of the clay minerals and a minor part of the Fe^{III} species is present in goethite α-FeOOH.

The reactivity of the shale with phosphate (PO_4) was studied in both homogeneous suspension ("batch reactor") and in hydrodynamic conditions ("column reactors"). A particular attention was devoted to determine both residual phosphate and metal species (Ca^{2+}, Mg^{2+}, Al^{3+} and total iron) released in solution after phosphate sorption. Kinetics experiments in "batch reactors" showed that the saturation of the shale surface by PO_4 occurred after ~24 hours of contact time. Adsorption isotherms led to a maximal PO_4 adsorption capacity of ~0.4 mg g^{-1} at neutral pH. The PO_4 removal capacity decreased with increasing pH and reached a minimum around pH = 10. In strong alkaline conditions, an increase of the PO_4 removal capacity was observed that was linked to an increase of the aluminum solubility. During the column experiments, the phosphate solution circulated continuously during a five days period and then was stopped during 2.7 days to study the effect of residence time on phosphate removal. This sequence was repeated several times in order to reach a quasi- saturation of the column by PO_4. The PO_4 breakthrough of the column was strongly dependent on the contact time. Interestingly, a correlation between the increase of PO_4 removal rate observed at longer contact time with an increase of Ca^{2+} and Mg^{2+} solubility was established. Therefore, these species could play a more important role than iron in the PO_4 removal mechanism of shale.

In conclusion the shale of Ivory Cost is an interesting material for PO_4 removal from wastewater. Nevertheless, it should be compared in terms of removal efficiency and cost to other readily available natural compounds, *e.g.* laterite and sandstone, or recently developed synthetic Fe^{III} nanocomposites [2].

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STRUCTURE STUDY OF Ge-AKAGANEITE USING RIETVELD REFINEMENT AND COMPUTATIONAL MODELLING

Donghoon Chung, Changyun Park, Jeacheon Shim, Yungoo Song*

Yonsei University, Seoul, Rep. of Korea

Akaganeite is one of the polymorph of FeOOH (β-FeOOH) like goethite, well-known as α-FeOOH, and has been reported as a main Fe-oxide component in some soil and brine deposits [1]. This akageneite has been interested as a means of preparing uniform nanocrystalline hematite particles (α-Fe_2O_3) [2,3] rather than as a catalyst and absorbent. It is because akaganeite can be synthesized as rod-like structures [4], but its structural ordering and stability is low, and then it is easily transformed to the more stable form, α-Fe_2O_3 (hematite) by dehydration or dehydroxylation [3,5]. Meanwhile synthesizing method of highly ordered Ge-incorporated akageneite was reported [6]. In this study, we perform Rietveld refinement and computational method to find structure model of Ge-akaganeite. Naturally occurred and synthesized akaganeite were refined by Post and Buchwald (1991) [7] and Post et al. (2003) [8]. The symmetry of Ge-akaganeite is based on I 2/m and the tunnel site was modelled with computational method with CASTEP. From the rietveld refinement, the model of 25% Ge existed in tunnel site substituting Cl and remains in Fe1 site substituting Fe is well-matched showing 0.0756 wRp value. The tunnel Ge is expected to $Ge(OH)_4$ because of synthesizing material, that lead to the position of OH should be calculated with the condition of geometrical optimization in CASTEP program.

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STABILITY OF ANTIBIOTIC INTERCALATED IN MONTMORILLONITE: GENTAMICIN INTERCALATED IN MONTMORILLONITE

Donghoon Chung (1), Young Goo Song (2), Il-Mo Kang (3), Woohyun Choi (1), Chaewon Park (1), Yungoo Song (1)*

(1) Yonsei University, Seoul, Rep. of Korea, (2) Gangnam Severance Hospital, Yonsei University College of Medicine, Seoul, Rep. of Korea, (3) Korea Institute of Geoscience and Mineral Resources, Daejeon, Rep. of Korea

Montmorillonite have isomorphous substitutions of divalent cation for Al in the octahedral sheet mainly induce a negative charge that leads the interlayer to be an active cation-exchangeable site with alkaline earth metal ions and positive organic molecules for charge compensation, indicating that montmorillonite could be used as a drug-carrying material [1,2]. Therefore, the use of montmorillonite-based biomaterial as a drug delivery vehicle has attracted great interest in recent years, and many studies have reported various drug-intercalated montmorillonite hybrids including donepezil [3], lincomycin [4], timolol maleate [5], vitamin B1 [6], chlorhexidine acetate [7], tetracycline [8,9], and metronidazole [10] for controlled delivery and release behaviours.

Gentamicin is a one of the aminoglycoside antibiotics which is widely used in topical therapy. This antibiotic is reported to have an effective MIC in *Helicobactor pylori* [11] but not used for oral administration by low bioavailability.

In this study, we develop gentamicin -intercalated montmorillonite hybrid and demonstrate the 16days of release test to measure the stability of gentamicin in interlayer condition.

The experimental conditions were chosen to 500 ml of 1.5 mg/ml gentamicin sulphate was vigorously mixed with 2g of montmorillonite (Bgp35, Bgp40) from Pohang, Korea. After 1-day mixing, settle downed complex was dialyzed and freeze-dried. The complex was tested 2-day interval release test with 100mg of complex to 20 ml of simulated gastric fluid (pH 1.2) ratio.

Comparing the result, each hybrid shows different aspect in stability that might be from content of Fe ion. Hybrid made by Bgp35 may be expected to prolong its gastrointestinal residence time by covering mucous membrane and these characteristics could be increase the bioavailability of antibiotic.

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NEUTRON REFLECTION FROM THE MICA/LIQUID INTERFACE

Finian Allen (1), Kathryn Browning (2), Stuart M. Clarke (1)*, Luke Clifton (3), Lucy Griffin (1), Philipp Gutfreund (4), Arwel Hughes (3), Maximillian Skoda (2), Rebecca Welbourn (2)

(1) Department of Chemistry and BP Institute, University of Cambridge, UK, (2) Department of Pharmacy, Uppsala University, Uppsala, Sweden, (3) ISIS neutron facility, Harwell Science campus, Oxon, UK, (4) Institute Laue Langevin, Grenoble, France

Recently we have enabled the study of the mica/liquid interface using the technique of neutron reflectometry. This approach will be shown to provide unique compositional and structural insight into this important interfacial system at molecular level and importantly it will be demonstrated that it is non-invasive. We are now able to probe the structural details of monolayers, bi layers and interesting electrostatics of surfactants and ionic liquids.

Neutron reflectometry has been used for a number of years to structurally characterise molecules such as surfactants at the air/water and particular solid/liquid interfaces (mainly silica). We have recently enabled this approach to be used for the study of a number of new surfaces particularly mica (1-4) and other minerals (5-6) in oil or water and hence have begun the study of adsorbed molecular systems with this method. The key advantages of neutrons over related methods, such as AFM, SFA and X-ray reflectometry are (i) its non-invasive nature and (ii) there is excellent contrast to observe the adsorption of similar species when looking at mixtures. This contrast arises from the very different scattering of hydrogen and deuterium allowing us to study complex mixtures of very similar materials, not possible with X-ray. In addition, neutron reflection averages over very large areas compared to other techniques, local probe techniques.

Using this method we have already observed a variety of behaviour and propose to outline the capabilities of this method with illustrations of adsorption of cationic surfactants, anionic surfactants and the layering of ionic liquids at the mica surface - a unique capability.

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VALORISATION OF PIETRA SERENA SANDSTONE SEWAGE SLUDGE IN MATRIX OF METAKAOLIN

Marina Clausi (1)*, Ana M. Fernández-Jiménez (3), Serena Chiara Tarantino (1,2), Michele Zema (1,2), Angel Palomo (3)

(1) Dipartimento di Scienze della Terra e dell'Ambiente, Università degli Studi di Pavia, via A. Ferrata 9, I-27100 Pavia, Italy, (2) CNR-IGG, Sezione di Pavia, via A. Ferrata 9, I-27100 Pavia, Ital, (3) Instituto Eduardo Torroja (IETcc), CSIC, C/ Serrano Galvache 4, 28033 Madrid, Spain
*marina.clausi01@universitadipavia.it

Many studies on alkali activated materials (AAMs) as alternatives to traditional construction materials, such as mortars or Ordinary Portland Cement (OPC), have been realized with a view towards the themes of sustainability and reuse of waste materials, derived by various human activities, producing economic and environmental benefits [1].

The aim of this work was to investigate a potential alternative to the disposal of sewage sludge, deriving from the cultivation of an Italian sandstone known as Pietra Serena, evaluating their use as precursors in the alkaline activation process.

Pietra Serena sewage sludge (sPS) were used as such and after a thermal treatment at 800 ºC for two hours. A synergic use with a high-quality kaolin, heated at 800 ºC for two hours to obtain the relative metakaolin, was also proposed with the aim to produce valid construction materials, being metakaolin one of the most studied precursors, due to its high reactivity and the good properties in terms of resistance and durability of the final products [2].

AAMs obtained by different proportions of binary mixtures of sPS and metakaolin were synthetized using 8M and 12M NaOH solutions and curing samples at 85 °C and 100% R.H. for 5 or 20 hours. Materials were characterized by X-ray power diffraction (XPRD), Fourier transform infrared (FTIR) spectroscopy, scanning electron microscope (SEM), colorimetry and mechanical tests.

Samples produced exclusively by using the untreated sludge (sPS) show low compressive strength (3.6(2) MPa). The mechanical behaviour of AAMs obtained from the binary mixtures of sPS and metakaolin denoted the sPS inefficiency as a filler and their low reactivity towards metakaolin.

The decarbonation process of the sewage sludge provided a useful tool for the valorisation of this type of waste, leading to a behaviour similar to those of pozzolanic cements, in which the calcium oxide produced is hydrated and reacts with the silica present in the material to generate a C-S-H gel with Al incorporated in its structure. In the mix produced using the calcinated sPS, an interaction occurs, giving rise to a mixture of N,C-A-S-H / C-A-S-H gels, similar to those produced in the so-called mixed alkali cements or hybrid cements.

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TALC SYNTHESIS ADVANCES: FROM BATCH TO CONTINUOUS PROCESSING

Marie Claverie (1)*, Angela Dumas (2), Cédric Slostowski (2), Guillaume Aubert (2), Christel Careme (1), Christophe Le Roux (3), Pierre Micoud (3), François Martin (3), Cyril Aymonier (2)

(1) Imerys, Toulouse, France, (2) CNRS, Univ. Bordeaux, ICMCB, UPR 9048, F-33600 Pessac, France, (3) Géosciences Environnement Toulouse, Toulouse, France
cyril.aymonier@icmcb.cnrs.fr, francois.martin@get.obs-mip.fr

The growing interest in the applications of synthetic talc, for instance, for polymer reinforcement (polypropylene, polyamide, polyurethane), coatings and new cosmetic formulations, has motivated research and development activities to propose novel synthesis routes. In this context, the synthesis process of talc has evolved noticeably leading to processes which could fulfill industrial requirements over the past 10 years [1-4].

This presentation introduces an innovative process representing a real breakthrough, which allows the synthesis of talc in a continuous process in only few tens of seconds [5,6]. This powerful, continuous and fast method to produce submicronic talc in mimicking natural environment is achievable through the use of supercritical hydrothermal flow synthesis. The properties of supercritical water (T_c = 374.0 °C, P_c = 22.1 MPa) make it a prime candidate to be used in material synthesis. Indeed, in the supercritical domain, reaction rates increase dramatically due to a drastic drop of supercritical water dielectric constant. Therefore, fine particles (e.g., metal oxides) are rapidly synthesized using supercritical water at the origin of the development of continuous processes.

Synthetic talc particles thus obtained were characterized by X-ray diffraction (XRD) to target optimal synthesis conditions by evaluating their degree of crystal order. Nuclear magnetic resonance, scanning electron microscopy and transmission electron microscopy were used to characterize the crystal structure of talc particles. The use of this innovative method has shown encouraging results by favoring the synthesis of a single-phase and highly pure product with a controlled composition displaying hydrophilic character, opposite to natural talc which is hydrophobic and often associated with other minerals and/or may contain other elements substituting into its crystal lattice. This hydrophilic character of this synthetic talc has resulted to the formulation of the first fluid talc filler.

From an academic point of view, this process offers the possibility to obtain a range of nanominerals differing in their degree(s) of crystal order just by adjusting synthesis time and/or temperature. Furthermore, from an industrial point of view, the decrease in synthesis time from few hours in batch reactor to few tens of seconds in continuous flow synthesis to produce submicronic talc particles represents a major technical breakthrough. This new route to synthesize talc is scalable and brought us on the route of the industrialization with our industry partner, the IMERYS company.

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EFFECT OF NATURE OF CLAY ON MORPHOLOGY, THERMAL PROPERTIES AND DEGRADATION DURING MELT PROCESSING OF POLY(LACTIC ACID)/VERMICULITE COMPOSITES

Mónica Cobos*, Mª Jesus Fernández, Mª Dolores Fernández

Department of Polymer Science and Technology, Faculty of Chemistry, University of the Basque Country, Paseo Manuel Lardizábal 3. 20018. San Sebastián, Spain
*monica.cobos@ehu.eus

Biodegradable polymers have been attracting much attention in recent decades due to increasingly environmental, biomedical and agricultural applications. Aliphatic polyesters are one of the most promising biodegradable plastics to solve the problems related to plastic waste accumulation. Among biodegradable polyesters, polylactic acid (PLA) has attracted the attention of industry for packaging and biomedical applications because of its biodegradability characteristics, in addition to its good mechanical and physicochemical properties.

Polymer nanocomposites are a new class of reinforced plastics formed by dispersion of nanoparticles in a polymer matrix which have received considerable attention in both scientific and industrial areas during the past decade. Of particular interest is the preparation of nanobiocomposites between PLA and inorganic nanofiller, such as layered silicate clays because they often exhibit concurrent improvement in several properties of neat PLA. The enhanced properties of polymer-clay nanocomposites are due to high interfacial interaction between the homogeneously dispersed nano-sized clay platelets and polymer matrix. Pristine layered silicates usually contain hydrated alkali or alkaline earth metal cations in the interlayer that are only miscible with hydrophilic polymers. The clay needs to be modified suitably with organic species in order to use it in the preparation of clay based polymer nanocomposites. The surface modification can be done by ion-exchange reactions with cationic surfactants such as organoalkylammonium salts. Additionally, the alkylammonium cations could provide functional groups that can react with the polymer matrix to improve the strength of the interface between the inorganic and the polymer matrix. PLA possesses inherent thermal/mechanical/hydrolytic degradation during extrusion when heated above its melting point. Among the factors that may affect the PLA decomposition during melt processing are residual metal catalysts, processing temperature, moisture content, oxygen environment, as well as the presence of clay.

In this study organoclays with different alkylammonium ions were prepared and compounded with PLA, forming PLA/clay nanocomposites via melt extrusion, natural vermiculite (VMT) was also blended with PLA. Natural VMT led to the formation of a microcomposite, while mainly exfoliated and intercalated nanocomposites were obtained with the incorporation of the organomodified VMTs. The molecular weight evaluation of PLA/clay composites was accomplished by using gel permeation chromatography technique. The level of degradation depended on the surfactant chemistry in organo-VMTs. In addition, the composite with better clay dispersion state experienced the most severe reduction in PLA molecular weight. DSC analysis showed that clay mineral accelerated the crystallization process of PLLA due to its nucleation agent effect. The thermal stability of the composites depended on the thermal stability of the added clay mineral.

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EFFECT OF CLAY TYPE ON PROPERTIES OF POLY(VINYL ALCOHOL)/CLAY/SILVER NANOPARTICLES NANOCOMPOSITES

Mónica Cobos*, Mª Jesus fernandez, Mª Dolores Fernandez

Department of Polymer Science and Technology, Faculty of Chemistry, University of the Basque Country, Paseo Manuel Lardizábal 3. 20018. San Sebastián, Spain
*monica.cobos@ehu.eus

Polymer nanocomposites are a new class of reinforced plastics formed by dispersion of nanoparticles in a polymer matrix which have received considerable attention in both scientific and industrial areas during the past decade. Polymer/clay nanocomposites have received considerable attention due to their potential for enhanced physical, chemical, and mechanical properties compared to conventional composites.

Metal nanoparticles are widely used for applications such as catalysis, electronics, optics, environmental, and biotechnology. Silver nanoparticles (AgNPs) are of particular interest because of their catalytic and antibacterial activity. AgNPs have been incorporated into other materials, such as clays and polymers, in order to minimize the aggregation process.

Poly (vinyl alcohol) (PVAL) is a semi-crystalline hydrophilic polymer with good chemical and thermal stability, highly biocompatible and non-toxic. PVAL has been used in a wide range of applications in medical, cosmetic, food, pharmaceutical, and packaging industries, due to its properties.

Vermiculite (VMT) is a 2:1 phyllosilicate clay mineral composed of hydrated magnesium-aluminium-iron sheet silicates, which consists of an octahedral sheet sandwiched between two Si tetrahedral sheets, and these three sheets form a layer. Al^{3+} or Mg^{2+} and Fe^{2+} are the normal octahedral ions, and in tetrahedral sheets Al^{+3} substitutes for Si^{+4}. The tetrahedral sheets are negatively charged as a result of Al^{3+} for Si^{+4} substitution, and this negative charge is balanced by interlamellar hydrated cations (usually Mg^{+2}) that are easily exchangeable with cations in an external solution.

In this work we report the preparation of PVAL-based nanocomposites with different amounts of natural-VMT/AgNPs and organically modified-VMT (OVMT)/AgNPs nanohybrids. The effect of the nanohybrid type and content on the structure and properties of the PVAL/VMT/AgNPs nanocomposites was investigated by XRD, DSC, TGA, TEM, and tensile testing techniques.

PVAL/VMT/AgNPs nanocomposites were prepared by solution mixing. The layers of natural-VMT/AgNPs were not delaminated in the PVAL at low concentrations and got exfoliated at higher concentrations. In the absence of AgNPs, layers of natural VMT were not delaminated in the PVAL. OVMT/AgNPs clay was intercalated at lower concentrations, and dispersed homogeneously into the PVAL matrix at higher concentrations.

Crystallinity of PVAL was altered upon addition of VMT/AgNPs hybrids, being reduced by the presence of all clays, and the more pronounced reduction was observed with the addition of VMT/AgNPs nanohybrid. The T_g increased slightly with clay addition. The melting transition (T_m) found in pure PVAL was essentially unaffected by the presence of organo-modified VMT/AgNPs, whereas the transition took place at a lower temperature for the PVA/VMT/AgNPs films. T_c of PVAL decreased significantly with addition of VMT/AgNPs, and was almost unaffected by the presence of organo-modified VMT/AgNPs. The thermal stability of PVAL was almost unaffected by the incorporation of VMT/AgNPs, while slightly enhanced in the presence of OVMT/AgNPs. The Young's modulus, tensile strength, and ductility were affected by the type of clay and content.

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IN SITU SYNTHESIS OF SILVER NANOPARTICLES ON UNMODIFIED AND ORGANO-MODIFIED VERMICULITE AND THEIR CHARACTERIZATION

Mónica Cobos*, Lidia Orduña, Mª Dolores Fernandez, Mª Jesus Fernandez

Department of Polymer Science and Technology, Faculty of Chemistry, University of the Basque Country, Paseo Manuel Lardizábal 3. 20018. San Sebastián, Spain
*monica.cobos@ehu.eus

Great effort has been given in the last years to the synthesis of new silver-based nanomaterials in order to develop materials with new or enhanced antibacterial, antifungal, and catalyltic properties. Vermiculite (VMT) is a clay mineral that occurs extensively in nature. It is a 2:1 clay, consisting of an Al octahedral sheet, sandwiched between two Si tetrahedral sheets, and these three sheets forma layer. Between the layers is the interlayer space containing exchangeable cations, mainly magnesium ions, to maintain electrical neutrality. The total quantity of those cations is called the cation exchange capacity (CEC). Compared with montmorillonite, hectorite and saponite, VMT is much cheaper and has larger CEC, between 100 mmol/100 g and 150 mmol/100 g.

The synthesis of silver nanoparticles (AgNPs) is carried out by the use of the metal precursor, and a reducing agent. During chemical reduction, Ag^+ receives an electron from the reducing agent and reverts to its metallic form (Ag^0) eventually clustering to form AgNPs. Silver nitrate ($AgNO_3$)is the most commonly used metal precursor due to its low cost and high stability. A variety of reducing agents have been used such as sodium citrate, sodium borohydride, hydrazine hydrate, ascorbic acid, polyols, monosaccharides, alcohol, formaldehyde, and also photoreduction by UV radiation. The preparation of uniform and stable colloidal dispersion of AgNPs can be carried out by the use of stabilizing agents such as polymers or surfactants. AgNPs can also beprepared on solid supports such as clays.

In this study, AgNPs were intercalated in VMT and organo-modified VMT by in situ chemical reduction method. AgNPs/VMT and AgNPs/VMT-quaternary ammonium salts hybrids were prepared. The effect of type of reducing agent (environmentally friendly) was studied. FTIR and UV-Vis spectroscopy, X-ray diffraction (XRD), scanning and transmission electron microscopy (SEM and TEM), X-ray photoelectron spectroscopy (XPS), Raman spectroscopy, and thermogravimetric analysis (TGA)were used to characterize the AgNPs/VMT nanomaterials.

The UV-VIS absorption spectra exhibited the characteristic silver surface plasmon resonance band between 415 and 435 nm, indicating that AgNPs were effectively dispersed in the VMT. The original interlayer basal spacing of VMT, 1.18 nm, was unaltered or slightly expanded to 1.23 nm by silver intercalation. All AgNPs/VMT nanomaterials exhibited the WAXS signals corresponding to Ag^o. SEM and TEM micrographs revealed AgNPs grown on the surface of VMTs. TEM images showed small spherical Ag nanoparticles well dispersed in the clay matrix located on the platelet rim, and in some cases minimum inter-Ag particle aggregates of submicron-size. The size of AgNPs was in nanoscale. XPS confirmed the presence of Ag^o, there was no signal due to Ag^+. The Raman spectra of AgNPs/VMT showed a group of vibrational bands in the 750-1600 cm^{-1} attributed to the AgNPs. In the case of organo-modified VMT, the VMT vibrations were barely visible since they were desactivated by the alkylammonium ions intercalated on VMT interlayers. The TGA thermogram of pristine VMT revealed three mass loss steps, being the last one in the temperature region of 500 and 700 °C attributed to the dehydroxylation of the hydroxyl groups covalently incorporated in the crystal lattice of VMT. In the case of AgNPs/VMT hybrids the dehydroxylation step was absent.

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Zn-Al-CO_3 LAYERED DOUBLE HYDROXIDES PREPARED FROM WASTES OF HOT DIP GALVANIZING PROCESS

Laura Cocheci*, Lavinia Lupa, Marius Gheju, Alin Golban, Rodica Pode

Politehnica University of Timisoara, Faculty of Industrial Chemistry and Environmental Engineering, 6 Parvan Blvd., 300223, Timisoara, Romania
*laura.cocheci@upt.ro

Hot dip galvanizing process is used worldwide to protect from corrosion the steel or iron pieces. This process is a large generator of waste, considered one of the so-called “dirty industries”. One of the important waste, in terms of quantity, is zinc ash that contains a mixture of metallic zinc and zinc oxide with a total content of zinc between 70-90%. The zinc ash is considered a hazardous waste and is treated by stabilization / solidification for appropriate landfill disposal or, in most cases, is treated for the recovery and recycling of zinc.

The aim of this study is the preparation and characterization of a series of Zn_R-Al (R = 2 - 4) LDH by using as zinc precursor the zinc chloride obtained after hydrochloric acid digestion of zinc ash.

The unit cell parameters of synthesized samples have values close to those of similar materials synthesized from analytical grade reagents. Impurities that are present in zinc chloride obtained from zinc ash (Pb, Fe, Ca) are found at traces in the synthesized materials.

By applying a new approach regarding the synthesis of LDH from precursors obtained by zinc ash treatment the wastes of a “dirty industry” are treated and a valuable product is added, keeping in mind that the layered double hydroxides have multiple utilizations at industrial scale as plastic additives, as flame retardant and as anion scavengers.

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STATISTICAL ANALYSIS AND 3D MODELING OF DIFFRACTION PATTERNS: ADVANTAGES FOR STRATIGRAPHIC APPROACHES

Rute Coimbra (1,2)*, Fernando Rocha (1), Maurits Horikx (3), Denise Terroso (1)

(1) GeoBioTec, Department of Geosciences, University of Aveiro, Portugal, (2) MARE, Earth Sciences Department, University of Coimbra, Portugal, (3) Institute of Geology, Leibniz UniversityHannover, Germany

Dealing with significant amounts of mineralogical information can be an overwhelming task. But this is often the case when addressing extended sedimentary successions, justifying the search for simple and fast solutions to interpret X-Ray diffraction datasets. Also, commonly used diffractogram interpretation methods are susceptible to user bias (peak identification of disordered phases, baseline adjustments, quantitative estimations), clearly benefiting from the use of objective automated methods.

Here we present the advantages of simple statistical methods (PCA) and three-dimensional (3D) modeling of diffractogram spectra to unravel complex sedimentary archives along ancient shallow-water carbonates (São Julião and Magoito coastal sections, Portugal). In coastal areas, competing sedimentary sources often result in complex facies successions that may in turn have different susceptibilities to post-depositional processes. Such records are therefore challenging for paleoenvironmental studies, but enclose valuable information. The selected lower Cretaceous coastal deposits comprise alternating sandstone/siltstones, limestones and clayey/marly horizons, ensuring a highly variable lithofacies distribution. The presented approach is equally valid for a wide range of materials, with greater benefits directly related to a higher degree of complexity of the dataset.

Principal Component Analysis (PCA) is able to depict meaningful differences from the large sets of diffraction patterns (here 130, comprising a total of ca. 400.000 data points) processing data in any of the widely available statistical software packages by an extremely fast procedure (within minutes). Apart from the qualitative interpretation of the datasets of interest, adding samples of well-known mineralogical composition (pure or composite mixtures of natural samples) allowed accessing the relative quantitative contributions of each mineral. For the São Julião section, the most significant principal components responded to the presence of quartz and calcite in variable proportions, accounting for 91% of the total mineralogical variability. The majority of the samples (61%) show less than 25% of quartz in their mineralogical composition, whilst only 22% presented quartz abundance higher than 75%. Interestingly, the third principal component responded to samples bearing dolomite along with the other competing mineralogies (quartz and calcite), accounting only for 5% of the total variability of the dataset. Dolomite occurs along 25% of the samples, mostly with abundance up to 25% and only rarely up to 50%. In clear contrast, the nearby Magoito section showed no significant contribution of dolomite, being dominated by quartz and calcite. Only 24% of the samples presented quartz abundance higher than 25%, attesting for the more distant paleogeographic position of this section in respect to São Julião. By stratigraphically plotting the resulting principal component scores, accurate lithofacies intervals were gained. This outcome bears a high potential to serve as correlation tool across different localities, but particular hydrodynamic forcing may obscure otherwise clear patterns.

As an alternative to stacking XDR spectra, 3D modeling offers interpolation and smoothing options to be fitted by the user, as well as to create a spatial grid that places each diffractogram at its exact and correct stratigraphic position by using 3D mapping and visualization software. This later feature is of high value for cases of discrete sampling approaches, so common when dealing with outcropping sedimentary successions. The resulting 3D blocks can then be rotated or magnified to gain better perspective. For the tested outcrops, the main features along each stratigraphic section were intuitively identified and easily compared to diffractogram datasets from other sections also represented as a 3D block. Paleogeographic and hydrodynamic differences along both depositional sites can be attributed to the observed mineralogical trends. Accordingly, the more proximal area at São Julião shows a higher and persistent contribution of detrital quartz, only detected at a few samples of the Magoito section. Furthermore, dolomitized horizons occur exclusively along the São Julião section. The fact that nearby sections are differentially affected by dolomitization processes deserves further attention.

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HALLOYSITE NANOTUBES AS SUPPORT FOR METAL NANOPARTICLES FOR CATALYTIC APPLICATION

Carmelo G. Colletti (1)*, Marina Massaro (1), Serena Riela (1), Giuseppe Lazzara (2), Yusuf Darrat (3), Yuri Lvov (3)

(1) Department of Biological, Chemical and Pharmaceutical Sciences and Technology (STEBICEF), University of Palermo, Palermo, Italy, (2) Department of Physic and Chemistry), University of Palermo, Palermo, Italy, (3) Institute for Micromanufacturing, Louisiana Tech University, Ruston, LA

Halloysite (HNT) is a natural clay that, in the last years, has shown an important increasing on various applications in different field of interesting.

Chemically similar to kaolin, it shows the predominately rolled shape, to form multilayers tubes of nanometric dimensions.

The different chemical composition of the inside lumen (Al-OH) surface and outside (Si-O) give to the tubes a partial negative charge outside and positive inside. In this way, it is possible to get different interactions of different molecules or systems selectivity on one or another surface.

The selective functionalization, covalent or not, of the HNT lumen or outer surface, gives the possibility to the nanotubes to further expand and modulate their properties, increasing the potential efficacy and the application fields.

Recently some studies are, also, focused on the edges and interlayer properties and potentials.

Among the countless applications of halloysite, is central the nanotube ability to interact with metals.

Metals ions are one of the worst pollutants in the environmental contest. Halloysite has shown interesting properties as starting point to make environmental recovery system.

Another important application of the ability of HNT of interaction with metals is catalysis.

Catalyst immobilization is a good opportunity to obtain materials that can be recovered and reused for several cycles with low leaching.

Several studies have been carried out on the use of ionic liquids as reaction media and as stabilizers for metal nanoparticles. In particular, great attention has been devoted to the use of supported ionic liquid phase (SILP)-based materials as heterogeneous recyclable palladium catalyst.

Herein are reported some recent developments about immobilization of metal nanoparticles on halloysite nanotubes and studies about the materials and applications.

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URANOPHANE - A LAYERED URANYL SILICATE MINERAL. A COMPUTATIONAL DFT STUDY OF ITS STRUCTURAL, MECHANICAL AND VIBRATIONAL PROPERTIES

F. Colmenero (1)*, V. Timón (1), L.J. Bonales (2), J. Cobos (2)

(1) Instituto de Estructura de la Materia, CSIC. C/ Serrano, 113. 28006 Madrid, Spain, (2) Centro de Investigaciones Energéticas, Medioambientales y Tecnológicas, CIEMAT. Avda/ Complutense, 40. 28040 Madrid, Spain

Uranyl minerals are very important because they are expected to be the main phases found as a result of alteration of irradiated $U^{IV}O_2$ reactor spent nuclear fuel (SNF). In particular, uranyl silicate minerals are relevant for understanding the genesis of uranium deposits, as well as fluid-rock interactions during the hydration-oxidation weathering of uranium deposits. Uranyl silicates are significant to the disposal of nuclear waste, since they are likely to be abundant in a geological repository. Structural characterization of uranyl silicate minerals forming due to alteration of nuclear waste is extraordinarily important to evaluate the possible incorporation of fission products and transuranic elements into their crystal structures. Their characterization is very important, and it is a great challenge due to its radiotoxicity. Mineral uranophane-α has been recognized as one of the main secondary phases resulting from alteration of SNF [1].

In this work, a natural sample of uranyl silicate mineral uranophane-α, $Ca(UO_2)_2(SiO_3OH)_2 \cdot 5H_2O$ obtained from Sierra Albarrana (Córdoba, Spain) [2] was studied by means of Raman spectroscopy and theoretically by periodic solid state calculations based on density functional theory (DFT) method using CASTEP software [3]. A new norm-conserving relativistic pseudopotential of uranium atom has been used in the calculations. This pseudopotential was previously generated by these authors and evaluated for a series of uranium-containing minerals including the uranyl carbonate mineral rutherfordine [4], the uranyl peroxide mineral sudtite [5], and the uranyl silicate mineral soddyite [6].

Uranophane-α is a layered hydrated nesosilicate that behave much like clay minerals. It is one of the earliest known uranyl minerals, identified in nearly all major and most of the minor uranium deposits in the world. Its structure, present in nature in a wide variety of compounds having the uranophane sheet anion-topology [7] is confirmed here for the first time by means of rigorous theoretical solid state calculations. Computed lattice parameters, bond lengths, bond angles, and X-ray powder pattern reproduce accurately their experimental counterparts. Mechanical properties of uranophane are predicted and the satisfaction of the mechanical stability Born conditions of the structure is demonstrated by means of calculations of the elasticity tensor. The Raman spectrum was computed by means of density functional perturbation theory and compared with the experimental spectrum obtained from a natural uranophane-α sample. Since the comparison was satisfactory, a normal mode analysis of the theoretical spectra was carried out and used with the aim of assigning the main bands of the Raman spectrum. Theoretical methods allowed us to assign the Raman spectrum bands to vibrations localized in different fragments within the crystal unit cell.

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CALCINED SMECTITE ALKALI ACTIVATED BINDER AS A POSSIBLE ALTERNATIVE TO PORTLAND CEMENT

Silvia Contessi*, Irene Chiossi, Maria Chiara Dalconi, Luca Valentini, Gilberto Artioli

Inter-Departmental Research Center for the Study of Cement Materials and Hydraulic Binders (CIRCe), University of Padova, Via Gradenigo 6, 35131, Padova, Italy

Today much attention is devoted to the production of binders based on waste industrial materials, such as slag and fly ash, with the aim of minimizing the consumption of raw materials and reducing the CO_2 emissions due to the production of Portland cement. However, the limited availability of these uncommon materials has lead researchers to focus on more readily available and cheap materials, such as calcined clays. Among calcined clays, metakaolin, readily available commercially, has been extensively investigated [1], as a precursor for alternative binders. In literature, limited information is available about other kinds of clays for alternative binder manufacture.

This study aims, firstly, at comparing the performance of a smectite-based alkali activated binder, with those of an equivalent kaolin-based material. Secondly, the possibility of using a low purity material, a natural clayey soil, for the production of a binder has been evaluated, with the aim of obtaining performances comparable with those given by the high-purity material.

The first part of the investigation aims at comparing mechanical performances of binders obtained from two pure commercial clays. To quantify the amorphous contribution given by calcination of clay and, subsequently, given by reaction of metaclay with the activating solution, the PONKCS method (Partial Or Not Known Crystal Structure, [2]) has been used. Results of compressive strength tests conducted on hardened specimens reveal higher values for samples containing smectite, especially for the ones calcined at 750 °C, which is in line with what demonstrated by a previous study [3]. Moreover, the addition of ground limestone further improved mechanical strength.

In the second part of the study, the impure smectitic soil was calcined at 750 °C, then mixed with ground limestone, keeping the clay/$CaCO_3$ ratio fixed at 70/30 and a liquid-to-solid ratio of 0.4 with the activating solution. The average value of compressive strength after 15 days is 7.7 MPa, which is comparable with that obtained by the high-purity clay binder. Furthermore, in a second batch of samples, sodium citrate solution (in a concentration of 150 g/L) was added in 1:9 ratio with the alkaline solution, giving a total liquid-to-solid ratio of 0.5. These specimens gave a compressive strength of 19.7 MPa, after 15 days.

The purpose of this investigation was, on the one hand, to study the performance of calcined smectite in comparison to metakaolin, for the production of an alternative alkali-activated binder and, secondly, to preliminarily assess the use of a widely available and economically affordable natural clayey soil for the same purpose. From this study, smectite clay, both characterized by high and low purity, reveals to have a high potential as a precursor for binder manufacture, giving better performances compared to kaolin, which can potentially be considered an alternative to Ordinary Portland Cement. Additional research will aim at investigating in more detail the contribution of sodium citrate addition, in terms of hydration products development and compressive strength of the hardened material, both at early and later ages of curing.

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ASSESSEMENT OF ACTIVATORS INFLUENCE IN GEOPOLYMERS PROPERTIES

Cristiana Costa (1,2), Ângela Cerqueira (1), Ana Velosa (2,1), Walid Hajjaji (1),
Fernando Rocha (1,2)

(1) GeoBioTec, Geosciences Department, University of Aveiro, Aveiro, Portugal, (2) RISCO, Civil Engineering Department, University of Aveiro, Aveiro, Portugal

Geopolymers arise due to concerns about the environment during the production of cement that entails high energy amount and high CO_2 release. The chemical composition of these materials is very different from the cements or lime. The exothermic reaction of geopolymerization generates a structure closer zeolites or aluminosilicates gels. This alkaline aluminosilicate material, generally amorphous is mainly produced from metakaolin (source of Si and Al) reacting with hydroxides or alkaline silicate solutions. Depending of raw material selection and processing conditions, geopolymers can have a wide variety of properties and characteristics, including high compressive strength, low shrinkage, fast or slow setting, acid resistance, fire resistance and low thermal conductivity [1].

Metakaolin is used in Portugal on a small scale, when compared with other countries like France, Brazil, India and USA. The raw material for its production is available in Portugal, mainly in the north-west littoral of the country. Metakaolin is produced from kaolin by calcination at temperatures between 650 ºC to 800 ºC [2].

The activators of the geopolymerization reaction have a key role on the final properties of the material.

Geopolymers can be activated with an alkaline solution usually potassium or sodium rich. The aims of this work is to determine the effects of alkaline solution type (K^+ or Na^+) and concentration and metakaolin replacement on the properties of geopolymers. The activatiors influence was assessed on mechanical properties and chemical resistance. The geopolymers activated with KOH solution have better mechanical properties when compared with the geopolymers containing NaOH solution. The better concentration of the alkaline solution is around 6 to 8 molar.

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STUDY OF THE INFLUENCE OF THE PARTICLE SIZE OF CLAY IN THE PROPERTIES OF CLAY BRICK WITH DIATOMS EARTH FROM BREWING INDUSTRY

Carmen Martínez García (1), Teresa Cotes Palomino (1)*, Juan S. Bueno Rodríguez (2), María Del Pilar Baena Rus (1), María Sol Bertoya (1), José Ferris Pérez (1)

(1) Department of Chemical, Environmental and Materials Engineering, Higher Polytechnic School of Linares, University of Jaén, 23700 Linares (Jaén), Spain, (2) Fundación Innovarcilla, 23710 Bailén (Jaén), Spain
*mtcotes@ujaen.es

Different nature mineral residues have been used as a substitute for clay in the manufacture of clay bricks baked by its low cost, and can lower the sintering temperature. A example of them is the diatoms earth, material abundant in the nature, of nature microporous, very employee in the industry as filter agent (61% of the world production of diatomite, [1]).

This work presents them results of a study whose objective is evaluate the influence that the particle size of the clay has on technological properties of ceramic bricks obtained with the addition of diatoms earth coming from the process of filtering of the beer. This residue has double nature inorganic and organic due to the organic matter retained after the process of filtration of the beer. The organic nature of the residue will manifest itself in the process of sintered of the specimens, since it will provide part of the energy required in the oven in the cooking process.

We work with a clays mixture from the industrial area of Bailén (40% black clay; 30% red clay; 30% white clay). Once in the laboratory, the clay is crushed in a hammer mill (GRUBER model DUPLEX 21A) and sieved to three particle size fractions of work: a) 0,25-0,5 mm; b) 0,5-1 mm; c) 1-2 mm. Then, mixtures of clays and waste were prepared at the percentages of 0, 5, 10 and 15% of beer diatoms, that are formed in a uniaxial press MEM-101/20-SDC, by adding the minimum amount of water required to prevent defects in the pressed, to 50 kN of pressure. The obtained pieces were dried in an oven at 105 ± 1 °C, before its sintering at 950 °C in an laboratory furnace NABERTHERM LA 60/14., with a ramp of 5 °C/min up to maximum temperature, maintenance of 1 h at 950 °C and cooling by convection.

Different testing of characterization of the starting materials were made. Clays mixtures to the different particle sizes underwent the Dilatrometric test. The calorific power was determined at the beer diatoms earths.

To the sintered specimens were determined the following technological properties: dry and sintered weight loss, dry and sintered linear shrinkage, water absorption (Standard UNE-EN 772-21 [2]), bulk density, open porosity and boiling water absorption (Standard ASTM C-373 [3]), and compressive strenght (Standard UNE-EN 772-1 [4]). Also was determined the color of the specimens to see whether the particle size influences this parameter.

The results indicated an improvement in the mechanical properties of the manufactured samples with smaller particle fraction (0, 25-0, 5 mm), decreasing the values of water absorption and boiling water absorption, and an increase in bulk density. However the color of the samples is not significantly altered by the particle size of clay.

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LIGHTWEIGHT AGGREGATES FROM CLAYS, OLIVE POMACE AND BIOMASS FLY ASH FOR USE IN THE DRAINAGE LAYER OF GREEN ROOFS

Carmen Martínez García, Teresa Cotes Palomino*, Rocío Cortés Jiménez

Department of Chemical, Environmental and Materials Engineering, Higher Polytechnic School of Linares, University of Jaén, 23700 Linares (Jaén), Spain
*mtcotes@ujaen.es

The action by the climate, the environment, the efficiency of resources and raw materials, is the fifth thematic priority of the social challenges on the Horizon 2020 programme, framework programme for research and innovation in the European Union (2014-2020). One of its lines of action is 'the fight against climate change and adaptation to it, the protection of the environment, and the sustainable management of natural resources, water, biodiversity and ecosystems' [1]. Moreover, the sector of the construction is one of the pillars of the economy to level world and one of them main managers of development; However, produces about 40% of solid waste reaching landfill, uses 32% of the total number of resources in the world, 12% of the drinking water, 40 percent of the energy consumed and generated 38% of GHG emissions greenhouse (Eurostat data) [2]. Against this background, are considering various initiatives to reduce the environmental impact of the buildings. The most advanced is the efficiency energy of buildings, with new strategies as the certification of 'sustainable building' that is starting to be implemented in the legislation of some European countries.

In this context arises the need to develop new building materials that are sustainable to the environment. The developed lightweight aggregates in this work have with a double objective. On the one hand replace part of traditional raw material in its manufacturing (clay) by waste industrial (biomass fly ash and olive pomace) and by another obtain a material with best benefits both physical as thermal, respect to the original material.

The work begins characterizing the clays (white and black) and waste employees by differential thermal analysis, elemental analysis, XRD, termogravimetrias and FRX. It has determined the calorific power to alpeorujo due to the character organic of the waste, that putting of manifest its nature fuel. Dilatometric tets to the clays mixture and ash from biomass have also been realized.

A time formulated the mixtures of clays, biomass fly ash and olive pomace to the different proportions, is proceeded to make the specimens using a uniaxial press MEM-101/20-SDC. Then, they led to stove to 105 ± 1 °C, and subsequently are sintered in a laboratory furnance NABERTHERM 60 / 14, to 1000 and 1150 °C. Once cooled specimens, they passed through the jaws crusher WEDAG EXPANOLA S.A to obtain the lightweight aggregates.

It is determinated the following physical properties to the lightweight aggregates obtained: a) weight loss after sintering; b) bulk density and voids volume (Standard UNE-EN 1097-3 [3]); c) dry particle density and water absorption (Standard UNE-EN 1097-6 [4]). Also are carried out measures of the emissions gaseous of the current of output of the sintered furnace. Finally, it was revealed its greater insulating power with respect to the traditional aggregate used in the drainage layers through thermal images made with a thermal imaging camera IR RayCAm CA 1886.

In conclusion, it has been obtained a less dense material with greater absortion of water than the traditional aggregate, which improves its insulating ability, and that can be considered lightweight aggregate according to the Norma UNE-EN-13055-1 [5].

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USE OF ALKALI ACTIVATED FLY ASH BINDER FOR CLAY SOIL STABILISATION: PHYSICOCHEMICAL EVOLUTION

Elodie Coudert (1)*, Michael Paris (2), Dimitri Deneele (2,3), Giacomo Russo (1)

(1) Department of Civil and Mechanical Engineering, University of Cassino and Southern Lazio, Via Gaetano di Biasio, 43, 03043 Cassino FR, Italy, (2) Institut des Matériaux Jean Rouxel (IMN), Université de Nantes, CNRS, 2 rue de la Houssinière, BP 32229, 44322 Nantes Cedex 3, France, (3) IFSTTAR, Institut Français des Sciences et des Technologies des Transports, de l'Aménagement et des Réseaux, CS4, route de Bouaye, 44344 Bouguenais Cedex, France
*elodie.coudert@unicas.it

Clay soft unsuitable soils are frequently encountered in construction sites and represent a critical issue in engineering project. To improve their engineering characteristics Portland cement and lime are commonly used but are associated with a significant environmental penalty. To address the competitiveness challenge of the construction industry to develop carbon-efficient geotechnical infrastructure, the use of a novel sustainable soil stabiliser has been explored. That is the development of alkali activated calcium-rich fly ash to stabilise clayey kaolin soil at ambient conditions.

In the present work, the physicochemical evolution of both the binder - an alkali activated calcium-rich fly ash - and the stabilised kaolin has been established. The aims are to understand (i) which phases from the original materials are dissolved and therefore accessible during process (ii) which secondary compounds are subsequently formed (iii) how the alkali activation process is modified when kaolin is added to the system. It is worth noting that the presence of calcium in the fly ash introduces additional complexity into the range of phases that can form. Indeed, a three-dimensional alkali aluminosilicate framework structure characteristic of geopolymer, as well as calcium (aluminium) silicate hydrate C-(A)-S-H found as cementitious product in lime or cement stabilisation can be expected. A set of complementary techniques specifically X-ray diffraction, Thermogravimetric analysis, Scanning Electron Microscopy, Fourier Transform Infrared Spectroscopy, ^{29}Si and ^{27}Al Nuclear Magnetic Resonance has been used to assess the physicochemical evolution of the reaction system.

The results of the investigation show that the overall calcium bearing phases and part of the vitreous phase of the fly ash are dissolved during alkali activation releasing Ca, Si and Al. Amorphous calcium silicate chain with possibly aluminium crosslinked to the structure has been identified as a secondary product by NMR spectroscopy. While the formation of a coexisting three-dimensional geopolymeric type framework cannot be confirmed. The presence of an additional aluminosilicate source to the binder system that is to say kaolin does not modify in our case the phases dissolved and the amorphous products formed. Nevertheless, SEM images show that small-sized kaolinite platelets are covering fly ash particles during the process which could inhibit the extent of reaction. In conclusion, the complexity of the system involving the release of various species in the reaction system implies the formation of hardly identifiable cementitious compounds whose structure varies from the ones usually observed in either cement or geopolymer products, and raise concerns about durability which will be further studied. Future work will also focus on microstructural investigation and mechanical behaviour in order to complete a multi-scale analysis.

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HYDRATION OF LAYERED DOUBLE HYDROXIDES PROBED BY NEAR AMBIENT PRESSURE X-RAY PHOTOEMISSION SPECTROCOPY

Romain Coustel (1),* Anthony Boucly (2), Fabrice Bournel (2), Jean-Jacques Gallet (2), Arnaud Di Bitetto (1), Erwan André (1), François Rochet (2), Cédric Carteret (1)

(1) Laboratoire de Chimie Physique et Microbiologie pour l'Environnement (LCPME)-UMR 7564, CNRS-Université de Lorraine, Villers-lès-Nancy, France, (2) Laboratoire de Chimie Physique-Matière et Rayonnement (LCPMR)-UMR7614, CNRS-Université Pierre et Marie Curie, Paris, France

Due to the short elastic mean free path of electron in gas phase, X-ray electron spectroscopy (XPS) has long been restricted to measurements in ultra-high vacuum (10^{-9} mbar). However, recent improvements enable to perform photoemission measurements up to Near Ambient Pressure (NAP-XPS, ~10 mbar) by taking advantage of synchrotron light brightness. NAP-XPS opens the way to characterize, in operando conditions, catalyst surfaces [1] as well as the surface of solutions [2] or wet environmental surfaces. For instance, it was shown that NAP-XPS can be used to probe the chemical environment of interlayer cations in the early stage of clay hydration [3].

Layered double hydroxides (LDH) consist of positively charged layers separated with hydrated anions, thus LDH can be regarded as complementary to the clay family. As evidenced from their general formula $[M^{II}_{(1-x)}M^{III}_{x}(OH)_2][(A^{n-})_{x/n}\cdot yH_2O]$ (where M^{II}, M^{III}, and A^{n-} are respectively a divalent metal cation, a trivalent metal cation, and a counteranion, and x is typically in the range of 0.2-0.33), LDH present a highly tunable chemical composition, which makes them suitable as anion exchange media, adsorbents [4], drug delivery systems [5] and so forth.

LDH functional properties depend on their hydration rate, so we performed at TEMPO beamline (SOLEIL synchrotron facility) a NAP-XPS study of the water insertion into the archetypal $[Mg_{0.66}Al_{0.33}(OH)_2][(Cl^-)_{0.33}\cdot yH_2O]$ LDH. An increase of water pressure (from UHV up to few mbar) leads to a drastic and reversible modification of the Cl 2p spectrum (a shift to higher binding energy) that reflects a change in the core-hole relaxation energy due to formation of a water solvation shell around the ion NAP-XPS measurements, together with vibrational spectroscopy, X-ray diffraction and gas adsorption measurements allow getting a further insight to LDH hydration to the early stages of LDH hydration.

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THE COORDINATION COMPOUNDS BASED ON Fe (II) INSIDE CLAYS AND ITS RELEVANCE IN THE SYNTHESIS OF AMINO ACID PRECURSORS IN THE GEOCHEMICAL CONTEXT OF THE EARLY EARTH

Romulo Cruz-Simbron (1,2), Miguel Angel Rojas-Capcha (1), Mario Hurtado-Cotillo (2,3), Ruth Estefany Quispe-Pilco

(1) Universidad Nacional de Ingeniería, Lima, Perú, (2) Sociedad Científica de Astrobiología del Perú, Lima. Perú, (3) Universidad Nacional Agraria la Molina, Lima, Peru

The continuation of the study of the origin of life, initiated by Urey and Miller in 1953, has enabled that many researchers propose new mechanisms for the synthesis of the building blocks of life such as amino acids. The experiments are of significance in relation to the formation of simple biochemical compounds such as carbon and nitrogen compounds formed under assumed conditions that existed during the early development of the earth's crust. Pioneering Jean Oró experiments (1959) have shown that heating a combination of formaldehyde and hydroxylamine generate various biochemical compounds, such as amino acids, hydroxyl compounds. All that set the main compound is glycine.

Current models suggest that there was a thermal shock associated with both lightning strikes and high-energy meteorites producing NO in the atmosphere which consequently had to be dissolved in the sea in the atmosphere of early Earth. In addition, according to the review article Olso H2S was undoubtedly the most versatile on the early Earth could produce significant organic compounds such as thiols molecule. The work of Eoghan P. Reeves shows that simple alkylthiol are actively produced in cold areas around hydrothermal systems. These compounds are most likely involved in the emergence of microbial life and metabolism primitive systems.

Srdjan Stojanovic shows in his work that an iron (II) can catalyze the conversion of NO dissolved in water to species nitrosonium (NO +) and nitroxyl (HNO / NO-). The iron (II) complex dinitrosilo combined with ligands thiols catalyses the formation of NO + resulting in the synthesis of S-nitrosothiols both in vivo and in vitro. The mechanism involves the presence of nitroxyl ion which under appropriate pH conditions and under anoxic conditions (similar to the conditions of the early Earth) leads to the formation of hydroxylamine (as reaction product of HNO / NO- with thiols).

The aforementioned previous studies allow us to previse the fundamental role of iron (II) with thiol ligands and NO and in the NO capture process that is still present as an ancient relic in today's living systems. By means of Ab initio molecular dynamics and classical molecular dynamics we seek to understand the formation and stability of iron complexes with nitrosyl and thiol ligands within the interlaminar space of the clays in order to understand their catalytic role.

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KAOLINITE FROM DIVERSE ACIDIC ALTERATIONS IN EARTH ANALOGUES FOR MARS

Javier Cuadros (1)*, Christian Mavris (1,3), Joe Michalski (2), Janice Bishop (3), Jose Miguel Nieto (4)

(1) Department of Earth Sciences, Natural History Museum, London SW7 5BD, UK, (2) Department of Earth Sciences, University of Hong-Kong, Hong-Kong, (3) The SETI Institute, Carl Sagan Center, Mountain View, CA 94043, USA, (4) Department of Earth Sciences, University of Huelva, 21071 Huelva, Spain

The Iberian Pyrite Belt, SW Iberian Peninsula, contains sites that can be used as natural analogues of Martian rocks that have been altered in acidic environments. Three localities in the Riotinto area and one in Tharsis were sampled for the laboratory investigation of the rocks and their clay constituents [1]. The rocks (Upper Palaeozoic) include mafic and felsic volcanics that have been subjected to a variety of processes (including hydrothermal alteration) with a final stage of acidic alteration (Miocene) produced by pyrite oxidation. The extent of the acidic alteration is not uniform, neither between sites nor within them. Investigation of the samples indicates that they all fall within the same geochemical trends, which are controlled by the intensity of the acidic alteration and are independent of the site location.

The rocks have a wide mineral suite corresponding to the intensity of the acidic alteration, from Fe- and Mg-rich chlorite to alunite and jarosite. Quantitatively, the most prominent feature in the clay components produced during the acidic alteration is the replacement of hydrothermal illite by kaolinite. Kaolinite appears mainly as an end-member, although there is some interstratified kaolinite-smectite. The end-member kaolinite coexists with other mixed-layer phases including chlorite, vermiculite, illite and smectite. This indicates (a) the heterogeneous character of the acidic alteration and (b) where the acidic alteration was sufficiently intense to form kaolinite, few or no relics of previous clay layers were preserved interstratified with kaolinite.

The sequence of illite replacement by kaolinite can be followed spectroscopically, using NIR data of the whole rock. The clay minerals and sporadic sulphates dominate some of the diagnostic areas of the NIR spectrum (2-2.4 μm). Kaolinite features become obvious at 7 wt% (from XRD) concentration (in the clay suite, not the whole rock mineralogy), and effectively overwhelm illite features at 20 wt%. However, the transition of the spectroscopic features is not linear, and indicates partial control by crystal-order of the phases, as suggested by comparison with XRD data.

The above observations are important to identify the occurrence and mode of acidic alteration on Mars. In particular, the observation of interstratified kaolinite-smectite, as recognized in some areas on Mars [2], may rule out acidic alteration as its origin because such alteration produces little or no mixed-layer kaolinite phases.

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STEVENSITE *VERSUS* ORGANIC SORBENTS (BIOCHARS): COMPARATIVE ADSORPTION OF TETRACYCLINES

Rafael Antón-Herrero (1), Carlos García-Delgado (1), María Alonso-Izquierdo (1), Gabriel García-Rodríguez (1), Felipe Yunta (1); Ana Isabel Ruiz (2), Raul Férnández (2), Jaime Cuevas (2)*, Enrique Eymar (1)

(1) Autonomous University of Madrid, Department of Agricultural Chemistry and Food Sciences, Madrid, Spain,
(2) Autonomous University of Madrid, Department of Geology and Geochemistry, Madrid, Spain

Tetracyclines (TCs) are one of the most widely used classes of veterinary and human antibiotics around the world. Antibiotics enter in the environment through animal and human excretion via wastewater. The conventional treatment of wastewater based on activated sludge is not completely efficient to remove antibiotics and their residues are still biologically active even at low concentrations. Therefore the implementation of advanced treatments to prevent the dispersion of antibiotics is necessary since they can cause resistances in bacteria due to their presence in raising concentrations. The objectives of this work were to assess the ability of two biochars and stevensite clay to adsorb TCs from water and to characterize the adsorption-desorption process of the most effective adsorbent.

The adsorbents tested were stevensite (tri-octahedral smectite) and two biochars made by pyrolysis of oak holm and forest pruning. Adsorption experiments of three TCs (oxitetracycline (OTC), tetracycline (TC) and chlortetracycline (ClTC)) were performed at initial TCs concentrations between 25 and 1000 mg L^{-1} in 0.01M $NaNO_3$ at pH 2 and equilibration for 24 h. The results were fitted to Freundlich and Langmuir models. After TCs adsorption, stevensite was analysed by IR spectrometry to characterize the adsorption process. In order to assess the desorption process, after TCs adsorption on stevensite, desorption was performed using 0.01 M $NaNO_3$ sequentially at acid (pH 2.0) and neutral (pH 7.5) pHs. Finally the adsorption of TCs on stevensite mixed with milled glass, was tested in continuous flow using pressurized columns. The initial composition of the effluent was: OTC, TC and ClTC at 50 mg L^{-1} in 0.05M $NaNO_3$ at pH 7.0. The analysis of TCs was performed by HPLC-PDA at 355 nm.

The two biochars tested presented maximum adsorption capacity of TCs between 11 and 44 mg g^{-1} according to Langmuir model. In contrast, stevensite showed higher maximum adsorption capacity for the three TCs tested, 126 mg g^{-1} for OTC, 127 mg g^{-1} for TC and 140 mg g^{-1} for ClTC. Therefore stevensite was the most effective adsorbent of TCs of the three adsorbents tested. IR spectrum showed the important role of amide and dimethylamino groups of TCs on the adsorption process on stevensite, therefore cation exchange and complexation are the main mechanism for TCs adsorption on stevensite [1]. Desorption at pH 2 and 7 of TCs followed the order: OxTC > TC > ClTC, therefore desorption experiments reflected the higher affinity of stevensite for ClTC than TC and OTC. Desorption at low concentrations of TCs (10 mg g^{-1}) were lower than 0.1% because of the re-adsorption phenomena. The maximum desorption (%) was obtained at pH 2 and at the highest concentration of TCs, the values were 23% of OTC, 19% of TC and 17% of ClTC. At pH 7 the maximum desorption was 10% of OTC, 8% of TC and 3% of ClTC after desorption at pH 2. The increment of pH from 2 to 7 did not increase the amount of TC and ClTC desorbed but the increment of pH promoted the desorption of OTC at concentration below 72 mg g^{-1} (57% of maximum adsorption capacity). The adsorption of TCs on continuous system reached 188, 319 and 505 mg of OTC, TC and ClTC, respectively on 10 g of stevensite. Total TCs adsorption was 101 mg g^{-1}. The removal rates of OxTC, TC and ClTC were 36, 43 and 55%, respectively of the total amount of each antibiotic. The data confirm that ClTC presented more affinity to stevensite followed by TC and finally OxTC. In conclusion, stevensite is more effective than biochars for TC removal from water. Stevensite showed high adsorption and low desorption capacity for TCs. The most probable mechanism of adsorption of TCs on stevensite is the cation exchange and complexation involving amide group. The results demonstrate the usefulness of the stevensite as an appropriate adsorbent of tetracycline antibiotics.

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TETRACYCLINE RETENTION POTENTIAL OF DIFFERENT NATURAL SOIL GEOSORBENTS

Nisael Diorcé, Felipe Yunta, Carlos García Delgado, Daniel González Santamaría, Ana Isabel Ruiz, Raul Férnández, Enrique Eymar, Jaime Cuevas*

Universidad Autónoma de Madrid, Facultad de Ciencias, Madrid, 28049, Spain

Tetracyclines (TC) are the most used antimicrobials for animal feedstock in the EU (1/3 of sales in 2014, [1]. They are also used for humans and plant agriculture [2]. The persistence of these emerging pollutants in the environment is due to their relative long half-life (1/2 years) in residual organic-mineral sludges susceptible to be accumulated in sediments and soils [3]. Residual water treatments are not efficient to reduce or degrade this and other pharmaceutical soluble products, being biowaste debris adsorption processes responsible for their fixation [4]. The risk associated with this persistence is the development of antibiotic resistance microbiota which can affect ecosystems and human beings. The aim of this work was to assess the adsorption rate of tetracycline onto natural geosorbents such as clays and iron hydr(oxides).

Several mineral materials were studied, without any pre-treatment, for screening their potential capacity to adsorb TC as a model for aqueous soluble emerging pollutants. These materials were: illite from Carboneros (Jaén, Spain), sepiolite from Madrid (Spain), five smectitic materials (beidellitic soil and stevensite from Madrid basin, Spain), montmorillonites (low charge MX-80 (USA), high charge (Almería, Spain), high charge (ideal iron absent montmorillonite, Santiago, Chile). We also tested a calcined sewage sludge. Moreover, two-line ferrihydrite and goethite were synthetized and tested as iron hydr(oxides) sorbents. In addition to basic mineralogical, physical and chemical (CEC or BET surface area) properties, point of zero salt effect (PZSE) was determined to evaluate the pH dependent speciation of TC (tetracycline hydrochloride) with the retention capacity of materials [5]. TC adsorption was studied through batch experiments. Adsorption capacity was assessed using different TC (33, 132, 322, 625 and 1,176) mg·L-1 on solid geosorbents (2.5 g for clays and calcined sewage sludge, and 4.0 g for iron oxides) at pH 4, 6 and 8. Adsorbed TC was quantified by UV spectrophotometry (250 nm) 30 minutes after interaction.

Clay minerals illite, smectite and sepiolite adsorbed more TC than any other materials. In contrast, iron oxides showed the lowest values in terms of maximum adsorption and adsorption intensity when high TC concentration were present in solution. Among phyllosilicates, ideal montmorillonite (fully octahedral charge, either low charge or iron absent high charge) showed the highest adsorption capacity surely due to their capacity to integrate TC in the interlayer region. There was not significant dependence of TC adsorption with the magnitude of CEC or solution pH. TC molecule is cationic at pH < 4 and maintain both negative and positive charged groups (zwitter-ionic) with a maximum at pH =5.5, being progressively lost up to pH 8. Then, strict ionic interlayer adsorption is enhanced at low pH in clays [6]. However, TC adsorption is favoured by polar interactions induced by the presence of hydrated divalent cations and the formation of hydrogen bridges within clay interlayers [7]. The best adsorption isotherm fitting with Freundlich model suggests the influence of physical processes as geometry or surface structure (electric charge distribution) as adsorption controlling mechanisms of tetracycline on these materials.

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STUDIES OF THE BIOCOMPATIBILITY OF LAYERED DOUBLE HYDROXIDE BY INTRAMUSCULAR IMPLANTATION: HISTOLOGICAL AND MICROCIRCULATION

Vanessa R. R. Cunha (1)*, Rodrigo B. Souza (2), Ana M. C. R. P. F. Martins (3), Ivan H.J. Koh (4), Vera R.L. Constantino (1)

(1) Departamento de Química Fundamental, Instituto de Química, Universidade de São Paulo - USP, São Paulo, Postal code: 05508-000, Brazil, (2) Departamento de Morfologia e Genética, Universidade Federal de São Paulo - UNIFESP, São Paulo, Postal code: 04023-900, Brazil, (3) Instituto Biológico, Secretaria da Agricultura e Abastecimento, São Paulo, Postal code: 04014-002, Brazil, (4) Departamento de Cirurgia, Universidade Federal de São Paulo - UNIFESP, São Paulo, Postal code: 04023-900, Brazil
ivankoh@terra.com.br, vrlconst@iq.usp.br

Due the recognized biocompatibility and low toxicity, among other properties essential to nanomedicine the Layered Double Hydroxides (LDHs) have been studied as potential resources for therapeutic and imaging purposes [1,2]. The main subject of this work was to evaluate the biocompatibility of the LDHs by *in vivo* assays *via* intramuscular tablets implantation in mice abdominal wall.

The materials were obtained by co-precipitation method and characterized by physico-chemical techniques: chemical elementary analysis, X-ray diffraction, mass spectrometry coupled to thermogravimetric analysis (TGA-MS), zeta potential, size and (IR and Raman) spectroscopy. The tablets are composed by chloride ions intercalated into LDH of magnesium/aluminum (Mg_2Al-Cl) and zinc/aluminum (Zn_2Al-Cl). According to the metal content analysis and the weight percentage of H_2O (obtained from TGA curve), the chemical compositions of LDHs material prepared in this work are $[Mg_{2.10}Al(OH)_{6.20}]Cl\cdot 2.3H_2O$ and $[Zn_{2.08}Al(OH)_{6.16}]Cl\cdot 1.7H_2O$. The medium hydrodynamic diameters of the magnesium and zinc LDHs particles are 85 nm and 104 nm, respectively.

Through the histological analysis of the post-implanted tablets (7 and 28 days) it was possible to evaluate the antigenicity and tissue integration capacity of the LDHs. Two major observations can be emphasis that is related to the absence of fibrous and inflammatory reactions for both materials. Additionally, the Mg_2Al-Cl induced multiple collagen invaginations (mostly collagen type-I) among its fragments while Zn_2Al-Cl promoted predominantly collagen type-III after 28 days of implantation. Therefore, the histological results, independently of the metals composition, demonstrated a good tissue repair with characteristic biocompatibility, promoted the deposition of collagen and the appropriate extracellular matrix remodelling. However, at the same time, the results suggest that depending on the target effect, the layers composition with different metal cation (magnesium or zinc) can induce the tissue remodelling to the desired collagen type. The microcirculation in tissue monitored in real time by the Sidestream Dark Field imaging, revealed overall integrity of the microcirculatory network neighbouring the tablets, with no blood flow obstruction, bleeding and/or increasing of leukocyte endothelial adhesion.

This work supports previous results in the literature about LDHs compatibility with living matter, endorsing them as functional materials for biomedical applications.

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CLAY DUNES IN THE MURRAY-DARLING BASIN, AUSTRALIA: ORIGIN, AGE AND PALAEOENVIRONMENTS

Matt Cupper

School of Earth Sciences, The University of Melbourne, Melbourne 3010 Australia
cupper@unimelb.edu.au

Clay dunes are widespread in the Murray-Darling Basin of southeastern Australia [1,2]. They are low, transverse aeolian deposits downwind of salt lakes where saline groundwater discharges from regional aquifers in the semi-arid basin depocentre. These source-bordering dunes range in height from 10 m to thin veneers less than 1 m thick draping older sand dunes, are up to 500 m wide and can be several kilometres in length. Dunes often curve around the lake margins, with this arcuate form reflected in their local name, *lunette* [1]. Those dune sediments stacked over earlier deposits are interspersed by red-brown earth palaeosols.

Laser particle size analysis, micromorphological thin-sections and XRF show dune sediments are up to 75% clay, with lesser proportions of quartzose or gypseous silt and sand, although some deposits have abundant quartz or gypsum with as little as 10% clay. Pedogenesis has often altered the sediments to depths of at least several metres. Original pelletal clay aggregates have typically fused, forming a clayey silty plasmic matrix around skeletal quartz sand grains. Sand grains are coated by argillans (clay skins).

Clay minerals will only be entrained by wind under specific environmental conditions. Salt lake surface sediments must be desiccated, with interstitial growth of salt crystals or shrinking and curling of sun-cracked, polygonal crusts, which break the clays into fragments tractable by wind currents [1-5]. Further mechanical breakdown may occur as sand-sized aggregates (pellets) of clay move by saltation or traction across the dry lake surface [1-5]. Saltating particles can become trapped in vegetation fringing the basin. Successive clay horizons in dunes stabilize as the clay aggregates coalesce. The minerals in these aggregates hygroscopically absorb moisture due to seasonal increases in humidity and periodic rainfall [2-5]. This causes the clay horizons to stabilize. Subsequent deflation deposits more thin layers of clay over the stabilized, pre-existing surfaces. This layered accretion produces planar beds with very low angle (<10°) dips conformable to dune topography.

Clay dunes are usually on the northeastern corners of the salt lakes. Their axes are aligned northwest-southeast, suggesting dunes were formed by southwesterly winds. Such climatic conditions predominate in the austral summer, the direst part of the year in southeastern Australia. This further supports the inference that the lakebeds lacked surface-water during dune emplacement, because the lakes are mostly dry in summer. Gypsum is present in the dunes as eroded clastic gypsarenite, indicating that the lakes were hypersaline prior to lake floor desiccation and deflation. *Wüstenquarz* (iron-coated quartz silt) also occurs, showing aeolian input from adjacent mobile sand dunes.

Optically stimulated luminescence (OSL) dating of quartz sand within the deposits shows clay dunes formed episodically, primarily during the late Pleistocene 48,000-36,000, 21,0000-16,000 and 14,000-11,000 years ago. Minor aeolian clay deposits also accumulated during periods of the Holocene at 7000-6000 and 3000-1000 years ago.

Desiccation of the lake floors and deflation of basin sediments to form clay dunes is interpreted to have occurred over the arid late glacial and to a lesser extent in drier intervals of the Holocene. The deflationary events are associated with fluctuating water-tables in the Murray-Darling Basin [6]. Clay dunes can therefore serve as proxy indicators of past moisture budgets, atmospheric circulation patterns and temperature.

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FORMULATION AND DURABILITY OF METAKAOLIN-BASED GEOPOLYMERS

Pouhet Raphaëlle, Cyr Martin

Université de Toulouse, UPS, INSA, Laboratoire Matériaux et Durabilité des Constructions, 135, Avenue de Rangueil,
F-31077 TOULOUSE Cedex 4, France

The main objectives of this study were to assess the formulation and durability of metakaolin-based geopolymers as an alternative to traditional Portland cement. A formulation assessment performed exclusively on geopolymer made from flash metakaolin and sodium silicate and hydroxide, has shown performances comparable to a CEM I 52.5 with a faster cure kinetics.

The achievement of concrete, up to precast plant, showed the ability of geopolymer to completely substitute known hydraulic binders, in terms of workability and compressive strength.

Durability issues related to the high alkali content in this matrix were assessed by studies on alkali-silica reaction and carbonation. The results obtained have concluded that the alkali-silica reaction would not be detrimental in metakaolin-based geopolymer, and that the very rapid reaction of the alkalis in the geopolymer pore solution with atmospheric CO_2 does not lead to a significant drop of the pH, thus limiting the appearance of corrosion issues due to carbonation.

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SUB- AND SUPERCRITICAL CONTINUOUS HYDROTHERMAL TECHNOLOGY FOR ADVANCED NANOSTRUCTURED CLAY MINERALS

Aymonier Cyril (1)*, Claverie Marie (2), Aubert Guillaume (1), Martin Francois (3), Careme Christel (2), Pascu Oana (1), Prevot Vanessa (4), Maria Diez-Garcia (5), Gaitero Jon (5), Delado Jorge (5)

(1) CNRS, Univ. Bordeaux, ICMCB, UPR 9048, F-33600 Pessac, France, (2) Imerys, Toulouse, France, (3) Géosciences Environnement Toulouse, Toulouse, France, (4) Université Clermont Auvergne, CNRS, SIGMA Clermont, ICCF, Institut de Chimie de Clermont-Ferrand, F-63000 Clermont-Ferrand, France, (5) Sustainable Construction Division, Tecnalia, Parque tecnológico de Bizkaia, C/Geldo, Edif. 700, 48160, Derio, Spain
*cyril.aymonier@icmcb.cnrs.fr

Supercritical fluids-based technologies are developed for more than 40 years. Years after years the sub- and supercritical fluids route finds new applications in the field of materials by design from organics to inorganics through carbon-based materials [1]. This continuous method is fast (few tens of seconds), sustainable and scalable and gives access to high quality nanostructured materials with unique physico-chemical properties; this means which can not be obtained with other synthetic methods [2]. More recently, supercritical continuous fluids technology, especially using water as solvent, has been investigated as an alternative and scalable approach for clay mineral processing [3,4,5]. This presentation proposes to introduce first the specific properties of supercritical fluids, with a focus on the ones of water, followed by the description of the principle of the processing of materials in supercritical fluids with the associated technologies [6]. The need to open the black box of the near- and supercritical fluids processes brought us to develop numerous tools for *in situ* characterizations to have a better insight into hydrodynamics, thermodynamics, chemistry and nucleation & growth [7]. This will be also described knowing that this is a key issue to better understand but also to better control. We have proposed the first proof of the synthesis in few tens of seconds of clay minerals, namely talc, in a continuous process [3]. This innovative route offers the possibility to obtain a range of nanominerals differing in their degree(s) of crystallinity and size just by adjusting synthesis time and/or temperature. Beyond the control of these characteristics, this synthetic talc exhibits unique properties as its hydrophilicity. This hydrophilic character of the synthetic talc has conducted to the formulation of the first fluid talc filler. More recently, we went one-step forward with the demonstration of the possibility to prepare highly crystalline geominerals in just a few seconds again but under thermodynamically metastable conditions. This will be illustrated with the synthesis of the torbermorite mineral which is not abundant in nature but very interesting in the construction industry [4]. As a result of the supercritical continuous hydrothermal synthesis, highly crystalline fibrillar tobermorite can be obtained in just a few seconds under thermodynamically metastable conditions at 400 °C and 23.5 MPa. In addition to chemistry, it is also possible to play with the process to develop multifunctional materials. Instant one-pot synthesis of functional LDH has been developed using a subcritical continuous hydrothermal multiple process for the preparation of i) pristine LDH with different compositions by varying the cation (Mg, Ni, or Zn) and the anion (CO_3, NO_3) and ii) functional LDH by varying the functionalization agent, for example large/long organic molecules (hybrid LDH), enzymes (bio-hybrid LDH) or still inorganic metal /oxide nanocrystals (inorganic-LDH) [5]. The benefits of the sub- and supercritical continuous hydrothermal route include not only better performances for advanced applications but also environmental issues associated with the synthesis process. We will also stress challenges towards the transfer at the industrial scale of this technology in a near future.

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SYNTHESIS OF GEOPOLYMERS FROM MECHANICALLY AND THERMALLY TREATED CARBONATE-RICH CLAY SEDIMENTS

Angela D'Elia (1)*, Daniela Pinto (1), Serena C. Tarantino (2), M. Pia Riccardi (2), Gennaro Ventruti (1), Giacomo Eramo (1), Marina Clausi (2), Annarosa Mangone (3), Rocco Laviano (1)

(1) Dipartimento di Scienze della Terra e Geoambientali, Università di Bari "Aldo Moro", via Orabona 4, 70125 Bari, Italy, (2) Dipartimento di Scienze della Terra e dell'Ambiente, Università di Pavia, via Ferrata 1, I-27100 Pavia, Italy, (3) Dipartimento di Chimica, Università di Bari "Aldo Moro", via Orabona 4, 70125 Bari, Italy
*angela.delia@uniba.it

Among the many aluminosilicate raw materials suitable for the synthesis of Alkali Activated Materials (AAMs) including geopolymers, the latest research on geopolymers is dealing with an increasing interest in the sustainable use of widely available raw materials and hazardous wastes recycling.

In the same vein, the involvement of Apulian illitic carbonate-rich clay sediments for geopolymer production may promote the knowledge on the use of natural clay deposits to produce AAMs, providing a more ecological intended use of such clays, which are currently involved in the local industry of cements and ceramic tiles.

Although illite/smectite clay sediments have been found to be suitable for AAMs, the complex mineralogical composition of Apulian carbonate-rich illitic clays open some challenges about the most effective processing methodology aimed at the increase of the clay reactivity for the synthesis of geopolymers and to produce a positive effect of calcium compounds on the final product strength.

Apulian carbonate-rich clay samples were subjected to thermal activation in red-ox atmosphere (temperatures between 400 and 900 °C), mechanical activation (milling for 5, 10 and 15 minutes) and to a combination of such treatments.

A preliminary geopolymer synthesis has been conducted on differently treated samples, selected on the basis of the highest amorphous content and Si and Al release in alkaline solution, to assess the effects of different clay pre-treatments on clay reactivity. Moreover, two solutions (NaOH 8M and Na_2SiO_3 with $SiO_2/Na_2O = 2.06$) were used as activators, to investigate how the presence of soluble silica influences the final reaction products and properties of geopolymers.

The preparation of the pastes started from mixing the treated clays and the two different activators, adopting the lowest liquid/solid ratio to ensure the minimum paste workability condition (L/S ranging from 0.5 to 0.8). The resulting geopolymers have been characterised through XRPD, FT-IR, SEM-EDAX analysis and compressive strength tests.

In particular, a positive correlation between the compressive strength and the amorphous content of the raw materials (and, subordinately, the sodium silicate/solid ratio) was observed.

The best strength results are observed for the geopolymers obtained after alkali activation with sodium silicate (L/S = 0.8) of the thermally activated clay at 800 °C in oxidising atmosphere, probably due to the contribution of the increased content of soluble silica and highly reactive lime and portlandite.

Additionally, the activation of treated clays with sodium silicate brought the geopolymers to show a more reacted and homogeneous geopolymeric matrix enriched in calcium, identified as (N,C)-A-S-H gel, compared to geopolymers obtained after clay activation by NaOH. In this latter case, low reacted matrix resulted in the formation of zeolites as secondary reaction products and in very low compressive strength values.

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MESOSCALE ANISOTROPY OF CLAY POROUS MEDIA: A COMBINED EXPERIMENTAL AND NUMERICAL STUDY

Thomas Dabat *, Arnaud Mazurier, Fabien Hubert, Emmanuel Tertre, Brian Gregoire, Eric Ferrage

IC2MP-Hydrasa, UMR 7285 CNRS, Université de Poitiers, 86073 Poitiers, France

Mutual arrangement of lamellar clay particles most often controls the anisotropic properties of natural clay materials by influencing the morphology of pore network, which in turn impacts the overall directional dependence of fluid transfer within. As a consequence a detailed characterization of the mesoscale properties of clay porous media (orientation of particles and associated shape and size of pores) is necessary in order to connect the mechanisms occurring at different length scales, i.e., from the nanoscale (inter-)layers to the macroscale (centimeter).

Our study is based on a combined use of simulated and experimental results aiming at refining our understanding of orientational properties of lamellar particles in clay porous media.

Virtual three-dimensional clay porous media were obtained using a sequential deposition algorithm of particles having disc geometry [1-2]. According to this algorithm, the one-by-one particle deposition is performed under a gravitational field according to the steepest-descent method. The obtained simulations allowed reproducing a wide range of virtual porous media as defined from the obtained order parameter S (S=0 for isotropic system and S=1 for perfectly aligned particles in the porous medium; [3]). By plotting the porosity of the media as a function of order parameter S a master curveis observed[2]. Moreover, the obtained virtual porous media can then be used to assess the size of the representative elementary volumes as well as the size and shape of the pores based on the chord length distribution analysis.

Experimental porous media were obtained by sedimentation of PTFE discs in a large column using different solvents. These media were analyzed by X-ray microtomography through the EasyTom XL Duo system (RX-solutions) set at the University of Poitiers. The porosity and S values from a sub-volume in the column was quantified by means of digital segmentation of pores and discs. The relationship between porosity and parameter S, obtained from both experiments and simulations are in good agreement. Such an agreement corroborates both the pore network morphology and the orientation density functions (ODFs) of clay particles derived from the virtual porous media with different degree of anisotropy. These ODFs are successfully compared with existing data obtained with more complex systems, i.e., from monomineralic clay material [4-6] to polymineralic shale samples [7] and provides sound constraints on the representativeness of the obtained virtual porous media.

The simulation of representative three-dimensional virtual porous media for clay materials represents an important step for a better understanding of anisotropic features in clay porous media, i.e., particle orientation and associated evolution of pore network morphology. Moreover the results obtained in this study could provide sound constraints for the design of upscaling schemes devoted to predict macroscopic properties of clay materials (e.g., diffusive, dielectric, and elastic properties) on the basis of properties of clay minerals commonly derived at the molecular and mesoscopic scales.

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THE USE OF NATURAL ALGERIAN PALYGORSKITE TO PRODUCE ZEOLITE TYPE A

LAMIA DALI YOUCEF (1)*, LALA SETTI BELAROUI (1,2), ABDELKADER BENGUEDDACH (1), ALBERTO LOPEZ GALINDO (3)

(1) Lab. of Chemistry of Materials (LCM), University of Oran 1, BP 1524 Oran El M'Naouer, Oran, Algeria, (2) Dep. of Pharmacy, Fac. of Medicine, University of Oran 1, BP 1510 Oran El M'Naouer, Oran, Algeria, (3) Instituto Andaluz de Ciencias de la Tierra (CSIC-UGR), Avda. de las Palmeras 4, 18100 Armilla, Granada, Spain

Zeolites are vastly used in the industry (i.e. adsorbents in gas purification, ion exchanger in detergents, petroleum refinement catalysis, or in petrochemistry), because their high ion exchange potential, high surface area distributed throughout pores with several diameters, high thermal stability and high acidity. Synthetic zeolites exhibit higher purity, crystallinity and uniformity of particle sizes than natural zeolites. They can be prepared from chemical sources of silica and alumina, but the process is expensive. This problem can be resolved and the costs can be reduced by using natural materials.

Palygorskite, a magnesium aluminum non-planar hydrous 2:1 phyllosilicate with modulated structure, exhibits a fibrous morphology, has great internal surface and contains exchangeable cations and reactive Si-OH groups on its surface. In the present study, an Algerian palygorskite [1,2] (Pal, Figure 1a) is transformed to silica source via acid activation, which is a simple and low-cost effective method.

The synthesis of low silica zeolites essentially consists of two steps; preactivation of Pal to get X-ray amorphous product and hydrothermal reaction of activated Pal with aqueous alkali and sodium aluminate. For this purpose, 1 g of Pal is activated using HCl solution (Figure 1b) at 4N. The obtained solid is dried and then mixed with NaOH solution of 5 N stirred with solid/liquid ratio of the clay and alkaline solution is 1 g/20 mL and 5 g of $NaAl_2O_3$ with 20 mL of deionized water. The obtained gel solution is fitted in an autoclave which is kept in a conventional oven (6, 18 and 24 hours). The synthesized products are washed with deionized water twice, and then dried at 80 °C and 24 h.

X-ray diffraction proved the presence of all characteristic peaks of zeolite A, and electron microscopy revealed the presence of the rhombohedra forms referring to zeolite A morphology (Figure 1c).

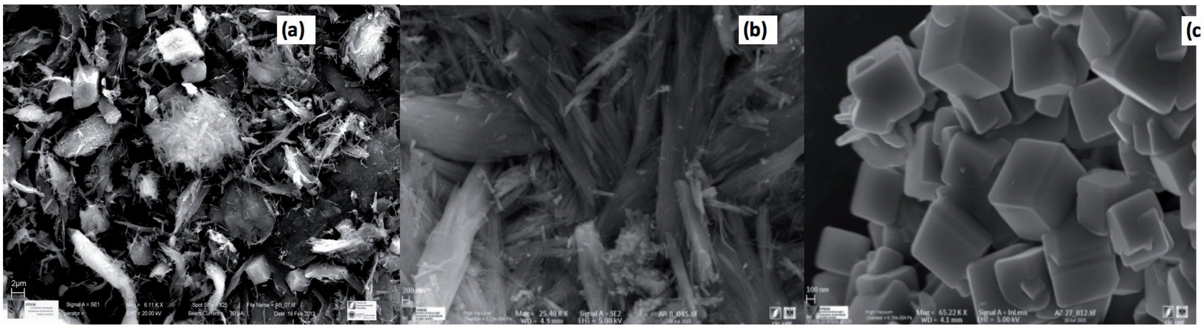

Fig. 1. The SEM images of: (a) the Algerian palygorskite (b) Actived palygorskite (c) zeolite A.

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CELLULOSE NANOFIBERS-SEPIOLITE BIOHYBRID MATERIALS

M. Mar González del Campo, Margarita Darder*, Pilar Aranda, Yves Huttel, Eduardo Ruiz-Hitzky

Instituto de Ciencia de Materiales de Madrid, CSIC, 28049 Madrid, Spain
*darder@icmm.csic.es

Bionanocomposites are a type of nanostructured biohybrid materials resulting from the assembly of naturally occurring polymers and inorganic solids with particle size in the nanometer scale [1], as for instance diverse clay minerals with layered or fibrous morphology [2,3]. Amongst biopolymers, there is a special interest in the use of polysaccharides for the preparation of bionanocomposites due to their abundancy in nature and their renewable and biodegradable character. In the recent years, many works are focusing on the use of cellulose, the most abundant polysaccharide on Earth, to develop new hybrid materials involving clay minerals [4-7]. Cellulose chains consisting of β(1→4) linked D-glucose units are arranged in crystalline and amorphous regions forming elementary fibrils, which are in turn assembled forming the cellulose fibers present in the cell wall of plants [8].

In this context, the current work explores the development of biohybrids based on the assembly of cellulose nanofibers (CNF) to the fibrous clay sepiolite. For this purpose, Pangel® S9, sepiolite from Vallecas-Vicálvaro of rheological grade commercialized by Tolsa SA, was used together with CNF (dimensions around 0.5-2 µm in length and 4-20 nm in diameter), which was prepared following a reported procedure [9] and gently provided by Prof. P. Mutjé (LEPAMAP group, Univ. of Girona, Spain). Aqueous suspensions of CNF and sepiolite were combined by means of shear force and ultrasounds energy in order to produce homogenous and stable gels, which can be dried by solvent casting or vacuum filtration leading to self-standing films [7]. The sonication treatment seems to be compulsory in order to obtain uniform films with a considerable degree of transparency. The characterization of these materials reveals the good interaction between both types of fibers of biological and inorganic nature. The decrease in intensity of the IR vibration band at 3720 cm^{-1}, related to the O-H stretching vibration of silanol groups in sepiolite, suggests a perturbation due to their hydrogen bonding interaction with hydroxyl groups in CNF. Accordingly, XPS results show a large perturbation in the C1s signal from CNF as a consequence of its interaction with sepiolite. Tensile modulus values of hybrid films show slightly higher values than those of the individual components, reaching a maximum value of 3.4 GPa for the material containing 20% sepiolite. The thermal stability was also improved as the sepiolite content increased, showing a shift in the thermal decomposition temperature towards higher values. The degree of hydrophobicity can be also controlled with the sepiolite content, and thus, water adsorption was reduced in hybrid films containing a small percentage of inorganic fibers in comparison to pristine CNF. The possibility of incorporating other nanoparticles allows the preparation of multifunctional materials [10]. For instance, multi-walled carbon nanotubes (MWCNTs) can be included in the CNF-sepiolite hybrids in order to provide them with electrical conductivity, allowing their application as active phase in sensor devices.

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CHARACTERIZATION AND AMINE BINDING CAPACITY OF NATURAL CUBAN ZEOLITE AS WELL AS ITS ORAL AND TOPICAL APPLICATIONS IN THE MEDICINE

Wilfried Dathe (1)*, Thangaraj Selvam (2), Wilhelm Schwieger (2), Richard P. Baum (3), Javiera Cervini-Silva (4), Stephan Kaufhold (5), Arturo Arjona Torres (6)

(1) Heck Bio-Pharma GmbH, Gerberstraße 15, D-73650 Winterbach, Germany, (2) Friedrich-Alexander-Universität Erlangen-Nürnberg, Institute of Chemical Reaction Engineering, Egerlandstraße 3, D-91058 Erlangen, Germany, (3) Zentralklinik Bad Berka GmbH, Clinic for Molecular Radiotherapy and Molecular Imaging, Robert-Koch-Allee 9, D-99437 Bad Berka, Germany, (4) Departamento de Procesos y Tecnología, Universidad Autónoma Metropolitana Unidad Cuajimalpa, México City, Mexico, (5) BGR Bundesanstaltfür Geowissenschaften und Rohstoffe, Stilleweg 2, D-30655 Hannover, Germany, (6) Hospital General Universitario “Vladimir Ilich Lenin”, Avenida Lenin No. 2, entre18 y 26, Holguín, Cuba
*daweidoc@gmx.de

The use of natural zeolites for medicine requires a detailed analysis of their chemical composition, phase purity, ion-exchange properties and microstructural harmlessness as described previously [1]. This Cuban zeolite contains clinoptilolite and mordenite as major phases (ca. 80%), exhibits large BET surface area (140 m^2g^{-1}), high histamine binding capacity of about 12 mg (pH 1) and 15 mg (pH 7) per gram of zeolite [1] and anti-inflammatory properties [2]. The medical application is focused to the gastrointestinal tract. Thus, in gastritis, the positive experience of potentiated clinoptilolite zeolite application [3] could be confirmed by several German general practitioners, who prescribe the natural Cuban zeolite. Furthermore, the high binding capacity of this zeolite against ammonia (about 10 mg/g) relieves the liver as the most important metabolic organ. In patients with renal failure this zeolite seems to be a helpful tool which improves living quality. In addition, patients who tookzeolite startedhemodialysis significantly later than the patients who did not take zeolite.

Serotonin is well known as the ‘hormone for fortune’ in the brain, but excessive peripheral blood levels (produced by neuroendocrine tumors, usually known as “carcinoids”) cause severe diarrhea. As zeolite is an anti-diarrheic drug [4], it has been applied to patients suffering from severe diarrhea. While histamine is nearly irreversibly bound to zeolite, serotonin shows initially a much higher binding affinity to zeolite which declines gradually over time. The use of zeolite in patients suffering from carcinoid syndrome can reduce significantly the number of bowel movements, but not in all patients.

An anhydrous zeolite paste for topical application (Detoxsan® Paste) has been prepared [5]. The formulation is based on petrolatum and contains additionally squalane as natural lipid component. The paste is used in mycosis, intertrigo, psoriasis and inflamed skin areas. In mycosis and intertrigo the improvement of skin area was visible after 2 to 5 days, in psoriasis between 1 and 3 weeks. The effect of this paste was not only investigated among the temperate climate of Germany but also under the tropical climate of Cuba;in both regions with good results. Thus, Detoxsan® Paste reduces inflammation promotors (histamine), prevents microbial growth (water adsorption) and promotes healing of the affected skin areas.

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LIQUID-CRYSTALLINE COLLOIDAL DISPERSIONS OF CLAY MINERALS

Patrick Davidson

Laboratoire de Physique des Solides, CNRS, Univ. Paris-Sud, Université Paris-Saclay, Orsay 91405, France

The purpose of this contribution is to introduce the most important concepts of liquid-crystals and to explain them with examples selected from the wide field of clay minerals. Although the notion of liquid-crystal is usually associated with organic matter, there are quite a few cases of minerals that can be used to elaborate liquid crystals and more cases are found every year [1,2].

Liquid-crystalline materials are substances that spontaneously organize in phases intermediate between crystals and usual liquids [3]. These liquid-crystalline phases (or “mesophases”) are, by definition, both fluid like simple liquids and anisotropic like crystals. Liquid crystal building blocks are generally anisometric, i.e. they have a rod-like or disc-like shape. Molecular liquid-crystals, used for example in display technology, display mesophases depending on temperature and are therefore called “thermotropic”. In contrast, colloidal liquid-crystals are obtained by dispersing anisometric nanoparticles in a solvent and are called lyotropic; then, the relevant control parameter is the nanoparticle concentration. Here, we will only be interested in this latter class of liquid crystals.

According to their symmetry, i.e. the kind of long-range order they display, liquid-crystalline phases can be classified into four main types: the nematic, lamellar, columnar, and cubic phases which have different physical properties. For all these mesophases (except the cubic ones), in a single domain, the building blocks are oriented in the same direction, which gives rise to optical birefringence. However, these phases differ by the dimensionality of their long-range positional order, which leads to very different x-ray scattering signatures.

As good examples of “soft matter”, liquid-crystalline phases usually show a large response to a small external mechanical or electromagnetic perturbation. For instance, mesophases readily respond to an electric field by aligning their anisotropic building blocks parallel (or perpendicular) to the field direction. This effect is at the basis of their electro-optic applications. Moreover, the presence of surfaces also has an aligning effect that can propagate in the bulk as far as several millimetres.

The most useful techniques to investigate liquid crystals are polarized-light microscopy and x-ray scattering. For the latter, in the case of colloidal liquid crystals made of mineral nanoparticles, the low concentration and the large particle size require using small-angle scattering instruments. The combination of these two techniques usually allows for the identification and the detailed characterization of liquid-crystalline order.

Colloidal dispersions of beidellite clay nanosheets and imogolite clay nanotubes will be used to illustrate all the ideas developed above as they are systems very well suited for this purpose [4,5]. We expect that many more mineral liquid crystals are still to be discovered.

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A LIQUID-CRYSTALLINE HEXAGONAL COLUMNAR PHASE IN HIGHLY-DILUTE SUSPENSIONS OF IMOGOLITE NANOTUBES

Erwan Paineau (1), Marie-Eve M. Krapf (2), Mohamed-Salah Amara (1), Natalia V.Matskova (1), Ivan Dozov (1), Stéphan Rouzière (1), Antoine Thill (2), Pascale Launois (1), Patrick Davidson (1)*

(1) Laboratoire de Physique des Solides, CNRS, Univ. Paris-Sud, Université Paris-Saclay, Orsay 91405, France, (2) LIONS, NIMBE, CNRS, Université Paris-Saclay, CEA-Saclay, Gif sur Yvette 91191, France

Colloidal suspensions of anisotropic, rod-like or disc-like, nanoparticles can spontaneously self-organize into liquid-crystalline phases according to their concentration. Although there are many more examples of such ordering displayed by organic compounds like polymers or detergents, the wide field of mineral nanoparticles provides quite a few cases of such phenomena [1].

Liquid-crystalline phases can be classified in four main types: the nematic, lamellar, columnar, and cubic phases. So far, it was shown that all of them can occur at very low volume fractions (i.e. ~1%), except the columnar phase. Very recently, we discovered a highly-dilute liquid-crystalline columnar phase in aqueous suspensions of imogolite clay nanotubes [2].

Imogolite nanotubes naturally occur in volcanic soils and can also be easily synthesized by sol/gel processes. In contrast with carbon nanotubes, they are highly hydrophilic and are readily dispersed in aqueous solvents. These suspensions were previously known to form a liquid-crystalline nematic phase [3] but we surprisingly observed by polarized-light microscopy an additional phase at very low volume fraction (~0.3%). Small-angle x-ray scattering experiments proved the columnar nature of this new phase where imogolite nanotubes organize on a 2-dimensional hexagonal lattice. The columnar phase has very strong positional order even though its lattice spacing is 15 times larger than the nanotube diameter. Moreover, this dilute columnar phase is so fluid that it is easily aligned in an a.c. electric field as the nanotubes orient parallel to the field. This feature could be exploited to prepare macroscopically oriented imogolite-based nanocomposite materials.

The dilute columnar phase is stabilized by electrostatic repulsions between the charged imogolite nanotubes in water at low ionic strength, which raises the question of its possible occurrence in other systems of charged rods, either mineral or organic such as carbon nanotubes or stiff biopolymers.

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HETEROSTRUCTURED MATERIALS BASED ON THE ASSEMBLY OF LAYERED DOUBLE HYDROXIDE TO LAYERED SILICATE FOR PHOTOCATALIC APPLICATIONS

Antonio de J. S. F. Júnior (1), Welton C. Sodré (1), Javier Perez-Carvajal (2), Cícero W. B. Bezerra (1), Ana C. S. Alcântara (1)*

(1) Universidade Federal do Maranhão, 1966, 65080-805, São Luís, MA, Brazil, (2) Instituto Catalán de Nanociencia y Nanotecnología (ICN2) / CSIC, 08193, Barcelona, Spain
*ana.alcantara@ufma.br

In recent years, organic compounds such as dyes from many industrial sectors have contributed to the contamination of several ecosystems, including water, damaging metabolisms of photosynthetic species [1]. In this sense, heterostructured materials based on clays or other silicates containing ZnO [2] or TiO_2 [3,4] nanoparticles appear as an attractive proposal to prepare adsorbents and catalysts that can be used in photodegradation of environments contaminated by such substances. Among these clay mineral-based porous solids, layered silicates such as magadiite, assembled to metal-oxide nanoparticles has been recently developed showing interesting surface properties, especially regarding their applications in the catalysis field [5,6]. Magadiite silicate shows a typical layered structure where the lamella surface presents an excess of negative charge counterbalanced by hydrated sodium ions located in the interlayer space. This silicate exhibits a broad range of properties, including adsorption of metal ions or organic molecules, cation exchange of interlayer sodium cations, intercalation reaction and organization of guest species [5]. On the other hand, layered double hydroxides (LDH), also considered as anionic clays, is a versatile compound which can be assembled with diverse type of nanoparticles such as clays, carbon nanotubes, magnetite or mesoporous silica for environmental or photocatalytic application [7]. In this work, a new type of heterostructured material based on the assembly of LDH to magadiite silicate was studied. For this purpose, MgAl and ZnAl LDH with different divalent/trivalent metal ratio were assembled to magadiite through the *in situ* co-precipitation method, where LDH lamellae are formed in presence of previously prepared magadiite. Diverse physicochemical techniques were employed to characterize the synthetized materials with the aim to ascertain the existence of interaction at the interface of the two components. Results obtained from XRD show typical reflections of LDH in magadiite, confirming the formation of layered hydroxide in the silicate surface. Interactions between both nanocrystalline moieties were evidenced by spectroscopy studies, where coupling between hydroxyl groups of each component take place. Magadiite-supported metal-oxide nanoparticles was prepared employing thermal decomposition of the LDH component in LDH/magadiite heterostructures, in view to obtain materials with highly disperse metal oxide catalysts supported on magadiite silicate. These materials were evaluated as photocatalysts using methylene blue as model dye molecule. Photocatalytic tests performed with the LDH/magadiite and their calcined products show an enhanced photocatalytic activity for degradation of methylene blue, where the concentration of dye is quickly decreased in a short time of exposure (ex. 10 min, 50% increase in dye degradation compared to photolysis). These results are likely due to synergistic effect resulting of the interesting textural features of the obtained heterostructures, making them promising photocatalysts in the degradation of organic compounds.

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CHARACTERISATION OF FREE SWELLING PROCESSES ACCOUNTING FOR SOLUTE CONCENTRATION EFFECTS

Gema De La Morena*, Laura Asensio, Ángel Yustres, Vicente Navarro

Geoenvironmental Group, Civil Engineering Department, University of Castilla-La Mancha, Avda. Camilo José Cela s/n,
13071 Ciudad Real, Spain
*gema.delamorena@uclm.es

Bentonites are planned to be an important part of engineered barriers in deep geological repositories for spent nuclear fuel. Therefore, during the last years the research activity to improve the characterisation of their behaviour has been very intense, and in particular, of their hydro-mechanical behaviour. Furthermore, much evidence of the influence of surrounding water salinity in the deformability of bentonites has shown that chemical processes must be considered. Therefore, nowadays the analysis of the behaviour of bentonites must be carried out from a hydro-chemo-mechanical perspective [1].

Recently, Navarro et al. [2] have developed a numerical model that accounts for solute concentration effects on the behaviour of bentonites. In that model, a double porosity approach was adopted, using the Barcelona Expansive Model [3] as a framework. To characterise the free swelling strains due to the destructuration of particles and aggregates, a state surface like the one used in Navarro et al. [4] was considered, adding the effects caused by the salinity conditions. The geochemical behaviour of bentonite was idealised assuming a simplified geochemical model that took into account sodium, calcium and chloride ions. The effect of salinity was considered on both the macrostructural and the microstructural waters, given the equilibrium between them is controlled by their chemical potentials. For this purpose, the osmotic terms were used [5], which depend on the ion concentration in macrostructural water and on the non-charge-compensating ion concentration in the microstructural water. The Donnan equilibrium relates the ion concentrations of both structural levels. An isothermal formulation was considered, assuming a constant gas pressure equal to atmospheric pressure. A flow model similar to that used in Navarro et al. [4] was considered, taking into account also the vapour flow (assumed to be diffusive only). The solute transport was also included to characterise the evolution of the system salinity. The proposed formulation was applied to reproduce the free swelling behaviour of a MX-80 bentonite under different water salinity conditions.

In the current study, the model proposed by Navarro et al. [2] is improved by adding the osmotic coefficients according to the procedure proposed by Muurinen et al. [6] to the osmotic terms.

A vertical free swelling test was simulated to illustrate the applicability of the model, using a water solution of 35 g/L that contains sodium and calcium chloride. The formulation was implemented in the multiphysics partial differential equation finite solver COMSOL Multiphysics.

The results demonstrate that the hydro-chemo-mechanical formulation significantly improves the predictions over models that do not account for salinity effects. Although it could be developed further, the proposed model allows for a consistent inclusion of the effect of water salinity on the behaviour of MX-80 bentonite.

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NONIONIC ORGANOCLAY AS A VERSATILE ADSORBANT FOR NUMEROUS MICROPOLLUTANTS

Tiago De Oliveira*, Régis Guégan, Mohammed Boussafir

Institut des Sciences de la Terre d'Orléans, CNRS-Universitéd'Orléans, Orléans, France

In contrast to ternary operation water treatment techniques such as UV irradiation, ozonation, advanced oxidation, adsorption represents a simple and easy process avoiding degraded or unwanted molecules showing a toxicity that may be worse than those of actual micropollutants. Among the materials matching the criteria for adsorption: a large specific surface area and a possibility of recycling; clay minerals and other layered materials analogous (layered double hydroxides, organoclays…) display particular interests for adsorption. Indeed, moreover to develop numerous accessible adsorption sites, these layered materials show ion exchange capacities and outstanding hydration properties with an exfoliation of the nanosheets that can self-assembled in liquid crystalline phases [1]. Surfactants used as chemical modifier and/or in association with clay mineral in solution generate a hydrophobic environment improving and enlarging the spectrum of adsorbed organic compounds [2-3].

In this present contribution, novel organoclays were synthesized using nonionic surfactants [4-5], and their efficiency for the adsorption of non-conventional micropollutants such as pharmaceuticals were compared to untreated clay minerals and cationic organoclays (i.e. organoclay prepared with cationic surfactants) for different experimental conditions with a control of pH, temperature, ionic strength… in order to mimic the natural context. The adsorption data correlated to the results obtained with complementary techniques (X-ray diffraction, small angle X-ray scattering, infrared spectroscopy, solid state nuclear magnetic resonance) reveals the importance of the hydrophobicity, charge density and the competition of the micropollutants. Finally, due to its dual hydrophilic/hydrophobic, non-ionic organoclays, unlike cationic ones and untreated clay minerals, represent the most polyvalent material for the adsorption of a wide range of micropollutants showing different chemical nature [6].

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LATE CRETACEOUS COOLING ENHANCED BY CONTINENTAL WEATHERING EXPRESSED BY CLAY MINERALS INCAMPANIAN SEDIMENTS

Elise Chenot (1), Jean-François Deconinck (1), Maxime Jaubert (1), Emmanuelle Pucéat (1), Pierre Pellenard (1), Myriam Boussaha (2), Nicolas Thibault (2), Théophile Cocquerez (1), Ludovic Bruneau (1), Ian Jarvis (3), Jean-Pierre Sizun (4), James Richard (4)

(1) Biogéosciences, UMR 6282, UBFC/CNRS, Univ. Bourgogne Franche-Comté, 6 boulevard Gabriel, F-21000 Dijon, France, (2) IGN, University of Copenhagen, ØsterVoldgade10, DK-1350 Copenhagen, Denmark, (3) Department of Geography and Geology, Kingston University London, Penrhyn Road, Kingston upon Thames, Surrey KT1 2EE, United Kingdom, (4) Chrono-environnement, UMR 6249 UBFC/CNRS, Univ. Bourgogne Franche-Comté, 16 route de Gray, F-25030 Besançon, France

The latest Cretaceous was marked by major changes in the ocean-climate system, with oxygen isotopes indicating a long-term cooling that seems to have accelerated during the Early Campanian [3], while ε_{Nd} data from ocean sediments demonstrate a contemporaneous reorganization of the overall thermohaline circulation [5]. A recent study performed on Campanian sediments of the Tercis-les-Bains section (Aquitaine Basin) and of the Poigny-borehole (Paris Basin) has shown evidence of detrital input of illite, kaolinite and chlorite that coincides with a global carbon-isotope negative excursion, the so-called “Late Campanian Event” [1]. Although conducted in a limited region of the western Tethys, this study hints toward possible modifications of continental weathering that may have affected climate through enhanced atmospheric CO_2 consumption. In order to better constrain the spatial extent of this event characterised by enhanced detrital inputs, we have analysed clay mineralogical assemblages of sediments from several additional sections and boreholes of Campanian sediments from the Tethyan and Boreal realms, along a palaeolatitudinal transect from 20° to 45°N (Danish Basin, North Sea, Paris Basin, Mons Basin, Aquitaine Basin, Umbria-Marche Basin, Saharan Platform). Our results show that the clay fraction of the Campanian sediments from all sections is largely dominated by smectites, which represent the background of Late Cretaceous clay sedimentation [2]. However, in several sections, intervals of significantly enhanced detrital input are evidenced by increased proportions of illite, kaolinite, chlorite, palygorskite and talc atvarious levels in the Upper Campanian.

These detrital inputs result from the erosion of nearby continental areas and thus reflect an intensification of continental weathering during the Late Campanian. This may be explained by a tectonic rejuvenation of exposed continental areas, triggered by closure of the Tethyan Ocean and the anti-clockwise rotation of Africa [4]. As this event seems to be recorded at a broad geographic scale in the Tethyan Realm, the associated increase in chemical weathering may have induced a decrease in pCO_2 levels, thereby contributing to the Late Cretaceous global cooling trend.

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FROM CLAY MINERALS TO THE GEOLOGICAL TIME SCALE: ASTROCLIMATIC CONTROL OF CLAY SEDIMENTATION IN CRETACEOUS SEDIMENTS - EXAMPLE OF THE LONG EXCENTRICITY CYCLE (405 KY)

Deconinck Jean-François (1), Martinez Mathieu (2), Pellenard Pierre (1)

(1) Biogéosciences, UMR 6282, UBFC/CNRS, Univ. Bourgogne Franche-Comté, 6 boulevard Gabriel, 21000 Dijon, France,
(2) MARUM: Center for Marine Environmental Sciences, Universität Bremen, Leobenstrasse 8, 28359 Bremen, Germany

The influence of climatic fluctuations induced by variations in the orbital parameters of the Earth on clay sedimentation is known since the 1980s. Many studies throughout the Tethyan and northern Europe areas have indeed documented the simultaneous rhythmicity between the clay mineral assemblages and the precession-induced marl-limestone alternations. Conversely, the imprint of longer orbital cycles on clay sedimentation has not been investigated yet. We introduce here three examples of the record of the long Milankovitch cycles on clay mineral assemblages in Cretaceous hemipelagic series: 1) in alternating marl-limestone deposits of the Hauterivian/Barremian transition in southeastern Spain (Río Argos section, Subbetic Domain, Moiroud*et al*., 2012); 2) in a much more homogeneous marly series of the Aptian (Marnes Bleues of the Vocontian Basin, southeastern France, Ghirardi*et al*., 2014) and 3) in a mixed Cenomanian succession, composed of marl-limestone alternations intercalated within homogeneous marly sediments (Blieux section, Vocontian Basin, Giraud *et al.,*2013).

On all three sections, samples taken each 20 cm have a clay fraction determined by X-ray diffraction consisting of chlorite, illite, interstratified illite/smectite(I/S R0) and kaolinite. The ratios of the areas of the diffraction peaks of each mineral species were calculated and the data processed by spectral analyses. These clearly show that the precession, obliquity and eccentricity are preserved in clay mineralogical data. In all analyzed cases, the imprint of the 405-ky eccentricity cycle is observed with high amplitudes. The period of this cycle is known with an accuracy of ±0.32%, so that it is applied as a geochronometer in the Mesozoic. The high-amplitude record of this cycle demonstrates the ability of the clay minerals tocalibrate the geologic time scale. Other tools like spectral gamma ray, $CaCO_3$ content and magnetic susceptibility provide comparable results, however, because clay minerals bear a clear climatic message, orbital signal from clay mineralogy is particularly significant.

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CHARACTERIZATION OF AUTHIGENIC Mg-CLAY MINERALS IN HYPERSALINE LAKES (CENTRAL SPAIN). IMPLICATIONS FOR THEIR BIOLOGICAL ORIGIN

Pablo Del Buey (1)*, Xabier Arroyo (2), Óscar Cabestrero (1), Esther Sanz-Montero (1)

(1) Departamento de Petrología y Geoquímica, Facultad de CC. Geológicas (UCM), C/ José Antonio Nováis, 12, 28040, Madrid, Spain, (2) CAI de Técnicas Geológicas, Facultad de CC. Geológicas (UCM), C/ José Antonio Nováis, 12, 28040, Madrid, Spain
*pablodelbuey@ucm.es

Playalakes in Central Spain representmodern hypersaline ephemeral environments where the crystallization of authigenicmineral assemblages in relation with microbial mats led to the formation of gypsum microbialites. Long termhydrochemical analyses reveal a Mg^{2+}-(Na^{+})-(Ca^{2+})-SO_4^{2-}-(Cl^{-}) brine composition (Cabestrero and Sanz-Montero, 2016). Salinity concentration ranges from 2 to up to 400 $g \cdot L^{-1}$in the driest season with pH values ranging from 8 to 10(Cabestrero, et al.2014). Those factors, in addition with microbial activity, enables the formation of a suite of authigenic minerals dominated by sulphates (with gypsum representing up to 80%) and to a lesser extent by carbonates and chlorides. Detrital minerals consist mainly of clays, quartz, feldspars and carbonate grains. A first study of the clay mineralogy of the playalakes was carried outby Cabestrero et al., (2014). The characterization of the phyllosilicatesby XRDrevealedthe occurrence of authigenic clay mineralsin relation with the organic matrix (Extracellular Polymeric Substance) of microbial mats. The present work goesa bit further in the characterization of clay minerals and their textural relations in order to understand accurately the genesis of authigenic clay mineral assemblages.

Semi-quantitative analysis by XRD shows that the bulk sample is made of up to 50% of phyllosilicates. Theauthigenic clay fraction from the total amount of phyllosilicates consist of sepiolite-palygorskite(up to 20%) associated with poorly crystalinesmectite (up to 23%). Systematic Chemical analyses of sepiolite-palygorskite and smectites crystals from a representative sample by AEM (TEM JEM 3000 F)indicate a continuous range of compositions for sepiolite-palygorskite assemblages. According to the classification proposed by Suarez and García-Romero (2013) samples ranged from ideal palygorskite $[Si_{12}O_{30}Mg_8(OH)_4(OH_2)_2]_0\,[Si_8O_{20}(Mg_2Fe_2)_{0.1}(Mg_2Al_2)_{0.9}(OH)_2(OH_2)_2]_1.nH_2O$ to Mg-palygorskite$[Si_{12}O_{30}Mg_8(OH)_4(OH_2)_2]_{0.4}\,[Si_8O_{20}(Mg_2Fe_2)_{0.05}(Mg_2Al_2)_{0.95}(OH)_2(OH_2)_2]_{0.6}.nH_2O$. Detailedobservations by SEM (FEI INSPECT) show the close relation between the lenticular gypsum crystals and palygorskite fibres that coatthe surface of the gypsum.

In the case of smectites, thetrahedralsusbtitution of Si for Al ($Si_{3.84}$, $Al_{0.16}$) to ($Si_{3.22}$, $Al_{0.78}$) wasobtainedin all analyses (14). This implies the incorporation of the rest of Al in the octahedral sheet with other cations like Fe, Mn, Ti and Mg (the most abundant octahedral cation). K is the most abundant interlayer cation, followed by Mg and Ca. These compositionssuggest that the studied smectites belong to the Di-to-Trioctahedralsolid solutionbetween beidellite (dioctahedral) and saponite (trioctahedral) end-members with structural formulas closer to the Mg-rich component. In addition, EDX analysis of EPS from microbial mats within which gypsum crystals nucleated and grow, consistently shows a similar chemical composition to smectites, particularly enriched in Si.

The present results onthe great compositional variability of palygorskites, grown on the surface of authigenic lenticular gypsum crystals, as wellas the existence of solid solution at low temperatures in poorly crystalline andmetaestableMg-rich smectitic phases, support that the formation of the authigenic clays took place belowground by processes of biomass transformation. Thus, the compositional variability of these phases could be considered as a biomarker in mineral precipitation.

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USE OF A PROTEIN AS FUNCTIONALIZALING AGENT TO PRODUCE LOW APPARENT DENSITY KAOLIN

Felipe Delgado*, Herley Casanova

Institute of Chemistry, University of Antioquia, Medellin, 050010, Colombia
felipe.delgado@udea.edu.co

Kaolinite is widely used in the paper, paint and polymer industries as extender or reinforcing material due to its laminar structure. This mineral shows a stack type microstructure, generated by a preferential interaction between basal planes of kaolinite particles. This compact microstructure could be destroyed by shearing forces to increase the kaolinite specific surface area, and therefore, the interactions with other components present in the system of interest. A procedure was developed to disaggregate the kaolinite stack structure (thickness ca. 20 μm) to generate laminar structures (thickness < 500 nm), by applying high shear to a kaolin aqueous suspension. Afterwards, protein was added to stabilize and functionalize the surface of kaolinite particles. The obtained suspension was spray dried to produce a dried powder of kaolin, which has an apparent density of 0.2 g/mL, this value is one third of the apparent density of a kaolin dried powder (ca. 0.66 g/mL). This significant decrease in the apparent density is due to the formation of spheroidal structures obtained after the functionalization and drying processes. It is possible to change the spheroidal structure by varying the protein concentration; at low protein concentration a compact and smooth surface is obtained due to interactions between basal planes of kaolinite particles, whilst at high protein concentration a porous surface is generated due to basal plane-edge interactions of kaolinite particles. These porous structures were used in the adsorption of hydrophilic and hydrophobic compounds with potential application in pharma, food and agrochemicals as a carrier material.

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MANGANESE OXIDES AND THEIR INCORPORATION OF HEAVY METALS IN BENTONITE DEPOSITS DEVELOPED FROM UPPER EOCENE VOLCANIC ASH, TEXAS, USA

Youjun Deng*, Ana Luisa Barrientos Velazquez

Department of Soil & Crop Sciences, Texas A&M University, College Station, TX, 77843, USA
*yjd@tamu.edu

Manganese oxides are important minerals in soil and sediments due to their strong oxidation power and their high capability of fixing micronutrients and heavy metals in their structures. Yet, the structures and the properties of manganese oxides in soils and sediments are poorly understood, mainly due to the low abundance of Mn in soils and sediments. The objectives of this study were to characterize the Mn oxides formed in bentonite deposits, and to investigate the incorporation of heavy metals during the formation of the Mn oxides.

The Mn oxide specimens were collected in two commercial bentonite deposits developed from the Upper Eocene volcanic ash in Gonzales county, Texas. The bentonites themselves are low in Mn and heavy metals, but Fe and Mn oxide coatings are common in the cracks of the bentonites. They stain the white bentonite to the red or black color. In certain places, Mn oxide coatings with a few tenths of millimeter thickness and several millimeters of width can be found along the cracks. During the site visits, three Mn-oxide enriched pockets were observed at the bottom boundary of the bentonite deposit and its bed sandstone. These pockets of materials contained Mn oxides as high as 290 g/kg. The Mn oxide coatings were hand-picked. The Mn-oxide rich pockets were sampled in large quantity. The chemical compositions of the specimens were analyzed with X-ray fluorescence, and the mineral composition were analyzed with X-ray diffraction, scanning electron microscope, and transmission electron microscope.

The Mn oxides are enriched in several heavy metals: e.g., ~18,000 ppm BaO, ~7,000 ppm Zn, 1,700 ppm Y, 800 ppm Co, 600 ppm, Ni, 600 ppm Sr, and 300 ppm Sn. Where these values in the hosting bentonite are much lower or close to zero. The elemental composition difference and occurrence location of the Mn oxides suggested they formed after the diagenesis of the bentonite. The X-ray diffraction and electron microscope analyses revealed the mineral compositions of the coatings were different from the Mn oxide pocket deposits, and the three deposit pockets had different Mn mineral composition too. Mn mineral identified include birnessite, rancieite, hollandite, todorokite, and possibly lithiophorite. These minerals showed different incorporation of the heavy metals. Energy dispersive spectroscopy analysis indicated that Ba and the rare earth elements were mainly associated with the tectomanganate minerals. Washing the specimens with Mg and K solutions indicated that the heavy metals and Ca in the Mn oxides were not responsive to the cation exchange reactions. Suggesting the stability of the cations in the structures of the Mn oxides.

The observations indicated the bentonite deposits recorded the various transformation stages of the Mn oxides and the associated heavy incorporation and fixation in their structures. The complexity of mineral composition within such a small spatial distance suggested the sensitivity of Mn oxides to their forming chemical environment. Under the dry conditions, the heavy metals are incorporated in the tectomangante minerals. As those heavy metals are relatively scarce in the bentonite deposits themselves, the origins of the heavy metals were attributed to ground water, which in turn, might be influenced by sediments from a much large spatial and temporal ranges.

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IONIC LIQUIDS - CLAY MINERALS NANOARCHITECTURES AND APPLICATIONS

Christian Detellier (1)*, Gustave Kenne Dedzo (2)

(1) Department of Chemistry and Biomolecular Sciences and Centre for Catalysis research and Innovation, University of Ottawa, Ottawa (Ont) K1N6N4 Canada; (2) Laboratory of Analytical Chemistry, Faculty of Science, University of Yaoundé I, B.P. 812, Yaoundé, Cameroon

Ionic liquids (ILs) are commonly defined as organic salts with melting points under or around 100 °C. They have been employed as substitutes for traditional organic solvents in chemical reactions. The most common ones are based on four types of organic cations: alkylammonium, dialkylimidazolium, phosphonium and *N*-alkylpyridinium. Because they are non-volatile, non-flammable, have a high thermal stability and are relatively inexpensive, ionic liquids are attractive as solvents, being often qualified as ‘‘green solvents’’ [1].

The functionalization of the interlayer spaces of clay minerals leads to a large variety of applications [2]. The melt process was largely used as a powerful method leading to intercalation, delamination and exfoliation of phyllosilicates with polymers, including the intercalation of polymers in kaolinite [2]. This paper will focus on one particular clay mineral: kaolinite. It will show how ILs, because of their unique characteristics, can be employed as building blocks for the creation of functional kaolinite nanohybrid materials having potential applications as sensors, nanocarriers and catalysts supports.

Given their liquid nature, ILs are good candidates to be used as solvent in the melt process, in which a pre-intercalate (urea, dimethyl sulfoxide…) would be replaced by salts of large organic cations. Examples of intercalation of salts, or intersalation, in kaolinite were scarce, being limited to potassium acetate and analogs. The intersalation of ILs would lead to highly functional kaolinite interlayer spaces.

In 2005, our group showed that ILs with quite large cationic organic units, pyridinium derivatives, could be melt intercalated in the interlayer spaces of kaolinite [3]. This was followed, *i.a.*, by the preparation of a series of highly nanostructured hybrid materials resulting from the intercalation in kaolinite of imidazolium ILs, showing ionic conductivity highly dependent on the structure of the intercalated imidazolium cation [4]. The next step was to graft the IL cation on the internal surfaces of kaolinite, so that it became resistant to deintercalation in water, and could be used for applications as electrode modifier [5]. In particular, these nanohybrid materials were used as electrochemical sensors for size-selective detection of anions [6] and of several ionic and neutral species.[7,8] ILs - kaolinite materials were also used as precursors of exfoliated nanocomposites.[9] ILs-kaolinite and ILs-halloysite were recently used as efficient catalysts (palladium nanoparticles) supports [10,11].

Given the large spectrum of chemical structures of ILs and because of the possibility to use them in melt intercalation processes, the creation of materials nanoarchitectures designed for specific applications becomes possible.

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KAOLINITE AGGREGATION INDUCED BY ADJUVANTS IN NON-AQUEOUS MEDIA

Rola Mansa (1), Guy B. Ngassa (1), Stepan Hlushak (2), Andriy Kovalenko (2), Christian Detellier (1)*

(1) Department of Chemistry and Biomolecular Sciences and Centre for Catalysis Research and Innovation, Ottawa (Ont), K1N6N4, Canada, (2) National Institute for Nanotechnology, National Research Council of Canada, and Department of Mechanical Engineering, University of Alberta, Edmonton (AB), T6G2M9, Canada

The clean recovery of bitumen from oil sands would strongly benefit from fully non-aqueous processes taking into consideration the efficiency of desorption of the bitumen from fine particles (mainly kaolinite and illite) as well as the efficiency of sedimentation of these fines. Specific adjuvants to the non-aqueous solvent, including, but not limited to, cellulose derivatives, show a remarkable dual effect, helping both desorption and fines sedimentation.

In that context, an understanding of the morphologies of clay mineral assemblies in dispersion in aqueous or non-aqueous media is of importance. It is also of importance in the control of a vast spectrum of applications and processes. An attempt was made at describing the organization of kaolinite platelets in non-aqueous media in comparison to aqueous media, and also in the presence of a selection of solubilized organic polymers. SEM images give the result of the assembly process taking place during slow solvent evaporation, and consequently, because the experimental procedure was rigorously identical in all the cases of this study, they reflect how platelets can interact in various media, leading to different morphologies under different environments, by comparison.

Theoretical studies of the interactions of organic polymers in non-aqueous as well as aqueous solvents were performed by using the 3D-RISM-KH molecular theory of solvation. This theory readily yields the molecular solvation structure and thermodynamics of these all-atom force field models of clays organic polymers in aqueous and non-aqueous solutions It shows the balance between aggregation and dispersion of the clay polymers at different temperature and pressure conditions. Analysis of the calculation results reveals the molecular forces driving phase behavior of clays in solution.

Quite spectacular morphological differences were indeed observed between aqueous and non-aqueous samples, particularly when organic polymers were present in an organic solvent. In contrast with water, where only small aggregates were observed upon slow evaporation, large booklets or vermiform aggregates were induced by the slow evaporation of some organic solvents when kaolinite was first dispersed into them. The aggregates were particularly large when an organic polymer was present in the solution. For example, top apparent surface areas of more than 3,000 μm^2 could be observed in the case of an ethyl cellulose solution in a binary mixture of cyclohexane and toluene. Other polymers, such as polystyrene or guar gum, a polysaccharide, gave similar results. The aggregation of the kaolinite platelets results from face-to-face interactions, as well as edge-to-face and edge-to-edge interactions.

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DETERMINATION OF PHYSICAL AND CHEMICAL PROPERTIES OF MODIFIED CLAYS FOR IMPERMEABLE BARRIERS

Gemmina Di Emidio (1), Mathijs Dumon (2), Eric Van Ranst (2), Adam Bezuijen (1), R. Daniel Verastegui Flores (3)

(1) Department of Civil Engineering, Laboratory of Geotechnics, Ghent University, 9052 Zwijnaarde, Belgium, (2) Department of Geology, Ghent University, Campus Sterre S8, Krijgslaan 281, 9000 Gent, Belgium, (3) iMMC, Université catholique de Louvain, Louvain-la-Neuve, 1348, Belgium
gemmina.diemidio@gmail.com, Mathijs.dumon@ugent.be, eric.vanranst@ugent.be

Clayey barriers are widely used for isolation of pollutants in landfill systems because of their low hydraulic conductivity (k) to water resulting from their small pore size and thick diffuse double layer (DDL) between clay platelets. However, prolonged exposure of the clays to polluted liquids leaching from landfills can drastically increase their k due to the compression of the DDL, which can cause enormous damage to the surrounding environment and human health. To overcome this problem, HYPER clay, a superior material with enhanced hydraulic performance able to resist chemical attack, was developed at Ghent University [1] by adsorbing an anionic polymer, Sodium-Carboxy Methyl Cellulose (Na-CMC), onto the surface of clay minerals. . The materials selected for this research were kaolin, sodium natural bentonite (CEB1), calcium bentonite (CEB3), sodium activated bentonite (CEB4) and dredged sediments (DS) and they were treated with 2%, 8% and 16% of the anionic polymer (Na-CMC), respectively, to create the HYPER clays.

The quality of bentonite as hydraulic barrier increases with increasing montmorillonite content, surface area, surface charge deficiency, and/or percentage of Na^+ on the exchange complex [2]. The effect of these factors on the quality of bentonite generally is indicated macroscopically by an increase in swell capacity, liquid limit (LL), and cation exchange capacity (CEC), with a consequent decrease of the k [2]. For these reasons, to assess the potential benefits of the HYPER clay treatment, a series of analyses, e.g. swell index test, LL test, X-ray diffraction (XRD) and CEC determination, were conducted on the different materials treated with various polymer dosages.

Due to the inverse relationship between swell index and k [3], the influence of polymer treatment was studied by a series of swell index tests using KCl and $CaCl_2$ solutions with different concentrations. Based on the Gouy-Chapman equation, the DDL thickness decreases with increasing concentration and valence of the permeating solution. For this reason, the swell index obtained in this research decreased with increasing the concentration of the solutions and the valence of the ions present (e.g. Ca^{2+} vs. K^+). Test results also showed that swell index increased with increasing polymer dosage, suggesting that also the k of these materials will decrease after treatment.

The LL of clayey materials can also reflect the hydraulic conductivity: the higher the LL, the lower the hydraulic conductivity that could be expected [4]. Test results showed that the LL of the materials analyzed increased with increasing polymer dosage, with a consequent potential increase of the k performance.

XRD patterns of the materials showed that the basal spacing increased with increasing polymer dosage. The XRD pattern of CEB1, for example, showed a shift of basal spacing (d= 1.332) compared to the untreated clay (d= 1.274), demonstrating the polymer intercalation in the interlayer. These results suggest the permanence of the polymer in the interlayer region after addition, with a consequent beneficial increase of the DDL thickness.

The HYPER clay polymer treatment also showed a positive impact on the CEC, that increased with increasing polymer dosage. An increase in CEC indicates, in fact, an increase of bentonite quality for hydraulic barriers [2].

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LIGHTS ON THE SPECTRAL SHIFT OF PORPHYRIN/CLAY INTERFACE

Eduardo Diaz Suarez (1), Av. Gil Rebaza (2,3), Filipe Dalmatti Lima (4), Vera R. L. Constantino (5), Helena M. Petrilli (1)

(1) Instituto de Física, Universidade de São Paulo, C.P 66318,055080, São Paulo, Brazil, (2) Departamento de Física, Facultad de Ciencias Exactas, Instituto de Física, Universidad Nacional de La Plata-UNLP, 1900 La Plata, Argentina, (3) Grupo de Estudio de Materiales y Dispositivos Electrónicos(GEMyDE), Facultad de Ingeniería, Universidad Nacional de La Plata-UNLP, 1900 La Plata, Argentina, (4) Instituto Federal de Educação Ciência e Tecnologia de São Paulo, 15991502, Matão, São Paulo, Brazil, (5) Departamento de Química Fundamental, Instituto de Química, Universidade de São Paulo, C.P. 26077, 05508, São Paulo, Brazil

The electronic spectra shift of tetracationic 5,10,15,20-tetrakis(1-methyl4-pyridyl)-21H,23H-porphyrin (TMPyP) upon adsorption on a clay surface is here investigated using ab-initio electronic structure calculations performed in the framework of the Density Functional Theory (DFT). Porphyrins are heterocyclic macrocycle organic compounds with many applications such as photosensitizers for light harvesting and chemical reactions, molecular electronics and enzymatic catalysis. They can be found in biological systems like photosynthesis of light, enzymes, and transport proteins. The porphyrins optical spectra can be characterized by the presence of a dominant so called Soret band plus a Q-band structure, whose positions and shapes offer a method to characterize porphyrins in various environments. The influences of the environment and DFT exchange-correlation functional on the UV-vis spectra of the model systems, here considered, are investigated. With this aim, the TmPyP/Montmorillonite interface is studied and these results are further discussed to tentative address the observed electronic spectral shift on TMPyP upon the TMPyP/Clay interaction. The results suggest that the mechanism is still controversial.

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SECONDARY CHLORITE IN THE METADOLERITE DIKES OF THE FRIDO UNIT (SOUTHERN APENNINES - ITALY)

Maria Carmela Dichicco*, Salvatore Laurita, Giovanni Mongelli, Giovanna Rizzo, Rosa Sinisi

Department of Sciences, University of Basilicata, 85100 Potenza, Italy
*maria.dichicco@unibas.it

In the Pollino Ridge (Calabria-Lucania border zone) the ophiolitic rocks of the Frido Unit are cross-cutted by metadolerite dikes showing different types of textures (intersertal, blastophitic and locally cataclastic to mylonitic, Sansone et al., 2011).

The metadolerites dikes have been affected by ocean-floor metamorphism under amphibolite to greenschists facies conditions (Sansone et al., 2012b). Further subduction, involving metamorphism under blueschist facies conditions affected the rocks during the formation of the Pollino Ridge (Sansone et al., 2012b).

This study focused on the different features of the chlorite minerals occurring in the metadolerite dikes. The relict igneous minerals are plagioclase and clinopyroxene. Metamorphic minerals are chlorite, green amphibole, quartz, white mica and the brown amphibole. Accessory phases are opaque minerals, Fe-hydroxides, zircon, and spinel. Metadolerites are commonly cutted by veins filled with metamorphic minerals including pumpellyite, chlorite, prehnite, albite, tremolite/actinolite, white mica, quartz, calcite, epidote, lawsonite, glaucophane, and chrysotile, which occur with various combinations within the same veins (Sansone et al., 2011; Sansone and Rizzo, 2012). The veins show a brittle and ductile deformation and are straight, a few millimetres thick, and are isolated or in closely spaced sets.

Chlorite is generally retained as forming during alteration of primary minerals. In the metadolerites, different varieties of chlorite are observed:

1) fan-felt-radiated aggregates, sometimes over-growing on clinopyroxene;

2) chlorite flakes or tabular show an undulose extinction, replacing amphibole, and occurring at the core of textural sites near blue amphibole rimming brown amphibole. Pale-green amphibole may form pseudomorphs after clinopyroxene together with chlorite and white mica;

3) felt-radiated aggregates or flakes filling veins;

4) pseudomorph on the plagioclase crystals associated to pumpellyite, prehnite and epidote with fine-grained aggregates.

Chlorite is classified according with Hey's nomenclature (1954) as a clinochlore and pycnochlorite as revealed by EMPA characterisation. Chlorite compositions from blueschists facies, compared with the chlorites from the greenschist facies, where the Al/(A1 + Fe + Mg + Mn) ratio ranges between 0.35 and 0.40 (Brown 1967; Cooper 1972), are characterized by Al/(A1 + Fe + Mg + Mn) ratio (0.28-0.31). Finally the occurrence of the chlorite + clinopyroxene in textural sites with the brown - green and blue-amphibole testify the crystallization under blueschist facies of the metadolerite dikes in the Pollino Ridge.

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MINERALOGICAL FEATURES OF FIBROUS TREMOLITE FROM THE POLLINO MASSIF

Maria Carmela Dichicco*, Salvatore Laurita, Giovanni Mongelli, Giovanna Rizzo, Rosa Sinisi

Department of Sciences, University of Basilicata, 85100 Potenza, Italy
*maria.dichicco@unibas.it

On the Pollino massif (southern Apennines, Italy) crop out the Frido Unit belonging to the Liguride Complex. This unit consists of ophiolites with large lens-shaped bodies of serpentinites. In these rocks, tremolite, an asbestos-like mineral, is typically intergrown with fibrous antigorite and chrysotile. Tremolite (ideal formula $Ca_2Mg_5Si_8O_{22}(OH)_2$) which is the calcic end-member of the tremolite - ferro-actinolite series, shows acicular, fibrous and elongated habitus. These minerals generally occur as naturally exposed friable fibres and can be easily released into the environment as a result of both natural processes and anthropogenic activities. From a toxicological point of view, this fibrous tremolite species exhibited high carcinogenicity. Several analytical techniques have previously been used to identify the amphibole minerals on the basis of their different structural and chemical properties. In the analyzed rocks, tremolite is present mainly in veins as much as in the matrix and also forming crowns around clinopyroxene porphyroclasts. The X-ray diffraction analysis (XRPD) of powdered bulk rock allowed clearly the recognition of the amphibole-like minerals (actinolite, d = 8.31 Å; tremolite, d = 2.94 Å) that are the dominant phases. In the μ-Raman spectra, the number and relative intensity of the bands represent pure tremolite and almost pure tremolite (Fe-tremolite) with a small percentage of Fe^{2+}. The presence of Fe^{2+} is confirmed by FT-IR spectroscopy. The electron microprobe analysis (EMPA) revealed that the average composition obtained on single crystals is clearly distinguished from the typical compositions of the tremolite, in particular our samples show high content of Al_2O_3 (5.18 - 15.46 wt%), FeO (2.47 - 5.06 wt%), Cr_2O_3 (0.95 - 1.41 wt%). The scanning electron microscope equipped with electron-dispersive spectroscopy (SEM-EDS) shows that crystals are homogeneous, without zoning, although some crystals show variations compositions of CaO, MgO, Fe_2O_3 in the rim and core.

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HYDROXY-INTERCALATED SMECTITE (HIS) SYNTHESIS FROM NATURAL BENTONITE. A MULTIANALYTICAL APPROACH

Jan Dietel (1)*, Jens Gröger-Trampe (2), Stephan Kaufhold (1), Kristian Ufer (1), Marko Bertmer (3), Reiner Dohrmann (2)

(1) Bundesanstalt für Geowissenschaften und Rohstoffe (BGR), 30655 Hannover, Germany, (2) Landesamt für Bergbau, Energie und Geologie (LBEG), 30655 Hannover, Germany, (3) Leipzig University, Institute of Experimental Physics II, 04103 Leipzig, Germany
*jan.dietel@bgr.de

The acidic weathering of soils causes transformation of primary silicates such as feldspars or layer silicates to intermediate phases, especially clay minerals including their interstratifications. Due to acidic soil solutions, often occurring in upper soil horizons, Al is mobilized as Al^{3+} leading to a cation exchange of expandable minerals such as smectite or vermiculite. Al^{3+} then polymerizes in the interlayer regions forming island-like Al-OH polymers (Hydroxy-interlayers, HI) that are irreversibly fixed, leading at times to a drastically reduced expandability of the clay minerals, and thus, a reduced soil fertility. These hydroxy-interlayered minerals, such as hydroxy-interlayered smectite (HIS), or hydroxy-interlayered vermiculite (HIV) and their interstratifications, are difficult to quantify.

The aim of the project is to quantitatively describe the soil mineralogy including HI minerals using X-ray diffraction and the Rietveld method with the software package BGMN. To be able to apply the Rietveld method, a crystallographically correct structural model of each mineral must exist. In order to test and prove the correctness of a structural model, such as HIS, it should be applied to a pure phase that is well characterized to validate the refined structural parameters and to be able to verify the goodness of the fit without overlap with other mineral reflections. Due to the similarity regarding the chemistry and the same particle size compared to the primary layer silicates, it is not possible to separate these phases by any chemical or physical method (e.g., particle size separation) to obtain a mineralogically "pure" sample of HI minerals. In this study, we, therefore, synthesized highly enriched HIS samples as a set of 7 subsamples with different degrees of HI.

As a starting material we used a natural bentonite from Milos (Greece) that was size fractionated to <2 µm and saturated with Na^+. To the resulting sample containing >90% w/w dioctahedral smectite with minor amounts of K-feldspar, plagioclase, quartz, and anatase (in decreasing abundance), 1.000% w/w zircon ($ZrSiO_4$) was added as an internal standard. The mixture was homogenized and split into 7 identical subsamples. 6 of the subsamples were treated with a 0.1 mol/L $AlCl_3$ solution and titrated to pH=5.5, using a 0.3 mol/L NaOH solution (endpoint titration), while 1 subsample was not treated with $AlCl_3$ solution to receive a 0% HI sample. The other 6 subsamples were treated differently regarding the volume of 0.1 mol/L $AlCl_3$ added and the total reaction time leading to a continuous sample set of 7 different samples ranging from 0% HI to almost 100% HI.

Characterization of these subsamples was performed using a multianalytical approach. A number of methods including X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), cation exchange capacity (CEC) determination, X-ray fluorescence (XRF), simultaneous thermal analyses coupled with mass spectrometer (STA-MS), and others were used to characterize the reaction products and to calculate the Al budget. XRD, STA-MS, and FTIR were used to estimate the proportion of crystalline $Al(OH)_3$ phases precipitated during the repeated addition of $AlCl_3$ solution. Chemical calculations of the Al budget were undertaken at first to estimate the maximum proportion of precipitated X-ray amorphous $Al(OH)_3$ which is extremely difficult to detect, and secondly to evaluate the amount of HI for each subsample as determined by the CEC.

Although no direct methods are applicable to determine the degree of HI and the proportion of both crystalline and X-ray amorphous $Al(OH)_3$ phases, the data show that an estimation of the degree of HI as well as the proportions of crystalline and X-ray amorphous $Al(OH)_3$ phases are possible. STA-MS results show decreasing dehydration and dehydroxylation temperatures, as well as a more continuous behaviour compared to the reactant that showed clearly distinguishable dehydration and dehydroxylation peaks. These results indicate increasing proportions of HI and crystalline and/or X-ray amorphous $Al(OH)_3$ phases. The synthesized sample set consists of a continuous series of HIS samples different degrees of HI. Although minor impurities are present such as feldspar, quartz, anatase, or newly formed $Al(OH)_3$ phases, these samples are highly enriched in homogeneous HIS phases and hence, suitable to develop a structural model of HIS.

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MINERALOGICAL CHARACTERISATION OF A CORRENSITE SAMPLE FROM AYRSHIRE, SCOTLAND, UK

Jan Dietel (1), Kristian Ufer (1)*, Stephen Hillier (2,3), Stephan Kaufhold (1), Reiner Dohrmann (1,4)

(1) Bundesanstalt für Geowissenschaften und Rohstoffe (BGR), 30655 Hannover, Germany, (2) The James Hutton Institute, Craigiebuckler, Aberdeen, United Kingdom, (3) Department of Soil and Environment, Swedish University of Agricultural Sciences, Box 7014, Uppsala SE-750 07, Sweden, (4) Landesamt für Bergbau, Energie und Geologie (LBEG), 30655 Hannover, Germany
*Kristian.ufer@bgr.de

Corrensite is a mineral which commonly occurs in sediments, hydrothermal altered rocks, under retrograde diagenetic conditions, and soils. Corrensite is a regular interstratification of trioctahedral chloritic layers with either trioctahedral smectitic layers (low-charged corrensite) or trioctahedral vermiculitic layers (high-charged corrensite). Detailed knowledge of this mineral is necessary to be able to develop structural models suitable to quantify corrensite in natural rocks and soils using XRD and the Rietveld method.

The present study presents the characterisation of a corrensite sample from Scotland to define its crystal chemistry and structural parameters such as the layer charge density. This particular sample was originally collected by Colin Farmer from the Hillhouse quarry, a hydrothermal altered basalt in Ayrshire. Even the bulk material is almost free of impurities and could be further purified by particle size fractionation and is, therefore, suitable for a detailed characterisation and to derive the required structural parameters.

The sample was identified as corrensite by XRD measurements of oriented specimen in air-dried and ethylene-glycol intercalated state. However, it could be shown that the d_{00l} spacings slightly deviate from an ideal rational series with a coefficient of variation of 0.25. XRD powder patterns proved the trioctahedral character of the sample based on the *060* peak position (d_{060}=1.542 Å). Most intensity maxima of the *hk* reflections were broad and asymmetric and could hardly be assigned to Bragg peak positions. This indicates strong rotational and translational disorder of the layers parallel to each other.

The sample was further examined by SEM, XRF, $Fe^{2+/3+}$ determination, STA-MS, FTIR, and the determination of the CEC. These data were used to characterize the corrensite, to identify impurities, subtract the influence of impurities on the chemical data, and to calculate a structural formula of the corrensite. This structural formula was used to calculate a theoretical CEC and mass loss by heating, which were compared to observed data. Additionally, the type of the smectitic layers were derived from these data and the corrensite determined as a low-charged corrensite.

The slight deviation from rationality of the basal reflections as well as the modulated intensity distribution of the powder pattern show that the sample contains strong structural defects. This can be most likely expected for all corrensites. The results of this study, therefore, are used as basis for further development of a structural disorder model suitable to describe the three-dimensional XRD patterns of corrensites in mixtures with the Rietveld method.

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THERMAL STABILITY AND TECHNOLOGICAL CHARACTERIZATION OF DUTHUNI KAOLINS (LIMPOPO PROVINCE) SOUTH AFRICA

Oscar Miyambu (1), Lawrence Diko Makia (2)*, Georges-Ivo Ekosse (3), André Van Niekerk (4), Portia Mahumapelo (4), Ndabenhle Sosibo (4)

(1) Geology Division, University of Limpopo, P/Bag x1106, Sovenga, 0727 South Africa, (2) Department of Mining and Environmental Geology, University of Venda, P/Bag X5050 Thohoyandou, 0959 South Africa, (3) Directorate, Research and Innovation, University of Venda, P/B X5050 Limpopo Province, 0950 South Africa, (4) Small Scale Mining Division, MINTEK, Private Bag X3015, Randburg, 2125, South Africa
*dikom73@gmail.com

Phase transformations and microstructural evolution of sintered kaolin are important considerations for industrial application. This study presents preliminary findings on the thermal decomposition and mechanical behaviour of kaolin from Duthuni, exploited for clay brick production. Thermal stability was investigated by simultaneous differential scanning calorimetry (DSC) and thermogravimetry (TG), while technological properties were assessed on the basis of flexural strength (σ), water absorption capacity (WA) and linear shrinkage (LS) at four firing temperatures (800 ^{o}C, 900 ^{o}C, 1000 ^{o}C, and 1100 ^{o}C). The DSC curve portrayed three endothermic peaks at 85 ^{o}C, 295 ^{o}C and 535 ^{o}C corresponding to elimination of adsorbed water, goethite dehydroxylation and formation of metakaolinite respectively. A weak exothermic peak was observed at 945 ^{o}C with a cumulative mass loss of 10.5%. Findings also indicated that σ, WA and LS were significantly altered with increase in firing temperature. Compared to other kaolins commonly employed for structural ceramic production, Duthuni kaolins showed moderate to good qualities. However in-depth studies are required to complement current findings.

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PALYGORSKITE STABILIZED PICKERING EMULSION

Jing Chen, Yeling Jin, Shijie Ding*, Lingli Ni, Jinlong Jiang, Tingting Xu

School of Chemical Engineering, Huaiyin Institute of Technology, Key Laboratory for Palygorskite Science and Applied Technology of Jiangsu Province, Huaian 223003, PR China
*chenjing6910@163.com, shijie105@sina.com

Pickering emulsion is a kind of emulsion system stabilized by solid particles instead of surfactant molecules. Current work has mainly focused on emulsifies based on spherical particles or plate-like particles. There have been few reports for the Pickering emulsions stabilized by fibrous particles. Herein we chose native fibrous palygorskite particles and grafted fibrous palygorskite particles as Pickering emulsifiers, respectively. Moreover, pH-sensitive composite microspheres were successfully prepared from a novel Pickering emulsion polymerization using palygorskite particles as a stabilizer. Then, the application of these pH-sensitive composite microspheres as drug carriers was investigated. Palygorskite based Pickering emulsions have also been applied for lipase immobilization. The main content and results are summarized as follows:

1. The effects of different factors, such as particles concentrations, the pH values, and salt concentrations, on the properties of palygorskite particles-stabilized O/W emulsion were investigated. It was found that the emulsion droplet diameter decreased with increased particle concentration. A three dimensional network formed by the particles in the continuous phase plays an important role in improving emulsion stability. The palygorskite-based Pickering emulsions can undergo several cycles of in-situ emulsification-demulsification by altering the pH of continuous phase. Even at high NaCl concentrations, the as-prepared emulsions still have a satisfactory stability and have been stable for over 3 months in storage.
2. Brushes of poly(N,N-diethylaminoethyl methacrylate) (PDEAEMA) were successfully grafted from the surface of palygorskite via single-electron transfer mediated living radical polymerization (SET-LRP). The effects of different conditions, such as particles concentrations, the pH value, and oil-to-water ratio, on the properties of palygorskite-PDEAEMA particle-stabilized W/O emulsion were investigated. The morphology of emulsions was observed using scanning electron microscope (SEM). It was found that the palygorskite-PDEAEMA particles, as a form of small, irregular bundles and nano-rod aggregates, were adsorbed at the oil-water interface. The type of emulsions can be controlled by changing the pH. Moreover, W/O emulsion—de-emulsion—O/W emulsion transitions can be realized simply by adding HCl/NaOH to tuning the pH, which can last at least 7 successive cycles. Therefore, palygorskite-PDEAEMA particles can be used as an excellent recyclable pH-sensitive Pickering emulsifier.
3. pH-sensitive composite microspheres were successfully prepared from a novel Pickering emulsion polymerization using palygorskite particles as a stabilizer. The release profile of the model drug (Rhodamine B) from composite microspheres was studied in the solutions at different pHs. Release mechanism was analyzed using the dynamic model. The pH-sensitive composite microspheres with average size of about 50 μm were obtained. The ektexine of composite microspheres consists of two layers: a palygorskite particle layer and a polymer layer. The as-synthesized composite microspheres exhibit good pH-responsive property. The release rates of Rhodamine B are greatly dependent on pH value. In addition, Higuchi's model is fit for Rhodamine B released from composite microspheres at pH 5, 7.4 and 10, which appeared to be diffusion controlled.
4. With the palygorskite based Pickering emulsion as a template, organic/inorganic composite microspheres were prepared by emulsion polymerization and then used as a support for the immobilization of lipase. The composition and morphology of the composite microspheres were characterized with FTIR, TGA, and SEM. The reaction conditions, the stability of immobilized lipase and its re-use were investigated. Then the lipase was applied as a co-emulsifier with the palygorskite for the preparation of Pickering emulsion. The stability of the emulsion formed, the mechanism of the synergistic stabilization for the Pickering emulsion and its biological catalytic performance were explored. Resolution of racemic 2- methyl -1- butanol catalyzed by the lipase was investigated. Comparison of the activity of the free lipase, of the immobilized lipase with composite microspheres, and of Pickering emulsion immobilized lipase was performed.

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LAYERED DOUBLE HYDROXIDE MATERIALS COATED CARBON ELECTRODE: NEW CHALLENGE TO FUTURE ELECTROCHEMICAL POWER DEVICES

Mohamed Amine Djebbi (1,2)*, Mohamed Braiek (1), Philippe Namour (1,3), Abdesslem Ben Haj Amara (2), Nicole Jaffrezic-Renault (1)

(1) Institut des Sciences Analytiques UMR CNRS 5280, Université Claude Bernard-Lyon 1, 5 rue de la Doua, 69100 Villeurbanne, France, (2) Laboratoire de Physique des Matériaux Lamellaires et Nano-Matériaux Hybrides, Faculté des Sciences de Bizerte, Université de Carthage, 7021 Bizerte, Tunisia, (3) Irstea, 5 rue de la Doua, 69100, Villeurbanne, France

Layered double hydroxides (LDH) have been widely used in the past years due to their unique physicochemical properties and promising applications in electroanalytical chemistry. The present paper is going to focus exclusively on magnesium-aluminum and zinc-aluminum layered double hydroxides (MgAl & ZnAl LDHs) in order to investigate the property and structure of active cation sites located within the layer structure. The MgAl and ZnAl LDH nanosheets were prepared by the constant pH co-precipitation method and uniformly supported on carbon-based electrode materials to fabricate an LDH electrode. Characterization by powder x-ray diffraction, Fourier transform infrared spectroscopy, scanning electron microscopy and transmission electron microscopy revealed the LDH form and well-crystallized materials. Wetting surface properties (hydrophilicity and hydrophobicity) of both prepared LDHs were recorded by contact angle measurement show hydrophilic character and basic property. The electrochemical performance of these hybrid materials was investigated by mainly cyclic voltammetry, electrochemical impedance spectroscopy and chronoamperometry techniques to identify the oxidation/reduction processes at the electrode/electrolyte interface and the effect of the divalent metal cations in total reactivity. The hierarchy of the modified electrode proves that the electronic conductivity of the bulk material is considerably dependent on the divalent cation and affects the limiting parameter of the overall redox process. However, MgAl LDH shows better performance than ZnAl LDH, due to the presence of magnesium cations in the layers. Following the structural, morphological and electrochemical behavior studies of both synthesized LDHs, the prepared LDH modified electrodes were tested through microbial fuel cell configuration, revealing a remarkable, potential new pathway for high-performance and cost-effective electrode use in electrochemical power devices.

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CYCLIC CHANGES IN CLAY MINERALS ASSEMBLAGES IN PALEOGENE POST RIFT CONTINENTAL SEDIMENTS OF THE SALTA BASIN (NW ARGENTINA)

Margarita Do Campo (1), Blanca Bauluz (2), Cecilia Del Papa (3), Timothy White (4), Alfonso Yuste (2), Maria Jose Mayayo (2)

(1) Universidad de Buenos Aires and INGEIS (CONICET - UBA), (1428) Buenos Aires, Argentina, (2) IUCA-Departamento de Ciencias de la Tierra, Universidad de Zaragoza, Spain, (3) CICTERRA, CONICET-Universidad Nacional de Córdoba, Córdoba, Argentina, (4) Earth and Environmental Systems Institute, The Pennsylvania State University, USA

The Salta Group was deposited in an intracontinental rift, the Salta Basin that evolved from the lower Cretaceous to the middle Palaeogene, and is subdivided intothe Pirgua, the Balbuena and the Santa Barbara Subgroups. The Maíz Gordo Formation (MG Fm) that is 200 meters thickis the middle unit of the Santa Bárbara Subgroup, corresponding to late post-rift sedimentation. These deposits mainly consist of sandstones, mudstones and limestones, plus several paleosol levels. We studiedthe mineralogy of fine-grained levels of the MG Fmby XRD and SEM in order to examine the connection between vertical changes in clay mineralogy in alluvial sediments and paleosol levels and global paleoclimatic changes registered during the Paleogene. The samples were collected in two stratigraphic sections, the Tin Tinand Obeliscosites, located in the west of the Salta Basin.

XRD revealed marked vertical changes in clay mineralogy and kaolinite/muscovite (Kln/Ms)ratios that according to [1] can be used as a palaeoclimatic indicator. In the basal level of the MGFm at the Tin Tin section illite-mica is very abundant whereas smectite relative abundance is around 25%, and kaolinite is absent (Kln/Ms=0). The next fine-grained level, 25 meters up section, depicts a sharp increase in kaolinite content together with a strong decrease in smectite and illite-mica abundances (Kln/Ms=0.68). Upwards kaolinite abundances gradually increase at the expense of illite-mica for the next 30 meters, except for slight fluctuations, reaching a maximum Kln/Ms ratio of 1.3. Then, kaolinite contents decrease sharply and Kln/Ms ratio decrease to 0.8 in few (five) meters. Towards the top of the unit another three cycles of increase/decrease in kaolinite relative abundances occur in shorter intervals, depicting, respectively, maximum Kln/Ms ratios of 2.7, 5.2 and 3.9. On the other hand, in fine-grained levels of the MG Fmat the Tin Tin site, smectite contents remain low, except for one bed with a peak value of 38%. At the Obelisco site the clay assemblages of the MG Fmshow a similar trend asat Tin Tin, with successive cycles of increase/decrease in kaolinite contents. Likewise, smectite contents remain less than 10% with the exception of a level in which smectite has a peak value of 29%. SEM showedeuhedral kaolinite plates forming well-developed booklets and smectite packets. Both clays grew from altered K-feldspar fragments indicating their authigenic origin.

For the paleosol levels occurring in the upper 15 meters of the studied sections organic matter carbon isotope data that records three negative carbon isotope excursions (CIE) were recently obtained [2], one of them was correlated bythese authors with the Paleocene to early Eocene Thermal Maximum. It is remarkable that the three CIEs match very well with the three levels depicting the highest Kln/Ms ratios mentioned above. Thecyclic increase in kaolinite abundance and Kln/Ms ratio indicate several climatic changes implying progressively higher hydrolyzing conditions. In fact, the increase in kaolinite relative abundances in the upper part of the profiles is in agreement with the rise in paleoprecipitacion and paleotemperature indicated by different proxies [2]. Thus thecyclicchanges in kaolinite relative abundances in the study sections of the MG Fmconstitute strong evidence of the occurrence of several short-lived hyperthermals during Paleocene-early Eocene time in the Southern Hemisphere coincident with well-establishedwarm episodes in the Northern Hemisphere [3].

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POST-DEPOSITIONAL EVOLUTION OF THE ORDOVICIAN SUCCESSIONS OF NORTHWESTERN ARGENTINA

Margarita Do Campo (1)*, Fernando Nieto (2)

(1) INGEIS (CONICET - Universidad de Buenos Aires) y FCEyN - U.B.A, Buenos Aires, 1428, Argentina,
(2) Departamento de Mineralogía y Petrología and I.A.C.T., Universidad de Granada, Granada, España

The thermal post-depositional evolution of metapelitic and metavolcanic rocks of the upper Cambrian-Ordovician succession of the Central Andes of northwestern Argentina was estimated through clay mineral analysis, Kübler index, SEM-EDS study of selected samples and chlorite geothermometry [1]. The study area comprise five representative regions in Cordillera Oriental and Puna, that are from east to west: Sierra de Santa Victoria (Nazareno and Santa Victoria river areas), Cordón de los Siete Hermanos (Yavi), Sierra de Cochinoca-Escaya and Sierra de Rinconada. Based on KI values and occurrence (or absence) of slaty cleavage the studied rocks can be divided in three groups: 1) Almost all the mudstones from Sierra de Santa Victoria show KI values in the range of deep diagenesis-low anchizone and a rough bedding-parallel microfabric (S_0). The clay mineral assemblages identified in these metapelites illite-muscovite + chlorite ± kaolinite, or illite-muscovite ± Chl/Sm ± I/Sm are in agreement with the diagenetic-anchizonal grade indicated by KI values. 2) To the west, slates from Yavi depict KI values in the range of high anchizone-epizone (0.30-$0.36\Delta°2\theta$) and rough anastomosing spaced cleavage (S_1) parallel to the sedimentary layering (S_0), or a crenulation cleavage (S_1) oblique to S_0. The clay mineral associations identified in these slates (illite-muscovite ± kaolinite ± chlorite ± smectite) do not represent equilibrium assemblages, neither are they consistent with the KI values indicating high anchizone to epizone. Consequently smectite and kaolinite probably represent retrograde-diagenetic products [2]. 3) Finally, slates and metavolcanic rocks from Puna show KI values from high anchizone to epizone (0.23-$0.35\Delta°2\theta$). In these slates a discontinuous crenulation cleavage (S_1) oblique to S_0 or an S_1 cleavage, mainly sub parallel to the sedimentary layering (S_0) is observed. Few samples of this group show clay-mineral assemblages comprising illite-muscovite and chlorite, in coherence with the anchizonal/epizonal grade indicated by KI values. On the contrary, most of the samples consist of complex clay-minerals assemblages comprising, in addition to illite-muscovite and rarely chlorite, diverse phyllosilicates like kaolinite, smectite, and various mixed-layers (Chl/Sm, Chl/Vrm and Chl/Mi) that are not stable in the anchizone and neither in the epizone. Consequently, these phases could not represent prograde metamorphic phases in these rocks. Furthermore, metaandesites from Sierra de Cochinoca-Escaya present strong evidences of hydrothermal alteration at optical microscope and SEM, such as phenocrysts of albite depicting dissolution voids, embayments filled with mixed-layered phyllosilicates, replacement by fine-grained white mica and sulfates of the alunite-jarosite family occurring in close association with goethite. Moreover, mixed-layered phyllosilicates form veinlets, sometimes associated with scarce anhedral quartz. Geothermometric calculations performed for the three chlorite-bearing samples yield temperatures from 124 to 199 °C for a mudstone from Nazareno (n= 6, average 138 °C) and values in the range from 179 to 339 °C (n= 18, average 273 °C) for Cordón de los Siete Hermanos . On the other hand, a wide range of temperatures from 151 to 322 °C (n= 28, average 231 °C) were obtained for chlorites from a slate of northern Puna. However, geothermometric calculations could not be accomplished for a significant number of chlorite analyses enclosed in the $\delta < 0.1$ p.f.u./Si < 2.5 p.f.u. window, that are outside the T range of applicability of Bourdelle's thermometer, and thus probably formed at T >350 °C. The paleotemperatures obtained with the chlorite geothermometer, in coincidence with KI values, showed an E-W trend from diagenesis/low anchizone in the eastern localities, to high anchizone/epizone in the Puna, with intermediate values in locality of Yavi. The common occurrence of kaolinite in the slates and the metavolcanic rocks of Sierra de Cochinoca-Escaya, coupled with the substitution of chlorite by interstratified lower-temperature phases (smectite, kaolinite, as well as interstratified Chl/Sm and Chl/Vrm) in most of these rocks and the occurrence of jarosite in a metadacite, indicate hydrothermal fluids with high H^+/cations ratios, producing acid type alteration, at temperatures between 100 and ~300 °C. The hydrothermal alteration should have been subsequent to the maximum burial and the attainment of epizonal metamorphism, and was very probably related with the posthumous activity of the Ordovician volcanic arc. This is, up to our knowledge, the first report of an extensive hydrothermal activity affecting not only the volcanic rocks but also the Lower Ordovician sediments of northern Puna.

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CATION EXCHANGE PROCESSES OBSERVED IN THE FEBEX FIELD EXPERIMENT

Reiner Dohrmann (1,2)*, Stephan Kaufhold (1)

(1) LBEG, Hannover, Germany, (2) BGR, Hannover, Germany

Bentonites are candidate materials for the encapsulation of radioactive waste in barrier systems in crystalline rocks. Their long-term behaviour of up to 1 million years is important to understand. Alteration of bentonites can be studied in natural analogues (illitization, alkaline plume) and in laboratory experiments at numerous conditions. Few natural analogues exist and laboratory experiments were usually performed at unrealistic conditions such as high solution/solid ratios and dynamic (batch) experiments. Important knowledge about bentonite performance is gained from large-scale experiments in different underground rock laboratories with different type of groundwater.

The “full-scale engineered buffer experiment” (FEBEX) experiment was installed in Grimsel, Switzerland, with a low salinity groundwater: Na-Ca-$HC0_3$-F type with 0.7 mM Na^+ and 0.14 mM Ca^{2+}. Other cations are present in traces: 2.1 µM Mg^{2+}, 2.3 µM Sr^{2+}, and 3.6 µM K^+; the pH in 9.6 (Degueldre, 1994, table 3 for GTS). The FEBEX experiment was heated up to 100 °C for 18 years of operation.

The Prototype Repository (PR) experiment (Äspö, Sweden) on the other hand reacted with a Na-Ca-Cl dominated groundwater (each ~ 2500 mg/L Na^+ and Ca^{2+}, ~ 8500 mg/L Cl^-, and ~ 500 mg/L SO_4^{2-}) with minor contents of Mg^{2+}, Br^-, and K^+ (all <100 mg/L). PR was heated to 65-85 °C (section 2) for 8 years.

Both experiments have been (partly) terminated recently. One of the fastest reactions that can be measured in order to study alteration of the buffer material is cation exchange. Cation exchange is important because it determines physical and chemical properties of bentonites [1].

The PR data were published before [2]. In the following this data is compared with the recently obtained FEBEX results. In the FEBEX experiment, the distribution of exchangeable cations was investigated in different sections. All different sections showed comparable trends.

- Exchangeable Mg^{2+} shows a sharp increase towards the heater. Near the heater exchangeable Mg^{2+} was higher compared to the reference values. This differs from the PR experiment where exchangeable Mg^{2+} values were always lower compared to the reference materials with a small increase at the direct contact to the heater [2].
- Exchangeable Na^+ values were more or less unchanged over a large distance from the cold side to the hot side (heater). Closer to the heater exchangeable Na^+ values decreased in both the FEBEX and in the PR experiment.
- Exchangeable Ca^{2+} values were lower at the cold (host rock) side in FEBEX and increased (linear trend) to the hot side whereas in the PR experiment (nearly) all values were higher than the reference values and the increase towards the heater was sharp.

The observed differences can possibly be explained by the different types of water, and secondly the maximum temperature which was lower for the PR experiment that for the FEBEX experiment.

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POTENTIAL RECYCLING OF ARGENTINIAN BORON SLUDGES IN CERAMIC TILES

Michele Dondi (1), Chiara Zanelli (1), Claudio Iglesias (2), Eduardo Domínguez (3)*

(1) CNR-ISTEC, Istituto di Scienza e Tecnologia dei Materiali Ceramici, Faenza, 48018, Italy, (2) Piedra Grande SA, Trelew, Chubut, 9100, Argentina, (3) Departamento de Geología, Universidad Nacional del Sur, Bahía Blanca, 8000, Argentina
*edomin@criba.edu.ar

Residues from beneficiation of borate ores have been extensively investigated in the last decade. The recycling of boron-containing wastes has been assessed in clay bricks, ceramic tiles, as well as ceramic frits and glazes. All these studies agree about the technological feasibility of the utilization of borate residues, even though with different amounts depending on the end-use.

Waste ceramic usage has been assessed in clay bricks (up to 30%wt), ceramic tiles (up to 8%wt), as well as in ceramic frits and glazes (up to 5%wt). Clay bricks can tolerate an amount of B_2O_3 widely spanning from around 1% to 5-6% that falls to ≤1% in the case of glazes.

This study is aimed at appraising the re-use of boron sludge, coming from the Argentinian production factories, in porcelain stoneware tiles, addressing key-points in processing and product performance. The rationale consisted in adding different waste amounts (2-5-10%wt), then testing their technological behavior at the laboratory scale and finally characterizing semi-finished and finished products in order to assess technological feasibility. The batches were designed by two different strategies: adding boron waste in replacement of ball clay in an “Argentinian-style formulation” and in replacement of sodic feldspar in an “Italian-style body”.

Argentina has an important boron production with a yearly output of 170,000 tons of borax and boric acid compounds. The waste sludge comes from the Tincalayu mine (67 ° 03’ W and 25 ° 16’ S) located at the western end of Salar del Hombre Muerto in the Salta province, Argentina.

The waste was taken directly during a routine industrial processing day; it came from the boric acid obtained after a hot water leaching for the borax solubilization. The waste sludge is characterized by a typical clay composition (65% of particle size <2 micron and 35% of silt), and composed of quartz (~20%wt), plagioclase (~50%wt), illite (~20%wt) and borate (~10%wt).

The percentage of iron oxide higher (~3%) and the relatively low loss in ignition (~11%) are the further features peculiar of the boron sludge. While the amount of iron is a limitation for its use in the white firing bodies, the latter is undoubtedly an advantage for its utilization in vitrification tiles. Boron sludge is characterized by a very strong fusibility, witnessed by a melting temperature close to 1100 °C, value almost 300 °C lower than the strongest ceramic flux currently used (i.e. nepheline syenite) and nearly 600 °C below than typical fluxes used in porcelain stoneware tiles.

Recycling the boron sludge in ceramic tile-making is possible only with a careful strategy of replacement (feldspar or clay) and controlled addition is done in the industrial practice. During some steps of the conventional technological process such as milling and shaping, a slight reduction of the powder moisture, a fluctuation of expansion after pressing (i.e. 0.3-0.6 cm/m) and improved compaction (bulk density of dry bodies increased for addition over 2% of waste) were detected. Moreover, the waste addition implies an increase of reactivity: the firing temperature can be reduced according to the amount of waste added. The introduction of the borate waste into porcelain stoneware bodies changes the technological behavior (during milling, pressing and firing) as well as the phase composition and technical properties of finished products. The recommended amount of waste varies from 2% to 5% wt depending on the body type and strategy of replacement. In addition, the waste ensures an increase of reactivity: the firing temperature can be reduced according to the amount of waste added.

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ELECTRIC FIELD MANIPULATION OF CLAY PARTICLES AND STRUCTURES AT LIQUID-LIQUID INTERFACES

Paul Dommersnes (1)*, Zbigniew Rozynek (1,2), Alexander Mikkelsen (1), Jon otto fossum (1)

(1) Department of Physics, Norwegian University of Science and Technology, Hoegskoleringen 5, N-7491 Trondheim, Norway (2) Adam Mickiewicz University, Faculty of Physics, Poznań, Poland

Colloidal and granular particles tend to adsorb strongly at liquid interfaces due to capillary interactions. Adding particles to an emulsion therefor generally results in particle covered drops, and stabilization of the emulsion [1]. Such particle coated drops have also be used to fabricate semi-permeable capsules [2]. Clay particles of various sizes are used in this context, and efficiently coat both liquid drops and bubbles [3,4,5]. Our own studies in this area show how electric field driven hydrodynamic circulation flows can be used to structure and dynamically control particle assemblies at drop surfaces [6,7,8]. This includes convective assembly of jammed colloidal 'ribbons', electro-rheological colloidal chains confined to a two-dimensional surface and spinning colloidal domains on that surface, and the dynamical 'pupil'-like openings in colloidal clays shells [7]. We also show that the synergetic action of electro-hydrodynamic flow and electro-coalescence can be used to build Janus and patchy colloidal shells [8].

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BRICK CLAYS: FROM GENESIS TO TECHNOLOGICAL PROPERTIES

Michele Dondi (1)*, Chiara Zanelli (1), Isabel Gonzalez (2), Vitor Lisboa (3)

(1) CNR-ISTEC, Institute of Science and Technology for Ceramic Materials, Faenza, Italy, (2) Departamento Cristalografía, Mineralogía y Química Agrícola, University of Sevilla, Spain, (3) LNEG, Laboratório Nacional de Energia e Geologia, Unidade de Recursos Minerais e Geofísica, Lisboa, Portugal

Clay bricks - the most ancient ceramic building materials - are widespread and apparently made up with whatever kind of clay raw materials. In reality, both technological behaviour during processing and technical performance of finished products strongly depend on clay features, particularly mineralogical composition and particle size distribution.

This contribution wants to draw attention to the *knowledge chain* existing along brick manufacturing:

- genesis of clay deposits (sedimentary environments and post-depositional events);
- clay composition (chemical and mineralogical composition, particle size distribution);
- clay exploitation (size and shape of deposits, compositional uniformity, geotechnical issues);
- technological behaviour of clays (plasticity, drying sensitivity, firing transformations);
- technical properties of finished bricks (porosity, mechanical strength, frost resistance, etc).

The main goal is to connect geological features (clay genesis and composition) to industrial manufacturing (clay exploitation and technological properties) to product performance and value (brick technical properties and possible defects). This knowledge chain can be most helpful on one side for clay exploration and drawing maps of "mineral deposits of public importance" [1]; on the other side, to improve resource efficiency and brick quality from the industrial viewpoint [2].

Examples of brick clays with different genesis are shortly overviewed: fluvial, lacustrine, fluvio-glacial, deltaic, and marine (platform, slope, submarine fan and deep-sea basin) along with shales and tectonic mélanges. Compositional features are related to geological issues and technological properties in order to address overall considerations for brick characteristics and performances.

The most important deposits of brick clays in Spain are in Neogene basins(marine, continental and lacustrine) with unlimited resources. The lithology consists of clays and marls composed of carbonates, phyllosilicates and quartz (gypsum, feldspars, iron oxides and carbonate nodules). The dominant phyllosilicates are illite and smectite (kaolinite and chlorite in minor proportions). The main ceramic industries are in Toledo and Bailén.

Fluvial and fluvio-deltaic sediments deposited in meandering systems are the major source of brick clays in Portugal. The clay bodies' morphology is basically lenticular with variable thickness (usually≤10m) and lateral extent (few to 100's m). The age of the economic deposits range from Upper Jurassic to Plio-Pleistoceneand the most important are dated from Tithonian, Lower Cretaceous and Plio-Pleistocene. Illite, kaolinite and quartz (order of these minerals' importance varies)constitute the most frequent mineral association; smectites, interstratified clay minerals and chlorites are frequently present; Fe oxi/hydroxides and feldspars occur as accessory minerals. Compositional trends are noticeable, such as: mineralogical zonation in Plio-Pleistocene clays, which tend to be more illite-rich in the country's northern area (north of river Mondego) and preferably kaolinite-rich in the south; Upper Jurassic and Lower Cretaceous clays tend to be kaolinite-rich. Almost all these clays are poor or devoid of carbonates.

Fluvio-glacial sandy-silty deposits of Upper Pleistocene, deeply weathered to relatively thin (<5 m) but laterally extended paleosols, are characteristic brick clays in northern Italy. They are peculiar because podzolisation left little or no carbonates and a smectite-rich composition, which brings about a good plasticity despite the coarse grain size. The resulting bricks are bright red in color and with a coarse pore size distribution usually ensuring excellent frost resistance.

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DIRECT MEASUREMENT OF NANO MECHANICAL PROPERTIES OF CLAY MINERALSWITH ATOMIC FORCE MICROSCOPY

Maoz Dor (1,2)*, Yael Mishael (2), Simon Emmanuel (1)

(1) Dept. Soil and Water Sci., Faculty of Agri., Food and Environ., The Hebrew University of Jerusalem, Rehovot, Israel, (2) Institute of Earth Sciences, the Hebrew University of Jerusalem, Jerusalem, Israel
*maoz.dor@mail.huji.ac.il

The elastic modulus of clay-minerals strongly affect the mechanical properties of natural materials, such as shales and soils. However, due to their tiny size, the direct measurement of the response of clay-mineralsto mechanical stress remains extremely challenging. In this study, we used anatomic force microscopy (AFM) technique to map the mechanical properties of clay-minerals at the nanometer scale. Tactoids of kaolinite and illite were measured in air, and the measured reduced Young's moduli (in the range 18-22 GPa) are in agreement with the calculated values reported in the literature. Clay-minerals within shales were found to have a stiffness in the range 18-40 GPa, which was stiffer than organic matter but softer than calcite grains. In addition to the analysis in air, we also carried out experiments in which clay-minerals were imaged with AFM in aqueous solutions with different ionic strengths. We found that the modulus of kaolinite dropped from a modal value of 20 GPa to 7.1 GPa when the fluid environment was switched from deionized water to a NaCl solution (100 mM). An increase in the ionic strength should decrease the electric double layer, reducing the Debye length, which may contribute to an alignment of the clay platelets into a more organized and compact structure. Such a structure may also clarify the lower modulus measured at high ionic strength since the resistance, of a card-like structure (face to edge) vs. an aligned structure, will be higher upon applying mechanical stress.

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SYNTHETIC SMECTITE FLUOROHECTORITE AS AN INOVATIVE DRUG CARRIER: CHARACTERIZATION AND CONTROLLED RELEASE STUDY OF CIRPOFLOXACIN

Éverton C. Dos Santos* (1,2), Zbigniew Rozynek (1,3), Elizabeth L. Hansen (1), Leander Michels (1), Alexander Mikkelsen (1,3), Tomás S. Plivelic (4), Heloisa N. Bordallo (2,5), Jon Otto Fossum (1,6)

(1) Department of Physics, Norwegian University of Science and Technology (NTNU), Trondheim, Norway, (2) Niels Bohr Institute (NBI), University of Copenhagen, Copenhagen, Denmark, (3) Faculty of Physics, Adam Mickiewicz University (AMU), Poznań, Poland, (4) MAX IV Laboratory, Lund University, Lund, Sweden, (5) European Spallation Source ERIC, Lund, Sweden, (6) Institute Pierre-Gilles de Gennes pour la microfluidique, Paris, France
*everton.santos@ntnu.no

Natural clay minerals, including laponite, montmorillonite and kaolinite, have been proven to be efficient drug carriers that provide high and long lasting drug concentrations owing to their adsorption capacity and ion exchange property [1,2]. Synthetic clays, however, are advantageous over the natural clay minerals in terms of purity of composition and controllable cation exchange, factors that contribute to improve reproducibility of the host system [3].

Here we demonstrated that the broad spectrum antibiotic agent Ciprofloxacin (CIPRO) can be intercalated into the interlayers of the synthetic clay mineral, fluorohectorite (Fh), likely replacing the native Li-cations. Via X-ray powder diffraction and UV-VIS spectroscopy we show that, under acid conditions, the degree of CIPRO incorporation in the synthetic clay fluorohectorite is at least 25% higher than for other systems reported in the literature [5].

Release experiments conducted in synthetic gastric acid, at different temperatures, shows a gradual and temperature dependent release, which increases on heating. By using the Kosmeyer Peppas model and the Arrhenius equation, we show that the release of CIPRO from the clay particles is anomalous and diffusion-controlled, being mostly thermally activated, in particular at body temperature [dos Santos E. C., Rozynek Z., Hansen E. L., Michels L., Mikkelsen A., Plivelic T. S., Bordallo H. N., Fossum J. O., Ciprofloxacin intercalated in fluorohectorite clay: High adsorption and controlled release rate, submitted.].

These results bring new advances to drug carrier encapsulation by adding the synthetic smectite Fluorohectorite as another promising material for such applications.

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APPLICATION OF POWDERED WASTE BUILDING MATERIALS IN SORPTION TECHNOLOGIES

Barbora Dousova (1)*, David Kolousek (1), Martin Keppert (2), Pavel reiterman (2), Miloslav Lhotka (1), Vladimir Machovic (1), Eliska Duchkova (1)

(1) University of Chemistry and Technology Prague, Technicka 5, 166 28 Prague 6, Czech Republic, (2) Faculty of Civil Engineering, Czech Technical University in Prague, Thakurova 7, 166 29 Prague 6, Czech Republic
*Barbora.Dousova@vscht.cz

Waste building materials have got into increased professional concern due to availability, low cost and appropriate properties. Analogously to aluminosilicates, they represent chemically stable and environmentally friendly silicate materials, which mean new potential in building and decontamination technologies [1].

Two types of powdered wastes originating in building materials production (waste brick dust (WBD) from the production of ceramic blocks and concrete slurry (CS) from prestressed poles production) were testified as possible adsorbents of ecologically risk (highly toxic or radioactive) cations (Cd, Pb, Zn, Cs) and anions (As, Cr, U) from contaminated waters. Favourable adsorption properties result from a proper chemical composition (Al, Si, Fe content), surface hydratation of aluminosilicate structure and/or a high specific surface area (S_{BET}) (Tab.1).

Table 1. Charcterization of waste building materials

sample	chemical composition (% wt)						mineralogical composition	S_{BET} (m^2/g)
	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO		
WBD	49.5	19.7	6.1	0.8	13.5	4.8	illite, feldspar, quartz, micas, hematite	3.3
CS	32.3	6.6	1.3	<0.1	46.9	1.8	muscovite, portlandite,	30.9-38.2
CS_{Fe} *)	26.6	4.3	29.8	0.4	18.7	2.1	calcite, quartz, (hornblende)	

*) surface modification with Fe^{2+}

Waste brick dust (WBD): The adsorption parameters calculated according to the Langmuir model for cations (Cd^{2+}, Pb^{2+}, Cs^{+}) and anions (As^{V}, As^{III}, Cr^{VI}, U^{VI}) indicated a wide sorption selectivity of WBD for both cationic and anionic contaminants. The adsorption stability and selectivity declined in the order: $Cd^{2+} \geq Pb^{2+} >> Cs^{+}$ for cations, and in the order: $U^{VI} >> As^{V} > As^{III} >> Cr^{VI}$ for anions at the adsorption efficiency of < 30% for As^{III}, Cr^{VI} and Cr^{+}, respectively, and > 90% for Pb^{2+}, Cd^{2+}, As^{V} and U^{VI}, respectively [2]. The WBD proved to be a selective sorbent of heavy metals (Pb^{2+}/Cd^{2+}) and U^{VI} as $[(UO_2)_n(OH)_{2n-1}]^{+}$ at a high adsorption efficiency and low sorbent consumption (<70 - 100 g per 1 g of contaminant), and a very good sorbent of As^{V} as AsO_4^{3-} with more than four times greater sorbent consumption. The adsorption of Cs^{+} and Cr^{VI} as CrO_4^{2-} on WBD was totally ineffective.

Concrete slurry (CS) was used in original and Fe-modified forms (the surface modification of aluminosilicates with $Fe^{II/III}$ was developed for the selective adsorption of anions from waters [3]). The adsorption of cations (Pb^{2+}, Zn^{2+}, Cd^{2+}) and anions (As^{V}, As^{III}, Cr^{VI}) on CS ran in the same manner as on WBD. The adsorption stability according to the Langmuir model declined in the order: $Cd^{2+} > As^{V} > Pb^{2+} \approx Zn^{2+} \geq As^{III} > Cr^{VI}$, at the maximum adsorption efficiency of >95% for As^{V}, 90% for As^{III}, 40-60% for Cr^{VI} and almost 100% for $Pb^{2+}/Zn^{2+}/Cd^{2+}$. The Fe-modification of CS raised up its adsorption efficiency to anions ($As^{III/V}$, Cr^{VI}) about 15. - 20% at less than a half sorbent consumption (80 - 200 g per 1 g of contaminant). The cations (Pb^{2+}, Zn^{2+}, Cd^{2+}) were adsorbed quantitatively on the initial CS at the sorbent consumption of 10 - 120 g per 1 g of contaminant. Their adsorption on CS_{Fe} did not exceed 15%. The CS/CS_{Fe} were found as promising sorbents of both heavy metals and toxic anions under appropriate technological conditions.

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HALLOYSITE NANOTUBES NANOCONTAINERS FOR SALICYLIC ACID: CHEMICO-PHYSICAL CHARACTERIZATION AND ANTIBACTERIAL ACTIVITY

Alessio Spepi (1), Lisa Ghezzi (2), Celia Duce (1)*, Alfonso Pedone (3), Davide Presti (3), José-Gonzalez Rivera (1), Caterina Cristiani (4), Monica Agnolucci (4), Manuela Giovannetti (4), Maria Rosaria Tiné (1)

(1) Chemistry and Industrial Chemistry Department, University of Pisa, I-56124 Pisa, Italy, (2) Department of Heart's Science, University of Pisa, I-56126 Pisa, Italy, (3) Department of Chemical and Geological Sciences, University of Modena and Reggio-Emilia, I-41125 Modena, Italy, (4) Department of Agriculture, Food and Environment, University Pisa, I-56124 Italy

The empty lumen of halloysite nanotubes (HNTs) has been used in literature as nanocontainer for a wide range of active chemical agents from antioxidants to antibiotics, anticancer and anti-inflammatory drugs, from proteins to enzymes [1,2]. Differently loaded HNTs have been then used in composites with smart functions and properties [3].

In particular, we are interested in HNTs loaded with antibacterial agents with possible applications as additives in packaging materials for food industry.

We set up a procedure for the loading of HNTs with salycilic acid (SA). SA is a natural antiseptic and bactericide used in pharmaceutical formulations and as an additive for food and cosmetics and it is used to model natural organic matter (NOM) in both experimental and theoretical studies of NOM adsorption on different kinds of mineral surfaces.

We characterized the HNTs empty and loaded with SA by a multi analytical approach including TG-FTIR, FTIR SEM, STEM and nitrogen adsorption/desorption isotherms measurements. Pristine HNTS were studied together with HNTS with enlarged internal lumen due to acidic etching. We obtained a maximum loading of 10% by using HNTs pretreated with H_2SO_4 2 M at 25 °C for 48 h. To improve the current knowledge of SA-clay interactions of interest for environmental and earth sciences, we deeply investigated the interaction of SA-HNTs at a molecular level by combining ATR-FTIR measurements and periodic density functional theory (DFT) calculations [4].

Preliminary results on the kinetics of the release of SA incorporated in the HNTs and on the effect of SA loaded HNTs on growth and metabolism of *Pseudomonas fluorescens* by using microbiological techniques and isothermal microcalorimetry (IMC) will be also presented. *P. fluorescens* was selected as food contaminating model microbe. IMC is a very sensitive technique which provides a real-time measurement of heat production related to the overall metabolism. In this study IMC was used to determine thermogenic growth curves *of P. fluorescens*, and to investigate its growth metabolism in the presence of SA loaded HNTs. We compared the thermokinetic parameters and microbial responses in order to assess the antimicrobial effect of the HNTs.

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CLAY MINERALOGY OF GLACIAL TILLS FROM MORASKO METEORITE RESERVE (WESTERN POLAND) - A RECORD OF SMALL METEORITE IMPACT?

Duczmal - Czernikiewicz Agata*, Muszyński Andrzej, Szokaluk Monika, Szczuciński Witold, Jagodziński Robert

Institute of Geology, Adam Mickiewicz University in Poznań, Poznań 61-680, Poland
*duczer@amu.edu.pl

Glacial tills in studied area are subjected to mineralogical researches hardly, by contrast to geomorphological scientific work, due to a meteorite fall, that left signs in the morphology of that region. The Morasko Meteorite Reserve is located in the northern part of Poznań (Western Poland), where meteorite formed several craters and elevations surrounding some of them. There occur glacial tills underlain by older (Mio-Pliocene) clay - silt sediments, known in Polish literature as the Poznań Formation [1,2].

This paper shows present results of mineralogical studies, which aimed to identify the mineralogical composition of sediments. Moreover changes of clay minerals were studied in samples from soil profiles, and from the trench located near the biggest crater (which exceed to 90 m). The studies indicated the mineralogical compositions, as an effect of the normal glacial processes and secondary weathering products rather, then effect of Morasko meteorite fall.

The main components of tills were determined by the use of microscopic and X-ray diffraction studies. Fine fractions of sediments are compose by clays and silts, with addition of sand and gravel fractions. Components in coarse fractions are as follows: quartz, feldspar, amphiboles, biotite and muscovite, as well as pebbles of igneous and methamorphic rocks. Fine fraction are dominated by the phyllosilicates: illite, kaolinite, smectite and smectite illite mixed-layered minerals and vermiculite-type minerals [3,4,5]. Secondary weathering processes resulted in development of modern soil profiles (humus, root fragments) and aluminum silicates of vermiculite - type minerals. Clay intercalations of the older rocks (Poznań Formation clays) into the younger ones, contain components typical for this Formation. Their fine fraction contains illite, kaolinite, smectite or smectite - illite minerals, accompanied by very fine-grained quartz and likely feldspars. The presence of clay intercalations in tills, can be referred to the meteorite fall. Glacial tills in the nearest part of craters are composed of illite, kaolinite, smectite and smectite - illite mixed-layered minerals. The depths of 80-120 cm are set apart from the other depths of profiles because of chlorite instead of smectite or smectite-illite phases content. The change of mineralogy is a possible indication of changes of the chemistry and physical conditions (temperature and/or pressure changes) in the nearest part of the meteorite fall.

The relatively homogeneity of the mineralogy of fine fraction on the top of soil profiles, could be the results of weathering processes. The weathering product of clays and tills seems to be very similar to each other products of weathering of Mio - Pliocene as well as Pleistocene sediments. Thus the present mineralogy of tills fine fraction are depend of both: primary composition of fine fraction, and the minerals formed during development of former and contemporary soils profiles.

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MINERALOGICAL AND MORPHOLOGICAL CHARACTERISTICS OF THE CRITICAL ZONE IN PALEOSOLS FROM MIO-PLIOCENE CLAYS OF POZNAN FORMATION (WESTERN POLAND)

Duczmal - Czernikiewicz Agata

Institute of Geology, Adam Mickiewicz University in Poznań, 61-680 Poznań, Poland
duczer@amu.edu.pl

The mineralogical and chemical composition of sediments results from numerous geological factors, including composition and weathering of the parent rock, supply rate, sorting during transport and deposition, and post-depositional weathering [1,4].

The purpose of the present study is to determine, on the basis of the mineralogical and chemical composition of the clays, paleoenvironmental conditions of the Mio-Pliocene Poznan Formation from deposits near Poznań (Witaszyce, Brzostów, Dymaczewo Stare, and Chodzież). Red and green clays have been studied. Fine fractions of the sediments consist of kaolinite, illite, smectite and mixed layered illite-smectite. In some samples halloysite also occurs and at the top of investigated profiles vermiculite-smectite type minerals were identified by XRD. The detrital and authigenic clay components were identified. Moreover, other secondary minerals (Fe - oxides and oxyhydroxides, gypsum and jarosite) and carbonate concretions were recognized in 3 separate levels, described as a sequence of several paleosols profiles [2,3,5].

The investigation included establishment of the distribution of clays in the Poznan Formation, their interrelationships, and their behaviour during weathering. Other issues dealt with in the present work include the identification of the burrows occurring partly in studied sediments and their meaning for Critical Zone. Based on a comparison of the mineralogical and chemical compositions of surficial deposits, the impact of weathering processes on the composition of the Poznań clays was also investigated.

All mineralogical and morphological features, the macro- and microstructures, biogenic burrows as well as the stratigraphic position of the investigated deposits suggest that the Poznań red clays owe their characteristics to pedogenesis.

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EARTHQUAKE INDUCED ROCK SHEAR THROUGH A DEPOSITION HOLE - LABORATORY TESTS ON BENTONITE BUFFER, DEVELOPMENT OF MATERIAL MODELS AND MODELLING OF THREE SCALE TESTS FOR VALIDATION

Lennart Börgesson (1), Ann Dueck (2)*, Jan Hernelind (3)

(1) Clay Technology AB, IDEON Science Park, SE-223 70 LUND, SWEDEN; (2) Clay Technology AB, IDEON Science Park, SE-223 70 LUND, SWEDEN, (3) 5T Engineering AB, Fornforskargatan 86, SE-723 53 VÄSTERÅS, SWEDEN
*ad@claytech.se

An earthquake induced rock shear through a KBS-3V deposition hole in a repository for spent nuclear fuel is an important scenario for the safety analysis since it may cause substantial damage to the canister hosting the spent fuel. Proper tools to simulate different shear scenarios and investigate the effects on the buffer and the canister are needed. This paper describes the laboratory tests conducted to develop a material model of the buffer to be used in the simulations [2], the material models that these tests have yielded and FEM simulations of three scale tests of a rock shear for comparison between modelled and measured results and validation of the material models and the calculation technique [1].

The laboratory study consisted of swelling pressure tests and tests to determine shear strength and stress-strain properties. The shear strength has been studied by conducting triaxial tests and unconfined compression tests on bentonite with different densities and at different shear rates. Shear rates between 0.1 mm/s and 4 m/s have been used for the latter tests.

The material model is elastic-plastic with a non-linear stress-strain relation. The model depends on the density of the bentonite buffer and is made a function of the strain rate. Three types of bentonites have been tested and the study also considers a reference case with MX-80Ca, i.e. MX-80 ion exchanged to Ca.

Three model shear tests of very high quality simulating a horizontal rock shear through a deposition hole in the centre of a canister with different shear rates were performed 1986. The tests simulated a deposition hole in the scale 1:10 with reference density of the buffer, very stiff confinement simulating the rock, and a solid bar of copper simulating the canister. The tests were very well documented. Shear force, shear rate, total stress in the bentonite, strain in the copper and the movement of the top of the simulated canister were measured continuously during the shear. After finished shear the equipment was dismantled and careful measurements and bentonite sampling were made.

The tests have been modelled with the finite element code Abaqus with the same models and techniques that were used for the full scale cases in the Swedish safety assessment SR-Site. Two element models were used. In one of them the bentonite was divided into three parts with different densities according to the measurements made during dismantling and sampling. In the other one the same density, corresponding to the weighted mean value, was used for all bentonite in the test. The reason for using both these models was to investigate whether the simplification done in SR-Site, where only one density was modelled and thus no consideration was taken to the incomplete homogenisation that remains after water saturation and swelling, would affect the results significantly.

The results show good agreement between modelled and measured results, in spite of the complexity of the models and the difficulties to measure stresses and strains under the very fast tests. In addition there was less than two per cent difference between the results of the simplified model with one density and the model with three densities. The modelling results of both models were thus found to agree well with the measurements, which validates the SR-Site modelling of the rock shear case.

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THE CRITICAL ZONE IN THE HAUT-KATANGA PROVINCE, D.R. CONGO: COMBINING PHYSICO-CHEMICAL, MINERALOGICAL AND MICROMORPHOLOGICAL OBSERVATIONS FROM A 40 M DEEP WEATHERING PROFILE

Mathijs Dumon (1), Els Timmermans (1), Isabel Van Driesche (2), Basile Basirake Mujinya (3), Geert Baert (1,4), Florias Mees (5), Eric Van Ranst (1)

(1) Department for Geology, Ghent University, Ghent, Belgium, (2) Department of Inorganic and Physical Chemistry, Ghent University, Ghent, Belgium, (3) Department of General Agricultural Sciences, University of Lubumbashi, Lubumbashi, D.R. Congo, (4) Department of Applied Biosciences, Ghent University, Ghent, Belgium, (5) Department of Geology and Mineralogy, Royal Museum for Central Africa, Tervuren, Belgium

We present physico-chemical, mineralogical and micromorphological observations for a 40 m deep profile taken beneath a termite mound (Macrotermes falciger) on talc-, chlorite- and mica-bearing parent materials in Lubumbashi (Haut-Katanga Province, D.R. Congo). Talc is a rarely reported constituent for soils, and very little information can be found about its weathering behavior in these environments [1,2,3] (Harris et al., 1984; Pérez Rodríguez et al., 1996; Zelazny et al., 2002). Therefore, this profile presents a unique opportunity to not only assess the influence and depth of termite activity but also to better understand weathering of talc in the Critical Zone.

The profile was described visually allowing for a first rough delineation of units which was used to make an initial sampling and characterisation. Two intervals at different depths were selected for a more detailed and fine-grained analysis (including X-ray diffraction and high-resolution TEM) providing a comparative, detailed view on weathered and relatively unweathered materials.

The soil that constitutes the upper part of the profile is classified as Plinthic Ferric Rhodic Luvisol. It shows micromorphological and other characteristics that are similar to those of Ferralsols, but is enriched in carbonates. Unlike chlorite and mica, talc shows no signs of mixed-layer formation, and HR-TEM imaging revealed that talc found at the top of the profile is nearly identical to talc found at greater depths. Combined micromophological and mineralogical observations indicate termite activity occurs up to a depth of 8 m.

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STUDY OF THE FEASIBILITY OF ALKALI ACTIVATED MATERIALS BASED ON THE COX ARGILLITE, WITH OR WITHOUT THERMAL TREATMENT

Ameni Gharzouni (1), Colin Dupuy (2)*, Isabel Sobrados (3), Nathalie Texier Mandoki (2), Xavier Bourbon (2), Sylvie Rossignol (1)

(1) Laboratoire SPCTS, Limoges, France, (2) Andra, Châtenay-Malabry, France, (3) CSIC, Madrid, Spain

French National Agency for the radioactive wastes (Andra) will excavates millions tons of COx argillite during the digging of the storage facility. Actually, there is no viable solution to revalue the argillite, which is referred as waste. The aim of this study is to use this argillite to elaborate alkali-activated materials. The first step is a thermal treatment of the COx argillite. Two calcination processes, flash and furnace, are used with different temperatures. Then, the COx argillite is activated with sodium and potassium silicate solutions. Then, samples are characterized with several methods (XRD, NMR …). Both calcinations involve structural transformations and then different reactivity. These differences are mainly related to the amorphous rate and the aluminium coordination number. Indeed, raw argillite does not have enough Al^{IV} and calcination is required to obtain sufficiently tetrahedral alumina. It is shown that is possible to elaborate alkali-activated materials with 100% of calcined COx argillite (flash and furnace) and with a mixture of 50% raw argillite and calcined argillite. For these activations, sodium and potassium silicate solutions can be used. Most of the samples present sufficient compressive strength, a structural change of the silicon connectivity and they can resist to water. Future studies will concern optimization of the formulations in the aim to adapt the reactive mixtures for specific uses in the storage facility.

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DISTINCTIVE DIFFUSION REGIMES OF ORGANIC MOLECULES IN CLAYS: (DE)COUPLED MOTION WITH WATER

Eduardo Duque-Redondo*, Hegoi Manzano, Iñigo López-Arbeloa

Molecular Spectroscopy Laboratory, University of the Basque Country UPV/EHU, Apartado 644, Bilbao, Spain

Clays provide a confining medium where the mobility of the species located in their interlaminar spaces is generally lowered. This is due to both geometrical effects and interactions with the confining clay surfaces, especially when they are charged. Swelling clays are considered excellent materials to immobilize mobile contaminants, including toxic hydrophobic organic compounds [1], CO2 [2], radioactive wastes [3], or ions [4], preventing their release into the environment. Clays also provides thermal, chemical and mechanical stability to the guest molecules. In photoactive molecules, such as dyes, may induce to an enhancement of the photophysical properties [5].

In order to understand diffusion mechanism of organic molecules located in the interlaminar spaces of clays, we have employed molecular dynamics simulations (MD). We develop host-guest hybrid materials based on Laponite and saponite to evaluate the effect of charge distribution in the clay structure, since the octahedral layer is charged in the former, whereas in the latter the tetrahedral is the charged one. We considered different organic molecules: polycyclic aromatic hydrocarbons such as benzo (a) pyrene, a common cigarette smoke carcinogen; surfactants with different charges and chain lengths, and dyes often employed in optical devices. We studied the diffusion properties with increasing water content, from 2.68% to 18.02% by mass. As the water content increase, the structure of the water molecules is transformed from a monolayer at low content to a bilayer at higher contents.

Despite the different nature of the retained species, their diffusion coefficients show two clear tendencies: slightly increase when a water monolayer is present and a sharp increase when water bilayer is arrayed. To determine the origin of this behaviour we have studied the motion of the species dissolved in the interlayer spaces. The results show that the motion of different species is coupled at low water concentration, whereas this motion is decoupled at higher water contents, increasing the freedom of the species and enabling higher diffusivity.

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THE EFFICACY OF TWO TYPES OF FILTRATION BED MATERIALS BASED ON MODIFIED CLAY FOR WATER DECONTAMINATION

Esperanza Durán (1)*, Salvador Bueno (2), Beatriz Gámiz (1), M. Carmen Hermosín (1)

(1) Instituto de Recursos Naturales y Agrobiología, Avda. Reina Mercedes nº10, 41012, Seville, Spain,
(2) Centro Tecnológico Innovarcilla, Calle los Alamillos, nº 25, 23710, Bailén, (Jaén), Spain
*esperanza.duran@irnas.csic.es

The presence of pollutants in surface and groundwater has increased due to the anthropogenic activities. Most of the decontamination techniques available are costly and time consuming, hence, to remove toxic compounds from the environments rapidly, efficiently and within reasonable costs is encouraged. The interest in clay minerals has grown as the development of nanoscience and nanotechnology has progressed. Due to their nano-sized layers and their customizable surfaces, they have been proposed as adsorbents to remove pollutants from water [1]. However, the morphological properties of clay need to be optimized to facilitate their industrial application as a component of filters for water decontamination. In this regard, the use of inert binder or support to increase the particle size of powder clay is required. The objective of this work was to prepare two types of filtering bed based on modified clays, obtained from a low value clay material, and compare their behavior to be used for water decontamination.

The adsorbent materials were prepared by the modification of a low value clay (CTI, smectite content, 30%) located in Bailén (Jaen, Spain) by saturation with Fe^{+3} (CTI-Fe) and hexadecyltrimethylammonium (CTI-HDTMA). A commercial organo-clay, Cloisite 10A (Clo10A, from BKG) was also used for comparison. These lected pollutants were three pesticides terbuthylazine, tebuconazole and MCPA, as representative compounds due to theirmarkedly different properties. Two types of filtering beds were prepared: clay-pellets (P) and anthracite-immobilized powder clay (AIC). The pellets (P) were made using carnauba wax (30% wt)as binder to granulated powder modified-clays through a ram extruderaftermixingat 90ºC; those pellets were mixed with anthracite at rate of 40% for the bed filter. The anthraciteimmobilized powder clays (AIC)were prepared by mixing the modified clays with carnauba wax and anthracite (14%/ 7%/78% wt) at 90 ºC. Anthracite was used in both cases to avoid clay losses and helps to increase the bed porosity improving the water flow. An adsorption experiment was performed to compare the behavior of the both filtering beds prepared by placing either P or AIC in a 40 L- water tank containing a solution with the three pesticides at initial concentration of 1 mg/L. The water flow was maintained constant through the closed system at 30 ml/min to obtain pressures of 1 bar. The adsorption kinetics was followed by sampling at selected times (15 min, 30 min, 1 h, 2 h, 4 h, 6 h, 8 h, 24 h) to determine the aqueous concentration of pesticides by HPLC.

The results revealed that the organic modified clays, Clo10A and CTI-HDTMA, were more effective than CTI-Fe for removing the pesticides in P filtering bed, with adsorption ranging between 60-100% and 40-100%, respectively. This fact contrasted with the adsorption reached by the inorganic modified clay pellets, where CTI-Fe was able to adsorb only between (15-40%). Similar trend was obtained in AIC, the organoclays also displayed greater adsorption towards the pesticides (60-100%) after 24h in comparison to CTI-Fe (20-80%). When assessing both types of bed, even AIC performed better than the P in terms of adsorption. This fact can be consequence of the greater amount of anthracitein AIC which facilitates the interaction between organoclays and pesticides in water by increasing the surface of modified clay exposed, as it has been observed in AIC by scanning electron microscopy (SEM) [2]. Additionally, anthracite also contributed itself (10-20%) to the adsorption of the pesticides. These results indicate that the organic clays (Clo10A and CTI-HDTMA) resulted in more efficient filtering materials (P and AIC forms) to remove the three pesticides from water, as compared with the inorganic Fe-clay (CTI-Fe). The anthracite immobilized clays are more efficient as final form forfiltering bed material.

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CAESIUM RETENTION IN SWELLING CLAY MINERALS: INFLUENCE OF LAYER CHARGE AND HYDROXY-INTERLAYERING

Liva Dzene (1)*, Éric Ferrage (1), Jean-Christophe Viennet (1), Héloïse Verron (1), Jean-Louis Robert (2), Alfred Delville (3), Laurent Michot (4), Emmanuel Tertre (1), Fabien Hubert (1)

(1) IC2MP-Hydrasa, UMR 7285, CNRS-Université de Poitiers, 86073 Poitiers cedex 9, France, (2) IMPMC, UMR 7590, CNRS-Université Pierre et Marie Curie-IRD-MNHN, 75005 Paris, France, (3) ICMN, UMR 7374, CNRS-Université d'Orléans, 45071 Orléans Cedex 2, France, (4) PHENIX Laboratory, UMR 8234, CNRS-Université Pierre et Marie Curie, 75252 Paris, France
*liva.dzene@uha.fr

Long-term soil pollution by radionuclides is one of the main problems after nuclear power plant accidents such as in Chernobyl and in Fukushima. To elaborate adequate remediation strategies for the contaminated sites, it is important to be able to predict the fate of pollutants such as ^{137}Cs in soil environments. Among various soil components swelling clay minerals are highly reactive and interact strongly with caesium. Soil swelling clay minerals displaya wide range of isomorphic substitutions in octahedral and/or tetrahedral sheet leading to significant differences in overall layer charge. Thus, in soils one can commonly find a wide range of layer charges ranging from low-charge (smectites) to high-charge (vermiculites) swelling clay minerals. Moreover, in acidic soil environments, such as in Fukushima area, these swelling clay minerals are subjected to weathering processes, resulting in the formation of hydroxy-interlayered minerals. The implications of both layer charge and presence of hydroxy-interlayerson Cs^+ mobility in soils remain difficult to predict due to the mixture of these minerals with other clay minerals and organic matter.

In this study, a series of synthetic saponites with well-defined layer charge and weathered vermiculite with known chemical composition were used. Regarding the influence of layer charge, combination of structure analysis and Cs^+ extractabilitymeasurements (with 1M CH_3COONH_4) shows that the fraction of highly exchangeable Cs^+decreases gradually for swelling clay minerals with layer charge of 0.7 per $O_{10}(OH)_2$ and higher. Quantitative structure analysis suggests that the amount of highly exchangeable Cs^+ can be related to a structure having one or two layers of water in the interlayer, while the fixed Cs^+ in these conditions corresponds to the amount of collapsed layers (zero layers of water in the interlayer). The proportion of collapsed layers increases with increasing layer charge. However, when hydroxy-interlayers are present in high-charge swelling clay minerals (vermiculite) Cs^+ cannot anymore be considered as fixed. In the case of weathered vermiculite, the formation of hydroxy-interlayers is accompanied by an increase in Cs^+exchangeability. Cs^+ in unaltered vermiculite layers is poorly exchangeable, while the extractability of Cs^+ is greatly enhanced in layers with hydroxy-interlayer aluminium.

The overall reactivity (cation exchange capacity, Cs^+ mobility) is then governed in both cases by the relative abundance of collapsed and non-collapsed layers. For saponite, collapsed layers are found to coexist with hydrated Cs^+-saturated layers, whereas for vermiculite, the overall reactivity is governed by the relative proportion between altered and non-altered layers. The proposed layer model for which two populations of caesium coexist could be useful for predicting the fate of caesium in contaminated soil environments.

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DEVELOPMENT OF CLAY-BASED FILMS WITH HIGH GAS BARRIER PROPERTIES

Takeo Ebina

Research Institute for Chemical Process Technology, National Institute of Advanced Industrial Science and Technology, Sendai, 983-8551, Japan

Phyllosilicate (clay) has been used as a filler to improve thermal stability and gas barrier property of plastic films. Clay is heat-resistant, and it is superior at resistively for chemicals, and can be supplied at reasonable cost. However, there has been a few film-preparation-trial using clays as a main component. The thermal stability and the gas barrier performance could be improved drastically if the layered clay crystals are highly ordered parallel to the film surface. An organic polymer is added as a binder, which improves the toughness of the film and has the effect of filling the pinholes lower the gas barrier property of the film. The films are obtained by coating and drying a paste composed of the clay, the binder and the solvent. These clay-based-films (CBF) are heat-resistant, and they have a high gas barrier property against various gases such as hydrogen, water vapor, and oxygen in the wide range of temperatures. The coefficient of thermal expansion is smaller than 10 ppm/K in the wide range of temperature. Moreover, a transparent film can be prepared using synthetic clay which doesn't contain colored impurities.

We actively conduct developments of composite materials using this technology to contribute to the realization of a sustainable society. The application products are wide-ranging such as, solar cell back sheet, hydrogen tank, gaskets, water vapor barrier film for displays, substrate for printable electronics, thermal insulation film, and so on. Latest achievements and future prospects based on academia-government agencies-industry collaborations will be introduced.

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SYNTHESIS OF LAYERED PEROVSKITE-TYPE NIOBATES DOPED WITH MAGNETIC ELEMENTS AND THEIR DELAMINATION INTO 2D OXIDE NANOSHEETS

Yasuo Ebina*, Yuichi Michiue, Takayoshi Sasaki

International Center for Materials Nanoarchitectonics, National Institute for Materials Science, Tsukuba 305-0044, Japan
*ebina.yasuo@nims.go.jp

Layered materials, e.g., clays, layered metal oxides, chalcogenides, hydroxides, can be delaminated into molecularly thin 2D materials, or nanosheets. They have attracted significant attention because they often exhibit new or enhanced physical properties based on their unique 2D structure. We have reported that a series of 2D oxide nanosheets with a progressively varied thickness were derived from a homologous family of layered perovskite niobates, $KNa_{n-3}Ca_2Nb_nO_{3n+1}$ (n = 3-6), through soft-chemical delamination processes [1]. In this work, we applied this synthetic strategy, or "solid-state templating method", to produce new homologous compounds, $ACa_2MNb_3TiO_{13}$ (A = K or Rb), doped with magnetic elements, e.g, M = Mn, Fe, Co and Ni. Then the obtained compounds were exfoliated into new perovskite-type oxide nanosheets.

A stoichiometric mixture of the layered perovskite, $ACa_2Nb_3O_{10}$ (A = K or Rb), and ilmenite-type oxide, $MTiO_3$ (M = Mn, Fe, Co and Ni), was heated at 1373 K. XRD data indicates the expansion of a basal spacing by ca. 0.4 nm, corresponding to the height of NbO_6 or TiO_6 octahedron. In addition, chemical analysis results were consistent with the target stoichiometry, indicating the successful formation of $ACa_2MNb_3TiO_{13}$, as the $n = 4$ member of homologous series of layered perovskites. Actually the Rietveld refinement of $RbCa_2MnNb_3TiO_{13}$ confirmed the layered perovskite structure having a host slab of $n = 4$. The obtained samples were converted into H^+-exchange forms, $HCa_2MNb_3TiO_{13}$, upon treatment with a 5 M HNO_3 solution, which were further reacted with an aqueous solution containing tetrabutylammonium ions. A turbid colloidal suspension was obtained. AFM observation after transferring the floating nanosheets by Langmuir-Blodgett method onto a Si substrate detected micrometer-sized 2D objects with a uniform thickness of ca. 2.1 nm, strongly suggesting the delamination into unilamellar nanosheets. In-plane and out-of-plane XRD data further support the full exfoliation of the layered perovskite compounds. These results indicate that new perovskite-type 2D nanosheets doped with magnetic elements can be obtained.

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MINERALOGICAL AND GEOCHEMICAL CHARACTERIZATION OF ARCHAEOLOGICAL CERAMIC FROM EL BADI PALACE, MOROCCO

Mouhssin El Halim (1)*, Lahcen Daoudi (1), Meriam El Ouahabi (2), ValérieRousseau (3), Catherine Cools (3), Nathalie Fagel (2)

(1) Laboratoire de Géosciences et Environnement (LGSE), Département de Géologie, Faculté des Sciences et Techniques, Université Cadi Ayyad, BP 549 Marrakech, Morocco, (2) UR Argile, Géochimie et Environnement sédimentaires (AGEs), Département de Géologie, Quartier Agora, Bâtiment B18, Allée du six Août, 14, Sart-Tilman, Université de Liège, B-4000, Belgium, (3) Ecole supérieure des Arts Saint-Luc de Liège, 41 Bd de la constitution, B-42000, Liège.Belgium

Historical monuments are tangible witnesses to the evolution of civilizations over time. Because of their historical, artistic and architectural interest, the management of historical heritage has become a priority in several countries. In Morocco, among the most fascinating historical sites, the El Badi Palace in Marrakech, declared World Heritage Site by the UNESCO in 1985, shows the beauty and perfection of Moroccan architecture of the Saadian dynasty (1554 to 1659), mosaic and ceramic used to decorate the building constitute one of the key elements of this exciting architecture. However, this building has now reached advanced deterioration phase and ceramic materials are increasingly weakened due to human impact over time. Several restoration attempts have been undertaken, but without success. In fact, traditional restoration methods that do not take into account the chemical and mineralogical characteristics of the raw materials are still practiced.

In this context, this study consists of characterizing the various types of ceramics used in the construction and decoration of the El Badi Palace. Three types of ceramics including decorative ceramics (zellige), brick masonry and ceramics from irrigation channelwere identified. Textural, mineralogical and chemical characterization of these ceramics has been investigated, in order to identify the appropriate materials and the development of a specific approach to the restoration, maintenance and enhancement of the ceramics of El Badi Palace. The methodology includes experimental data on different ceramic shreds and glazes (Cathodoluminescence, optical microscopy, SEM, XRD and XRF) as well as firing tests.

The obtained results show that the calcareous clay raw material was used to manufacture these three types of ceramics. For the zellige, the used clay material comes from the region of Fez (Benjellikh site), whereas for bricks and irrigation channel, the raw clay material was collected in the Marrakech area. The firing temperature was different for these three types of ceramics; zellige and irrigation canal ceramics were fired at a maximum temperature of 700 °C in oxidizing atmosphere, while bricks were fired at 900 °C. Several observations of zellige samples indicate that the glaze mixture has been previously applied to the fired clay shards and then a second firing was applied. Subsequently, the pieces were carved into small pieces like puzzles. This technique is still used by the artisans in the site of Fez, i.e. the main center of production of the zellige in Morocco. The zellige pieces used in the construction of the Palace El Badi are therefore either imported from Fez or manufactured locally in Marrakech according to the current standards and procedures in Fez. The low firing temperature for zellige facilitates the pieces cutting but it is responsible for their poor quality due to absence of the vitreous phases.

Keywords: archaeological ceramics, raw materials, characterization, manufacturing process, El Badi Palace, Morocco.

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TRADITIONAL MOROCCAN POTTERY: INSIGHT INTO PHYSICO-CHEMICAL AND TECHNOLOGICAL PROPERTIES

Meriam El Ouahabi (1)*, Lahcen Daoudi (2), Mouhssin El Halim (2), Hicham El Boudour El Idrissi (2), Nathalie Fagel (1)

(1) UR Argile, Géochimie et Environnement sédimentaires (AGEs), Département de Géologie, Quartier Agora, Bâtiment B18, Allée du six Aout, 14, Sart-Tilman, Université de Liège, B-4000, Belgium, (2) Laboratoire de Géosciences et Environnement (LGSE), Département de Géologie, Faculté des Sciences et Techniques, Université Cadi Ayyad, BP 549 Marrakech, Morocco
*meriam.elouahabi@ulg.ac.be

The clay reference samples are suggested as standards for archaeological pottery studies because their chemical composition and the mineralogy of fired clays are more like those of the artefacts. Such samples may provide a basis for correlating archaeological studies throughout the Mediterranean. This study focuses on the characteristic and the evaluation of the clayey raw materials from the main Moroccan traditional pottery centers. The objective is to establish reference samples that will help in the sourcing investigations for archeological ceramics in the western Mediterranean regions as well as in the choice of the appropriate materials for restoration of historical monuments. For this context, physical, chemical (X-ray fluorescence, XRF), mineralogical (X-ray diffraction, XRD) on bulk and clay fraction (<2 µm), grain-size distribution, plasticity index (PI), plasticity limit (PL) and liquid limit (LL) were performed on the clay-rich materials from the main rural pottery center which is specific to the northern regions (Oued Laou in northern east) and the city pottery sites which are the most common in Morocco (Meknes and Fez in northern east, Safi in centre west). Samples have been prepared by shaping and fired in the range of 500 - 1100 °C, then bulk water absorption capacity (WAC), loss on weight and mineralogical transformations were determined with the aim of evaluating the technological properties.

For the most of the sites, highly plastic clays were mainly composed of illite, smectite, kaolinite and mixed-layer clay minerals. Quartz, calcite, dolomite and feldspars were also detected. However, the rural pottery site (Oued Laou) indicates moderate to high plastic clays, comprising illite, kaolinite, muscovite, quartz and feldspars. Chemical composition of the samples indicates that the main oxide compositions were SiO_2 (41.0 -51.1%), Al_2O_3 (10.1 - 28.3%), CaO (0 - 34%) and Fe_2O_3 (4 - 11.7%) whereas other oxides were present only in small quantities.

Fired clays exhibited wide differences in water absorption capacity decreasing from 17 - 22% to 6 - 8% for 800 and 1100 °C, respectively. A sharp decrease in WAC values occurred from 800 and 1000 °C for Fez bodies due to glassy phase formation. All technological properties exhibit significant densification at temperatures from 1100 °C. The transformed mineralogical phases allow confirming densification with the appearance of Ca-sillicates (diopside) and spinel for the most fired clays, while spinel and mullite for the non-calcareous rural pottery. Formulations are necessary to enhance the workability of some plastic clay mainly for Meknes and Oued Laou raw materials.

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AMIK LAKE LEVEL FLUCTUATIONS DURING THE LAST 4000 YEARS (SOUTHERN TURKEY): HUMAN-CLIMATE INTERACTIONS

Meraim El Ouahabi (1)*, Aurélia Hubert-Ferrari (2), Jacqueline Vander Auwera (3), Gilles Lepoint (4), Volkan Karabacak (5), Sabine Schmidt (6), Nathalie Fagel (1)

(1) University of Liège, Department of Geology, U. R. Argiles, Géochimie et Environnements, Liège, Belgium, (2) University of Liège, Department of Geography, Liège, Belgium, (3) University of Liège, Department of Geology, Pétrologie, géochimie endogènes et pétrophysique, Liège, Belgium, (4) University of Liège, Département des Sciences et Gestion de l'Environnement, Liège, Belgium, (5) Eskisehir Osmangazi University, Department of Geological Engineering, Eskisehir, Turkey, (6) Departement of Geology and Oceanography, UMR5805 EPOC, University of Bordeaux 1, Talence Cedex, France

Within a Mediterranean context, the study investigates the upper sediments infilling the central part of the Amik basin in southern Turkey. Continuous human occupation is attested in the Amik Basin since 6000-7000 BC. The Basin also is crossed by The Dead Sea Fault (DSF), a major neotectonic structure in the Middle East extending from the Red Sea in the south to the East Anatolian Fault Zone in the north. The study focuses on the sedimentary record of the Amik Lake occupying the central part of the Basin. Our objective is to constrain major paleo-environmental changes in the area over the last 4000 years and assess possible human impact.

The lake has been drained and progressively dried up since the mid-50s so that it is not watered during the summer season and constitutes a unique opportunity to collect sediment records. Sediments were collected at 1 cm to 2 cm intervals in a trench and in cores up to a depth of 5 meters in the clay deposits. A diverse array of complementary methods is applied to study the records: magnetic susceptibility, grain size, organic matter and inorganic carbon (L.O.I), XRF geochemistry, mineralogy, carbon and geochemistry. The age of the record is constrained combining radionuclide and radiocarbon dating. The sedimentary record clearly shows two periods indicating strong soil erosion in the Lake catchment. The most recent erosion phase is Roman to modern period. The oldest one would have occurred during late Bronze period. Furthermore, several structural disturbances was affected the lake sediments and tell settlement related to earthquake shaking events, with major earthquakes from the 6th to the 9th century AD due to the Hasipasa Fault rupture.

Significant pedogenesis transformations are evidenced, especially during the Islamic/Ottoman periods suggesting intense chemical weathering conditions related to climate change. Fluctuations in water level of the Amik Lake occurred. In particular, an increase in potassium represents a lake development phase associated with a wet phase, it's would be due to overflow of the Orontes River which deposits of clays. By contrast, increased calcium and strontium corresponds to a low lacustrine level and a drier period. Lowstand with little external occurred during the Bronze and Iron/Hellenistic Age indicated by the high SrO percentage and small amount of clay size particle.

Keywords: Climate, Weathering conditions, Land erosion, Clay mineralogy, Lake sediment, Last millenia.

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INVESTIGATION OF USE OF COAL FLY ASH IN ECO-FRIENDLY CONSTRUCTION MATERIALS

Dolores Eliche-Quesada (1), Juan Antonio Sandalio-Pérez (1), Sergio Martínez-Martínez (1)*, Luis Pérez-Villarejo (1), Pedro José Sánchez-Soto (2)

(1) Department of Chemical, Environmental, and Materials Engineering. University of Jaen, Campus Las Lagunillas, s/n, 23071 Jaén, Spain, (2) Materials Science Institute of Sevilla (ICMS), Joint Center Spanish National Research Council (CSIC)-University of Sevilla, c/Américo Vespucio, 49, 41092 Sevilla, Spain

Sustainable use and disposal of industrial wastes could help to reduce their negative effects on the environment. The thermoelectric power plants in Spain generate more than 9.5 million tons per year, of which only 20% is used for different applications [1]. A significant quantity of the coal fly ash, mixed with heavy metals and toxins [2], is currently stored in landfills and ash lagoons, thus, can result a risk to the surrounding environment causing significant environmental impacts.

A considerable effort is being made worldwide on the reuse of coal combustion fly ashes as a source of alternative raw materials to produce new materials such as cement, concrete, zeolites, glass-ceramics, adsorbents for cleaning of flue gas, lightweight aggregate, road subbase, and clay bricks [3].

On the other hand, fly ash is pozzolanic thus its vitreous phase can react with lime to form hydration products that contribute to the development of the mechanical resistances in cementitious systems. The lime manufacturing process produces large CO_2 emissions due to its chemical transformation and the amount of energy required for incineration at high temperatures.

In this work is investigated the use of coal fly ash as raw material for the manufacture of two construction materials: fired clay bricks and silico-calcareous bricks. Fired clay bricks were manufactured using different waste ratios (0-50%), moulded at 10 MPa and fired at 1000 ºC (4 h). Silico-calcareous bricks were prepared using as raw material two wastes: coal fly ash (CFA) and “geosilex”(G), a lime which comes entirely from acetylene industry waste. Different proportions coal fly ash (80-20 wt%) - geosilex (20-80 wt%) were investigated. Raw materials were moulded at 10 MPa and cured in water 28 days. Some physical, mechanical and environmental properties of -CFA-clay bricks and CFA-Geosilex bricks were studied following standard procedures. The results indicate that the incorporation of up to 20 wt% of CFA produced fired clay bricks with physical and mechanical properties similar to control bricks without waste. However, additions of a higher residue amount (30-50 wt%) resulted in a more pronounced decrease in mechanical properties (between 25-50%) due to the increase in open porosity.

The technological characterization of the silico-calcareous bricks indicated that as the coal fly ash content decreases, the bulk density and water absorption are reduced. Silico-calcareous bricks containing between 40-60 wt% of coal fly ash have the highest values of compressive strength (between 45.8-42.8 MPa). These silico-calcareous bricks, 60CFA-40 G, 50CFA-50 G and 40CFA-60 GC, presented the optimum amount of pozzolanic materials (SiO_2 and Al_2O_3) present in the coal fly ash and calcium hydroxide present in the geosilex to give rise to calcium silicate hydrates and calcium aluminate hydrates, responsible for the mechanical resistance of the construction materials.

Therefore, CFA-clay bricks and silico-calcareous CFA-G bricks presented optimal technological properties that meet the quality standards.

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CLAY MINERALS FROM MICRO TO NANO-SIZE: THEIR ROLE IN IMPROVING DRILLING FLUID RHEOLOGY FOR HIGH-PRESSURE HIGH TEMPERATURE WELLS

Salaheldin Elkatatny (1), Fahd Alakbari (1), Mohammad Mahmoud (1), Reyad Shawabkeh (2), Ibnelwaleed Hussein* (3)

(1) Department of Petroleum Engineering, King Fahd University of Petroleum & Minerals, Dhahran, 31261, KSA, (2) Department of Chemical Engineering, King Fahd University of Petroleum & Minerals, Dhahran, 31261, KSA, (3) Gas Processing Center, College of Engineering, Qatar University, PO Box 2713, Doha, Qatar

Gel strength property plays a key role in drilling multilateral and long horizontal reservoir sections. Losing the gel strength will accumulate drilled cuttings and as a result, sticking of the drill string. Solving this issue takes long time and increase the total cost of the drilling operations. It was observed that, by increasing the temperature to 200 °F, the gel strength of calcium carbonate water-based drilling fluid reached zero lb/100 ft^2.

The objectives of this paper are to: (1) assess the effect of using clays (bentonite and nano-clay) to solve the gel strength problem associated with the current field formulation of calcium carbonate water-based drilling fluids, (2) optimize the weight percent of clays, (3) evaluate the stability of the drilling fluid constituents using zeta potential measurements, (4) determine the rheological properties of calcium carbonate water-based drilling fluid over a wide range of temperature (80 to 200 °F), and (5) evaluate the removal efficiency and the possibility of formation damage after adding clays to the drilling fluid formulation.

Zeta potential results showed that calcium carbonate was not stable over a wide range of pH while clay (bentonite) was stable over a wide range of pH (4 to 12). This can be attributed to the low electronegativity values of the elemental composition of bentonite. Rheological properties confirmed that the gel strength of the calcium carbonate water-based drilling fluid reached zero lb/100 ft^2 by increasing the temperature to 200 °F. This issue was solved by adding different concentration of bentonite. The optimum concentration of bentonite was 6.66 wt.%, which yielded a flat rheology profile of the gel strength. The filtrate volume decreased by 40% and the filter cake thickness decreased by 60%when bentonite was used. These results confirmed that the rheological properties of the water-based drilling fluid were optimized by using clays (bentonite).

The novelty of this research is the complete investigation of the drilling fluid properties especially the gel strength with time over a wide range of temperature. Development of a cheap solution without any side effect problems. Relating the electronegativity with zeta potential and XRD analysis to understand the stability of different components.

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SYNTHESIS OF METAL(LOID)S-BEARING PHYLLOSILICATES PHASES: A WAY TO BETTER ASSESS HEALTH RISKS FROM POLLUTED SITES

Monneron-Gyurits Matthias*, Joussein Emmanuel, Soubrand Marilyne, Courtin-Nomade Alexandra

Université de Limoges, GRESE "Groupement de Recherche Eau Sol Environnement", Limoges, France

Soil contamination is mainly caused by the presence of human-made contaminants from industrial and mining activities, agriculture, or improper disposal of wastes. The most common and problematic contamination involves metals and metalloids from mining wastes. The concern over soil contamination stems primarily from their potential health risks to humans. Human health risks linked tocontaminated soils depend on the feasibilityforthe contaminant to be extracted from the soil to eventually reach the human bloodstream [1]. Classically, the main approach concernsthe oral/ingestion pathway, namely bioaccessibility, which is based onto an operational chemical methodology miming the systemic circulation of the human body through oral ingestion of soil particles and finally causing toxic effects. However, this approach presents some methodological problems. Indeed, it is difficult to evaluate (i) the reactivity of each bearing phases in the case of a multi-element contamination and (ii) the most realistic potential risk due to the lack of physicochemical data of these specific "endemic" phases. Since polluted soil system is complex, it seems necessary to simplify it to better understand the associatedhealth risks of each bearing phases. For this purpose, it has been proposed to synthesize, at temperature up to 200 °C, some representative metal-bearing phases to assess their reactivity in supergene context. In this paper, we focus on (i) two phyllosilicates i.e., chapmanite, a 1:1 layers (ideal formula $Si_2O_8(OH)Fe^{3+}{}_2Sb^{3+}$) as well as a 2:1 layer structure namely sauconite (ideal formula $Zn_3(Si,Al)_4O_{10}(OH)_2$), and two others phases (ii) franklinite (ideal formula $ZnFe^{3+}{}_2O_4$) and beudantite (ideal formula $PbFe_3(As,SbO_4)(SO_4)(OH)_6$). Each synthesized product was characterized by XRD, XRF, FTIR, Raman and SEM-EDS, and the synthesis protocols were all adjusted. Then, the synthetic phases (similar grain size) were subjected to the bioaccessibility BARGE protocol (i.e., gastric fluid mimic, 37 °C) to assess the metal(loid)s geochemical behaviour. The results were compared to the stability of bearing phases obtained from physicochemical tests from 1 to 12 pH unit values so that the behaviour at every environmental supergene (as well organism one) condition can be evaluated. The discussion will focus on the metal(loid)s behaviour as well as the reactivity and stability of each phase in terms of health risks, and eventually the management of polluted sites and soils.

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MINERALOGICAL SEQUENCE OF Zn-RICH MINERALS IN AIN KHAMOUDA KARSTIC SYSTEM: EVIDENCE OF FRAIPONTITE NEOFORMATION

Lazaar Sonia (1,2), Joussein Emmanuel (1)*, Courtin-Nomade Alexandra (1), Soubrand Marilyne (1), Lajmi Amira (1,2), Mehdioub Mounir (2)

(1) Université de Limoges, GRESE “Groupement de Recherche Eau Sol Environnement”, Limoges, France, (2) Université de Sfax, Sfax, Tunisie

The miocene karstic system of Aïn Khamouda (central Tunisia) was known as a Pb-Zn deposit which was exploited during the 20th century. This depositis a carbonate-hosted zinc deposit and often exhibits as much Fe oxides as Zn mineral phases such as hemimorphite and smithsonite as well as phyllosilicate fraipontite mixed with halloysite. Actually, the nature and the origin of zinc-based clays are poorly understood. Fraipontite is a 1:1 clay mineral with the ideal formula $(Zn,Al)_3(Si,Al)_2O_5(OH)_4$. It was shown that Al was able to occupy both the octahedral and tetrahedral positions in this phase. The aim of this study is to characterize the neoformed minerals in the karstic system through the mineralogical sequence of alteration of each Zn-phases taking into account neoformed clay minerals i.e., fraipontite and halloysite. Chemical analyses of bulk samples were performed by XRF. Then clay fraction was separated according to the Stokes law. Each sample (bulk and after fractionation) was characterized by XRD (bulk powder and oriented tiles), FTIR, Raman and SEM-EDS. The rare trioctahedral 1:1 Zn clay mineral fraipontite was identified with minor amounts of halloysite, quartz, micas, hemimorphite, smithonite, goethite and hematite. Some traces of sauconite is observed in this more common supergene Zn minerals. The FTIR spectra of fraipontite as well as EDX analyses are quite similar to those reported in the literature. Together with XRD results, it seems that zinc is mainly located within the octahedral sheets. Halloysite occurs as spheroidal and tubular morphologies. These results support the partial dissolution of hemimorphite leading to release of Si and Zn and then the interaction between phases promoted the formation of Zn-rich clays as well halloysite thanks to meteoric fluids. Finally, the sequence will be discussed in terms of Zn-clay stability and neoformation.

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EFFECT OF LAYER CHARGE ON HYDRATION, WATER CONTENT, DEHYDRATION TEMPERATURE AND SWELLING PRESSURE OF DIOCTAHEDRAL SMECTITES

Katja Emmerich (1)*, Nicolas Giraudo (2), Florian Schnetzer (2), Rainer Schuhmann (1), Peter Thissen (1)

(1) Karlsruhe Institute of Technology, CMM, Karlsruhe, Germany, (2) Karlsruhe Institute of Technology, IFG, Karlsruhe, Germany

The deep geological disposal of radioactive waste is internationally agreed the safest option. Most repository concepts consist of a multi-barrier system that comprises an engineered barrier of bentonite. Still, open questions remain with respect to observed heterogeneity in swelling behaviour of bentonite and prediction of swelling pressure. The present study focuses on heterogeneous hydration and swelling of dioctahedral smectites, which are the main component of bentonites.

The amplified water uptake and retention by swellable clay minerals results from hydration of interlayer cations. Swelling of compacted bentonites in a confined space induces swelling pressures up to several MPa. Thereby, the water binding mechanisms are complex due to structural heterogeneity of smectites and are determined by layer charge density and location of substitutions. Several experimental studies deal with the water uptake of smectites [1] and heating conditions for full dehydration or swelling pressure in dependence of dry density [2]. Nevertheless, there is a lack in quantitative understanding of stable hydration states in dependence of layer charge covering the full range from (0.125) 0.2 and 0.6 cmol(+)/fu and the related volume change during innercrystalline swelling that determines dehydration and the magnitude of the swelling pressure.

The Na-saturated smectite / water interface for the montmorillonite-beidellite series is investigated in the present work within the density functional theory (DFT). Layer charge is varied between 0.125 and 0.5 per formula unit $[O_{10}(OH)_2]$ by substitution of Al^{3+} by Mg^{2+} in the octahedral sheet (montmorillonites) and by substitution of Si^{4+} by Al^{3+} in the tetrahedral sheets (beidellites). Starting from the water free supercells (with integer molar ratios), the number of water molecules is increased discretely. Stable hydration states (1H to 3H) do not necessarily correspond to the formation of water layers (1W to 3W) in the interlayer, which is deduced from the development of the basal spaces during hydration. With the help of ab initio thermodynamics, the energy states are related to temperature, and partial pressure of H_2O and the resulting phase diagrams revealed hydration state in dependence of relative humidity (RH) as well as necessary temperatures for full dehydration to determine the true water content. Thereby it was shown that 2:1 layer silicates with a layer charge of 0.125 are swellable but reach only the 1H state even at 100% RH, but the removal of water molecules from the interlayer requires temperatures >110 °C and partial pressures of water <100 Pa. In contrast water uptake of smectites with layer charge 0.375 requires RH of >11% at room temperature, but dehydration occurs at moderate heating. Swelling pressure calculations are under way.

Our results now provide the possibility to predict water uptake, swelling pressure and dehydration conditions for determination of the true water content for smectites, whose layer charge and layer charge distribution varies not only between samples but also for 2:1 layers within a distinct sample.

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THE CONTROL OF DESORPTION OF ADSORBED Cs^+ FROM THE NATURAL ZEOLITE

Masatoshi Endo*, Koki Togashi, Takuya Miura, Atsushi Sasaki

YamagataUniversity, Yonezawa, Japan
*endomasa@yz.yamagata-u.ac.jp

The zeolite known as good adsorbent has characteristics such as ion exchange capacity, molecular sieve and adsorptive capacity and it is used as drainage treatment and soil conditioner. Because the natural zeolite produced in Itaya, Yonezawa, Japan has good quality and bountiful reserves. Natural Itaya-zeolite is composed mostly of clinoptilolite, containing some mordenite. From its characteristic, zeolites are used for the removal of radioactive Cs^+. It was thought that natural zelite has utility value for being often produced and good quality. About adsorption of Cs^+ by zeolite has often been studied. But about effect of desorption of Cs^+ from zeolite has not been much reported. Therefore the study of suppression of desorption is required. Itaya zeolite mainly elute ions of K^+, Ca^{2+} and Mg^{2+} by ion exchange when adsorbed Cs^+. In addition, Cs-137 becomes Ba-137 by beta decay. So in this study Itaya zeolite absorbed Cs-133 was tested how it behave when solution of K^+, Mg^{2+}, Ca^{2+} or Ba^{2+} as desorbent was induced desorption. It was thought that zeolite adsorbed Cs^+ is suppressed desorption by burning. Desorption of Cs^+ was influenced in the order of $K^+>Ba^{2+}>Ca^{2+}>Mg^{2+}$. This means to affect desorption as the ionic radius of desorbent is larger. Desorption rate of non calcinated zeolite was 0.8%, in contrast desorption rate of calcinated zeolite was 0.008%, therefore, desorption was suppressed 1/100. The melting point of zeolite is 900 °C. Therefore zeolite was fired at 1100 °C was able to be immobilized Cs^+ that was adsorbed because the pores collapsed by melting.

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TEM OBSERVATION OF ORTHO-TYPE POLYGONAL SERPENTINE AND ORTHOCHRYSOTILE

Satomi Enju*, Seiichiro Uehara

Department of Earth and Planetary Sciences, Faculty of Science, Kyushu University, 744 Motoka, Nishi-ku, Fukuoka 819-0395 Japan

Serpentine minerals are 1:1 type phyllosilicate with ideal composition $Mg_3Si_2O_5(OH)_4$. They take various crystal structure due to the misfit between sheets. Chrysotile have cylindrical nanotube like structure and is divided into clinochrysotile (chrysotile-$2M_{c1}$) and orthochrysotile (chrysotile-$2Or_{c1}$) by the β angle. Polygonal serpentine (PS) have a unique multi column shaped structure. It can also be divided into two types; "clino-type PS" with XRD pattern similar to clinochrysotile and "ortho-type PS" similar to orthochrysotile (Middleton & Whittaker, 1976; Krstanović, 1997). Pure orthochrysotile is very rare, and mostly occur as mixture with clinochrysotile (Whittaker & Zussman, 1956). Ortho-type PS also seems to be rare, since most reports are done on clino-type PS (e.g. Mugnaioli et al., 2007). Their observation is insufficient compared to the clino-type structures. In this study, we researched the mineralogical properties, especially crystal structure and microtexture, of ortho-type PS and orthochrysotile, to discuss their relationships and formation process, which reflects the late stage hydrothermal environment in serpentinization.

The samples were analyzed by X-ray diffraction (XRD), electron microprobe analyser (EPMA) and transmission electron microscope (TEM) in Kyushu university ultramicroscopy research center. Ortho-type PS are from 3 areas (Shimotake, Fukami, Wakayama) in Kurosegawa belt, Japan. Orthochrysotile from Sir R. Bond's mine, Newfoundland (sample #M15100; Wicks & O' Hanley, 1988) was provided by Royal Ontario Museum. The samples are endmembers (free of clino-type components) in powder XRD.

The ortho-type PS specimens were collected from yellowish to pale green vein in host serpentinites, which are liner and splintery (Shimotake and Fukami) or irregular with space filling texture (Wakayama). All the samples were composed of ortho-type PS with minor orthochrysotile and/or clinochrysotile. PS was generally 200-300 nm, and some fibers around 100 nm showed polygonal sectors. The number of sectors were always 15, and 30 sectored PS were only rarely seen in Wakayama. The textures and stacking sequence differ through out the localities.

The observed orthochrysotile specimen is a fibrous cross fiber vein with silky luster. It was composed of aligned fibers below 50 nm in diameter. Some fibers were partially polygonised, and sector angles were similar to those of 15 sectored PS. The center of the fiber was composed of interlaced pack of layers, in addition to the cylindrical core. Stacking is not always continuous from center to rim. The layers always act as packets of 4 to 10 layers, sometimes bridging several fibers.

From our observation, ortho-type series starts to polygonize at very small diameters (50-100 nm), and tends to stop development at relatively small diameters (200-300 nm) than former studies (Baronnet & Devouard, 2005; Mugnaioli, 2007). This indicates that the formation of ortho-PS cannot be explained by only the overgrowth of chrysotile. As proposed in polyhedral serpentine (Andreani et al., 2008) trivalent ions may play an important role, but difficult to define a clear border, since ortho-type PS and orthochrysotile take various Al contents (0.01-0.09 *apfu*).

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MINERAL SURFACE CHEMISTRY CONSIDERATIONS FOR PREBIOTIC POLYMER FORMATION: PEPTIDES ON LAYERED HYDROXIDES

Valentina Erastova (1)*, Matteo Degiacomi (2), Donald Fraser (3), Chris Greenwell (1)

(1) Department of Earth Sciences, Durham University, South Road, Durham DH1 3LE, UK, (2) Chemistry Research Laboratory, Department of Chemistry, University of Oxford, 12 Mansfield Road, Oxford, OX1 3TA, UK, (3) Department of Earth Sciences, University of Oxford, South Parks Road, Oxford, OX1 3AN, UK
*valentina.erastova@durham.ac.uk

The role of clays in the origin of life, first proposed by John Desmond Bernal some seventy years ago, has been the subject of much research. While majority of clays carry negative charge, layered double hydroxides are positive, making them an ideal host for amino acids in early Earth's reducing environment. In this work we examine the role layered hydroxides could have played in prebiotic peptide formation. We demonstrate how highly ordered layered double hydroxides can concentrate, align and template amino acids and, during wetting-drying cycles, promote peptide bond formation. We propose a mechanism for peptide growth, supported by layered double hydroxides in an early Earth environment. Our work provides new insights into the potential role of mineral surfaces in mimicking aspects of biochemical reaction pathways.

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UNDERSTANDING SURFACE INTERACTIONS IN AQUEOUS MISCIBLE ORGANIC SOLVENT TREATED LAYERED DOUBLE HYDROXIDES

Valentina Erastova (1)*, Matteo Degiacomi (2), Dermot O'Hare (2), Chris Greenwell (1)

(1) Department of Earth Sciences, Durham University, South Road, Durham DH1 3LE, U.K., (2) Chemistry Research Laboratory, Department of Chemistry, University of Oxford, 12 Mansfield Road, Oxford, OX1 3TA, U.K.
*valentina.erastova@durham.ac.uk

Layered materials are of interest for use in a wealth of technological applications, many of which require a high surface area for optimal properties and performance. Recently, an industrially scalable method to create high surface area layered double hydroxide (LDH) materials, which may be readily dispersed in non-polar solvents, has been developed [1]. This method involves treatment of LDHs with aqueous miscible organic (AMO) solvents. Here, molecular modeling is exploited to elucidate the AMO solvent-LDH interactions to understand how the dispersion process is facilitated by the AMO treatment. The simulations show how hydrogen-bond networks within the LDH interlayer are disrupted by AMO solvents, leading to delamination [2].

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OCCURRENCE OF TONSTEIN TYPE KAOLINITE LAYERS INTERCALATED WITH COAL SEAMS IN THE NEOGENE LACUSTRINE TUNÇBİLEK BASIN, KÜTAHYA, WESTERN TURKEY

Hülya Erkoyun (1)*, Selahattin Kadir (1), Jennifer Huggett (2)

(1) Eskişehir Osmangazi University, Department of Geological Engineering, TR-26480 Eskişehir, Turkey, (2) Natural History Museum, Department of Earth Sciences, London, UK
*hlerkoyun08@gmail.com, skadir.euroclay@gmail.com, info@petroclays.com

Abundant of beige and white kaolinite in claystone layers have 2-50 cm thickness of Tunçbilek basin characterize tonstein which is suitable for ceramic and tile industries. Up to date there is no detail study on origin of this material. Thus, the aim of this study is to determine mineralogical, geochemical characteristics, and genesis of clays which have economical potential associated with coal seams in order to identify their precipitation environment. The Miocene units in the Tunçbilek coal deposit comprise organic-rich shale, organic-rich marl, marl, claystone, silty claystone, siltstone, sandstone, coal seam, and conglomerate deposited in a fluvial and lacustrine environment, associated with tuff and tuffite. Sanidine, plagioclase, biotite, chlorite and serpentine are partly to completely argillized and clay cemented in the rhyolitic to rhyodacitic tuff/tuffite, sandstone, organic-rich shale, and serpentinite host rocks of the coal deposit. Abundant of kaolinite and quartz associated with smectite, illite, opal-CT, feldspar, calcite, dolomite, siderite, pyrite, barite, gypsum, and olivine. Development of oriented halloysite tube on/in altered volcanogenic materials associated with kaolinite, and occurrence of vermiform type kaolinite edging disordered kaolinite, locally siderite and pyrite crystals may suggest formation of kaolinite under acidic condition following the procedure of: volcanic glass+feldspar+biotite ® 7 Å halloysite ® kaolinite. The slight enrichment of light rare earth elements (LREE) compared to heavy rare earth elements (HREE) with a positive Eu anomalies based on Upper Continental Crust (UCC) normalized values reflects fractional crystallization of feldspar and amphibole. Alteration of feldspar, biotite, serpentine and volcanic glass resulted in the concentration of Al, Si, Fe, Mg, and K in a stagnant envrionment and precipitation of kaolinite precipitated in an acidic open hydrological system, smectite and illite in an alkaline environment. The Al_2O_3/TiO_2 and low Cr/Ni ratios suggest that felsic source rocks. The trace elements ratios such as Ni/Co, V/Cr, Cu/Zn and U/Th among the basement complex source rocks units also suggest oxic and suboxic and anoxic conditions. Association of argillization and silicification with coal, pyrite, and gypsum indicates a swampy environment and partial hydrothermal processes. This interpretation is corroborated by the calculated formation temperatures from stable isotope analysis of 148.8-168 °C for kaolinite and 145-169.2 °C for smectite. The low δS isotope values of pyrite (-19 - 2.9‰) and high positive values of gypsum (11.5 - 21.7‰) indicate a mixed diagenetic and hydrothermal origin for the sulphide and sulphate mineral.

Keywords: Kaolinite, Coal seam, Neogene, Tunçbilek coal deposit, Turkey.

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ADSORPTION OF GLYCINE AND GLYCINIUM IN MONTMORILLONITE

Elizabeth Escamilla-Roa*, F. Javier Huertas, Alfonso Hernández-Laguna, C. Ignacio Sainz-Díaz

Instituto Andaluz de Ciencias de la Tierra (CSIC-University of Granada), Armilla (Granada), Spain

Clay minerals are common minerals on the Earth surface, particularly in soils and sediments, where they play a key role in limiting the movement of nutrients and toxins through soils and sediments. Adsorption is a potentially important process in natural environments because it can lead to preferential removal of some ions and molecules from the natural solutions, and so sorption may affect their transport processes in soils and sediments. Among clay minerals, montmorillonite exhibits one of the largest adsorption capacity. The interaction of proteins and amino acids with clay mineral surfaces has also a very significant impact on several aspects of natural or anthropogenic processes occurring in soils. Clays were present in large amounts on the prebiotic earth crust after the formation of the hydrosphere and may have played an important role in the process of chemical evolution.

In this work, the adsorption of glycine molecule into the interlayer space of potassium montmorillonite was studied by means of quantum mechanical methods based on Density Functional Theory. The cation exchange of potassium by glycinium and hydronium cations was also explored and the adsorption of glycine in presence of these cations was also studied. Different levels of hydration were explored.

Our calculations indicate that the hydration of montmorillonite is an energetically favorable process at all levels of hydration, where the adsorption energy shows an exothermic process. Neutral glycine is adsorbed inside montmorillonite in dry and hydrated conditions. This molecule is transformed spontaneously to a zwitterionic configuration and the adsorption energy shows that this adsorption is an exothermic process. The cation exchange of glycinium is exothermic, maintaining the same hydration levels. Interesting hydrogen bonds between glycine, glycinium and hydronium with the basal tetrahedral O atoms are observed. The IR spectroscopy properties were studied. Frequencies of the main vibrational modes were calculated and compared with experimental results observing interesting frequency shifts depending on the intermolecular interactions in the interlayer space of montmorillonite. This computational study confirms the experimental behavior that during the adsorption of glycine in montmorillonite a certain exchange of glycinium cation can be produced [1].

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SELF-ASSEMBLING TUBULAR STRUCTURES OF MAGNESIUM OXYHYDROXIDE AND SILICATE

Elizabeth Escamilla-Roa*, C. Ignacio Sainz-Díaz, Julyan H. E. Cartwright

Instituto Andaluz de Ciencias de la Tierra (CSIC-University of Granada), Armilla (Granada), Spain

Silicates are common minerals particularly in soils and sediments in Earth and also are present in the interplanetary space. Silicates minerals have been widely studied in several technology areas, due to their versatility, absorption capacity and catalytic properties. Natural silicates can be formed by self-organizing reaction-precipitation processes [1]. By means of this process, tubular structures can be formed. These forms have great importance in the formation of micrometer-scale fibers, biomineralized shells, mineral deposits in caverns and hydrotermal vents on the ocean floor [2]. Besides, these tubular structures can be a good print of the presence of water in extreme conditions like in Mars and other planets [3]. An study is presented simulating the formation of self-assembling tubular structures of Mg oxyhydroxide from reactions of silicate in alkaline conditions and Mg salts, to produce MgO/MgOH crystals. We obtained tubular structures in two phase: solid-liquid and liquid-liquid (injection of diluted salts). Tube and crystals growth in the interior surface of the tubular structure was also characterized by means of environmental scanning electron microscopy (ESEM), Micro-Raman spectra and X-ray diffraction. Our results show the evidence of formation MgO and MgOH in the inner surface of the tube.

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FROM FLOW TO FRACTURE IN LAPONITE

Gustavo Estevam Gimenes*, Elisabeth Bouchaud

PSL Research University, ESPCI-Paris, UMR Gulliver, MMN, 6 rue Jean Calvin, 75005 Paris Cedex 05, France
*gustavo.gimenes@espci.fr

Fracture of clays is an important issue in a number of fundamental and applied problems. Of particular interest is the hydraulic fracturing of oil reservoirs. However, its direct observation at mesoscopic and microscopic scales is complicated by the experimental challenges of gripping and imposing a controlled load on a very soft material and the complexity of viscoelastic processes inducing large deformations [1].

To this end, we use two experimental setups previously developed for the study of biopolymer gels [2] to investigate the mechanical response of synthetic hectorite clay *Laponite RD* gels and an analogous colloidal system composed of *Ludox TM-50* silica nanoparticles. The first device consists in a Hele-Shaw-like cell with a built-in notch. By connecting a hole over the notch to a water syringe pump, a flow rate controlled crack is initiated. The second consists of a closed, rigid chamber where the gel sample is surrounded by an immiscible oil. By sucking the oil out of the chamber, a rate of displacement proportional to its flow rate is imposed to the oil-gel interfaces, and a mode I crack appears at a notch. Both setups are fabricated using microfluidic stickers technology [3].

A wide range of behaviors can be observed on *Laponite* dispersions as a function of the solid concentration and ionic strength, from a fluid which flows under load to an elastic solid which breaks [4]. The crack opening displacement is obtained from its shape in the tip vicinity, while the displacement field is determined using Digital Image Correlation. In this plane stress configuration, it allows for the determination of the stress intensity factor and the energy release rate. Also, birefringence in nematic phases is used: observations are carried out through crossed linear and circular polarizers. By comparing the results of various compositions and cracks propagation velocities, we can have insight into the dissipative mechanisms and fracture properties of clay gels.

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CLAY-SUPPORTED Ni/Fe BIMETALLIC NANOCOMPOSITE USED FOR DEGRADATION OF ORANGE II IN AQUEOUS SOLUTION

Naeim Ezzatahmadi (1,2)*, Godwin A. Ayoko (2), Graeme J. Millar (2), Yunfei Xi (1)

(1) Institute for Future Environments, Queensland University of Technology (QUT), Brisbane, QLD 4000, Australia, (2) School of Chemistry, Physics and Mechanical Engineering, Science and Engineering Faculty, Queensland University of Technology (QUT), Brisbane, QLD 4000, Australia

Azo dyes are a major environmental concern due to their toxicity, widespread usage and biorecalcitrance for conventional aerobic wastewater treatment. Hence, the development of cost-effective technologies for degradation of azo dyes in aqueous solutions is of significant scientific and public interest. Advanced oxidation processes (AOPs) have become effective mechanisms for removal of azo dyes [1]. These processes involve a radical reaction, which can efficiently oxidize and degrade hazardous contaminants to completely harmless products. Recently, reactions using catalytic materials have drawn a great attention in wastewater treatment or groundwater remediation [2]. Of particular interest is the exploration of clay-supported bimetallic nanoparticles, which have proven to be promising remediation materials for the removal azo dyes due to their high catalytic efficiency and great reactivity [3,4]. In this study, we synthesized a palygorskite-supported Ni/Fe bimetallic nanocomposite catalyst (P-Ni/Fe), which exhibited a high capability for degradation of Orange II (OII) azo dye from aqueous solution. Batch experiments indicated that 97.4% of OII was removed using P-Ni/Fe, while only 83.1% and 4.9% of OII, were removed using either Ni/Fe bimetallic nanoparticles or palygorskite, after 6 h of reaction, respectively. Characterization by X-ray diffraction (XRD) and scanning electron microscopy (SEM) suggested that the use of palygorskite as a support material decreased the aggregation of Ni/Fe nanoparticles, thereby enhancing the surface area of these particles. A possible mechanism for degradation of OII by P-Ni/Fe was proposed based on the adsorption of OII on P-Ni/Fe, followed by degradation using Ni/Fe bimetallic nanoparticles. This study demonstrated that palygorskite may be a suitable support material for Ni/Fe bimetallic nanoparticles and the resulting palygorskite-supported Ni/Fe composite could be a promising catalyst for the remediation of dye-contaminated wastewater.

Keywords: palygorskite; Ni/Fe nanoparticles; Orange II; degradation.

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POLYMER-MODIFIED BIOCOMPATIBLE HALLOYSITE NANOTUBES-DOPED COMPOSITES FOR DRUG DELIVERY AND TISSUE ENGINEERING APPLICATIONS

Gölnur Fakhrullina, Elvira Gayazova, Ekaterina Naumenko, Anna Danilushkina, Marina Krychkova, Elvira Rozhina, Ivan Guryanov, Ramil Fakhrullin, Farida Akhatova, Svetlana Batasheva, Rawil Fakhrullin*

Bionanotecnology Lab, Institute of Fundamental Medicine and Biology, Kazan Federal Univeristy, Kreml uramı 18, Kazan, Republic of Tatarstan, Russian Federation, 420008

Halloysite clay nanotubes have become a promising and very popular material in fabrication of biomedical materials [1]. Here we report our recent results on fabrication, nanoscale characterisation and practical in vitro and in vivo applications of halloysite nanotubes for drug delivery and tissue engineering applications. First, we evaluated the toxicity of halloysite nanotubes in vivo using *Paramecium caudatum* protists [2] and *Caenorhabditis elegans* nematodes [3]. Our results indicate that halloysite nanotubes are biocompatible and non-toxic material. We have also perfumed detailed characterisation of pure and polymer-modified halloysite nanotubes using a selection of characterisation techniques.

Next, we demonstrate the selective prototype anticancer drug delivery into selected human cell lines using polymer-modified 50-nm diameter halloysite nanotube delivery vehicles [4]. We have produced versatile dextrin end stoppers to secure the intracellular release of several anticancer preparations (brilliant green, paclitaxel). We found that drug-loaded halloysite nanotubes penetrate through the cellular membranes and reside in cytoplasm. The uptake efficiency for halloysite nanotubes depends on the cells growth rate, for example, faster proliferating cells internalise larger amounts of nanotubes. We also found that the intracellular glycosyl hydrolases-mediated decomposition of the dextrin stoppers stimulates the release of the lumen-loaded brilliant green. This resulted in the preferable elimination of human lung carcinoma cells (A549), in comparison with hepatoma cells (Hep3b). The enzyme-activated intracellular delivery of loaded drugs using dextrin-coated halloysite nanotubes is a promising platform for anticancer treatment, which we elaborated into the more complex systems.

We also produced porous biopolymer cross-linkers free hydrogels doped at 3-6wt % with halloysite nanotubes using the freeze-drying method [5]. Our results confirm the enhancement of mechanical strength (doubled pick load), better water uptake and improved thermal properties in chitosan-gelatine-agarose composite hydrogels doped with halloysite nanotubes. Electron and atomic force microscopies have shown the even and uniform distribution of halloysite nanotubes within the tissue engineering scaffolds. We also utilised for the first time enhanced dark-field microscopy to visualise the distribution of halloysite nanotubes in implantation area in vivo (in rats). Our results confirm the increased in vitro cell adhesion and proliferation of cells on the nanocomposites. Importantly, no changes in viability and cytoskeleton formation were detected. Biocompatibility and biodegradability of implanted scaffolds (in rats) has confirmed that the scaffolds promote the growth of novel blood vessels around the implantation areas. The implanted scaffolds were fully resorbed within six weeks after subcutaneous implantation. Our results indicate that the halloysite-doped scaffolds are biocompatible as demonstrated both in vitro and in vivo and may find applications as promising candidates for tissue engineering applications [6].

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HOW PAINT WAS MADE BY ARTISTS? INTERACTION BETWEEN CLAYS AND PROTEINS

Agathe Fanost (1,2), Alice Gimat (1), Laurence de Viguerie (1), Philippe Walter (1), Augustin Lavirotte (1), Jean-Pierre Korb (2), Guillaume Mériguet (2), Anne-Laure Rollet (2), Maguy Jaber (1)*

(1) Sorbonne Universités, UMR 8220, Laboratoire d'Archéologie Moléculaire et Structurale, Paris, France, (2) Sorbonne Universités, UMR 8234, Physicochimie des Electrolytes et Nanosystèmes interfaciaux, Paris, France
*maguy.jaber@upmc.fr

Since the ancient times, humans have developed painting techniques with various materials such as earth or ochre for pigments and wax, egg, or animal glue for binding media. The *tempera* technique, which mixes animal glue or egg with pigments, was widespread during the Middle Age. Around 1420, thanks to Van Eyck, oily medias spread and superseded the *tempera*. It was the most used technique during the Renaissance. However, some artists like Pieter Brueghel the Elder (16thc.) and Nicolas Poussin (17th c.) reused the old technique in some of their artworks. What were their motives? What are the properties of such a painting technique?

To understand these mixtures, painting recipes were studied. They enabled to prepare model samples. The selected systems are based on green earths composed mostly of mica and smectite. Grinding at different levels the later allow, after mixing with biomolecules present in animal glue or eggs, to obtain special rheological properties. Several spectroscopy and microscopy techniques are used to characterize the materials. NMR relaxometry is used in this study to understand these interactions by investigating the proton dynamics on a wide timescale.

The preliminary results obtained by NMR relaxometry measurements highlight the dynamic of water in the minerals. T1 and T2 relaxation times point out the mobility/rigidity of sorbed water. Intensive grinding of the green earths leads to important structural changes leading to amorphous materials. The latter present different relaxation behaviour as attested by T1 and T2 measurements. The addition of the binders based on albumin or rabbit skin glue to the green earths affects the rheological properties of the obtained pigments. The water dynamics is deeply modified. The interactions between the inorganic and the organic part were investigated by vibrational spectroscopy.

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EXPERIMENTAL EVALUATION OF BENEFICIAL USE OF RANCE RIVER DREDGED SEDIMENT IN GEOPOLYMER BINDER

Rémi Farges (1)*, Baptiste Anger (2), Ameni Gharzouni (1), François Thery (2), Emmanuel Joussein (1), Sylvie Rossignol (1)

(1) Science des Procédés Céramiques et de Traitements de Surface (SPCTS), 12 rue Atlantis, 87068, Limoges Cedex, France,
(2) EDF R&D, Département Éco-Efficacité et Procédés Industriels (EPI), Les Renardières, 77818 Moret-sur-Loing, France

Sediment dredging is sometime necessary in order to keep a satisfactory level of functionality of ports, waterways and reservoirs. In a circular economy approach, there is an interest to use land-stored sediments in order to protect natural resources. In this logic, EDF R&D is working with the SPCTS to value sediments which come from hydroelectric dams or marine power plant as aluminosilicate source to develop geopolymer matrices. These new mineral binders, whose manufacture emits low CO_2, are interesting for various applications. This study uses fine sediments from “Lyvet’s sediment trap” in the estuary of the river Rance (Brittany, NW France). The physical, chemical, structural and thermal characteristics of the raw and heat treated sediments were determined to estimate their reactivity. A feasibility study was then initiated to evaluate the quantities of raw or treated sediments to incorporate in geopolymer formulations. Furthermore, the optimal formulations have been studied by FTIR spectroscopy in order to understand geopolymerization reactions.

The results show that the mineralogy of these sediments is mainly composed by quartz, carbonates and clay minerals (kaolinite, illite, micas, ...). After calcination at 650 °C, kaolinite is transformed to metakaolinite which is more reactive in an alkali medium. This observation is confirmed by the possibility to substitute about 50% of metakaolin by fine calcinated sediments to realize geopolymer binders with sufficient mechanical properties *i.e.* an unconfined compressive strength higher than 50 MPa.

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RESIDUE VALORIZATION, SUSTAINABLE CLAY LIGHT WEIGHT AGGREGATES AS GROWING MEDIUM AND CONTROLLED RELEASE FERTILIZERS

Romina D. Farías (1)*, Teresa Cotes Palomino (1), Fernanda Andreola (2), Luisa Barbieri (2), Carmen Martínez García (1), Isabella Lancelllotti (2)

(1) Department of Chemical, Environmental and Material Engineering, High Polytechnic School of Linares, University of Jaen, Linares Scientific and Technological Campus, Cinturón Sur, s/n, 23700 Linares, Spain, (2) Department of Engineering "Enzo Ferrari", University of Modena and Reggio Emilia, Via Pietro Vivarelli 10, 41125 Modena, Italy
*romina.d.farias@gmail.com

This research is focused on the valorization of agro-industrial residues (waste/by-products) and municipal post-treated cullet glass [1-3]dry sewage sludge (DSS, providedbylocal industries, as a replacement of virgin raw materials to elaborate lightweight aggregates (LWA$_S$) for their use in agronomic field as growing media and controlled release fertilizers. The incorporation of bio-based pore-forming agents into a clay formulation has been investigated in order to increase material's porosity, toboth reduce sintering temperature by means of the exothermic reaction produced bythe organic matter oxidation, and to reduce energy requirements during the firing process, finally as alternative to landfilling. It also seeks to develop sustainable LWA$_S$ capable of controlled release of nutrients for plants growing, through the valorization of different organic and inorganic wastes.

For the production of LWA$_S$ were used three types of clays (white, black and red) in two different clay-based mixtures: WB (30 wt% white-70 wt% black clay) and RC (100 wt% red clay). White and black clays were provided from a clay-pit in Bailen, Jaen Province, Spain, they are rich in quartz and calcite, predominating the phyllosilicates like illite and smectite type. In contrast, red clay provided from a clay-pit from Roncobotto at Apennines region, Modena province, Italy, contains few carbonates, predominating phyllosilicates being illite with low amount of kaolinite. The residuesused were added at the two clay-mix bases in different percentages: sludge from beer-wastewater treatment plant (SB) at 15 wt% as pore forming[4] and, as source of P and K,10 wt% of cattle bone-ash (CBA) or a fertilizer glass obtained in laboratory with glass cullet(42 wt%), CBA (40 wt%) and 18 wt% potassium carbonate (K_2CO_3)[5]. The materials were characterized in terms of chemical (XRF) and mineralogical (XRD) analyses, as well as their thermal behavior (TGA/DTA/DSC). The LWA$_S$obtainedwere subjected to drying process at 105±5 °C for 24 hours and thermally treated at 1000 °C for 1 hour in laboratory kiln. Technological parameters such as weight loss, bulk and absolute density, total porosity, water absorption, pH and electrical conductivity were determined. XRD and SEM analyses were performed for completing the samples characterization. The nutrient (P and K) release capacity was determined by leaching test according to European regulations in two different conditions: in water for 30' by using whole aggregates and in citric acid (2%), with two timeframes: 30' to ensure the immediate release of nutrients, whole and powdered aggregates, and 21 days, only whole, to verify the slow release. The eluates were analyzed by ICP-MS. The results of leaching test show the capacity of controlled nutrient release in composition containing glass, in particular for phosphorus, unlike the bone ash that releases more quantity in short time (test of 30'). The research indicates the feasibility of high-quality lightweight aggregatesmanufacturing for agronomic application, using relatively simple processing and lowsinteringtemperature and less environmental impact and economical savings.

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DELETERIOUS EFFECT OF CLAYS ON FROTH FLOTATION

Saeed Farrokhpay

University of Lorraine, GeoRessources Laboratory, 2 rue du, Doyen Roubault, 54518 Vandoeuvre-lès-Nancy, France

The increased beneficiation of progressively more complex low grade sulphide ores highlights the importance of developing strategies to process ores containing various clays. It is known that the reactivity of clays and variety of these reactions are greater than any other known colloidal material. The deleterious effects of clays in mineral processing performance are widely acknowledged but the mechanisms and concentrations involved for different minerals are not clearly established. Flotation is widely used to separate valuable mineral. While it is acknowledged that clay minerals can cause problems in mineral flotation, the literature contains conflicting evidence. In this paper, the latest findings about deleterious effect of clays on froth flotation will be discussed and the area that need further investigation will be identified. In addition, strategies to improve the process performance when clays are present will be also discussed.

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PHYSICOCHEMICAL AND UREA ADSORPTION-DESORPTION STUDY OF CHITOSAN-MONTMORILLONITE AND CHITOSAN-SAPONITE MICROSPHERE FOR SUSTAINED RELEASE FERTILIZER

Is Fatimah (1), Septian P. Yudha (1), Lusi Sopia (1), Ayu Puspita (1), Gunarti Pratiwi (1), Shaobin Wang (2)

(1) Chemistry Department, Universitas Islam Indonesia, Kampus Terpadu UII, Jl. Kaliurang Km 14, Sleman, Yogyakarta, Indonesia, (2) Chemical Engineering Department, Curtin University, Perth, Australia

The feasibility of modified clays as a carrier for slow release of nitrogen (N) was investigated. Montmorillonite and saponite kaolinite were modified using chitosan biopolymer and methenamine over intercalation method. Modified materials were thoroughly characterized using X-ray diffraction, Fourier transform infrared, differential thermal analysis and scanning electron microscopy to study the effect of surfactant modification. Adsorption-desorption study of N from urea was observed. The desorption experiment was performed in the constant flow percolation reactor. The study reports that modified clays give the better adsorption and also give longer time N supply compared to raw clays. Kinetics and thermodynamic of the adsorption-desorption study in relation to the physicochemical character of the material is presented.

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PREPARATION OF SYNTHETIC SAPONITE FROM BIOGENIC SILICA

Is Fatimah (1)*, Septian P. Yudha (1), Lusi Sopia (1), Shaobin Wang (2)

(1) Chemistry Department, Universitas Islam Indonesia, Kampus Terpadu UII, Jl. Kaliurang Km 14, Sleman, Yogyakarta, Indonesia, (2) Chemical Engineering Department, Curtin University, Perth, Australia

This work describes the process for synthesis of saponite by using biogenic silica. Saponite was prepared by sol-gel method using silica hydrogel extracted from bamboo leaves ash and rice husk ash under varied methods: hydrothermal and microwave irradiation method. The prepared materials derived from varied Si/Al content and time of aging were characterized by chemical analyses, thermogravimetric analysis (TGA), x ray diffraction (XRD), Fourier transform spectroscopy (FTIR), scanning electron microscopy and energy dispersive spectrometry (SEM/EDS). The results represent a formation of clay that was affected by the method in that hydrothermal gives better crystallinization and specific surface area compared to microwave method and the physicochemical parameter is the function of Sil/Al ratio.

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RUTHENIUM-IMMOBILIZED SAPONITE AS CATALYST FOR SOLVENTLESS MICROWAVE ASSISTED REACTION OF CITRONELLAL

Is Fatimah (1), Septian P. Yudha (1), Lusi Sopia (1), Shaobin Wang (2), Sim, Yoke Leng (3)

(1) Chemistry Department, Universitas Islam Indonesia, Kampus Terpadu UII, Jl. Kaliurang Km 14, Sleman, Yogyakarta, Indonesia, (2) Chemical Engineering Department, Curtin University, Perth, Australia, (3) Chemistry Department, Universiti Tungku Abdur Rahman, Perak, Malaysia

Green catalysis is a popular topics in green chemistry. Citronellal conversion to menthol is an interesting reaction for some toiletries, pharmaceutical and food industries. A tandem cyclization-hydrogenation is developed in this research by focusing on the synthesis of heterogeneous catalyst with high performance for a solventless conversion of citronellal. Catalyst was prepare by intercalating ruthenium bipyridinium complex into saponite interlayer and characterization was carried out by means of XRD, BET measurements, SEM-EDX and surface acidity by using pyridine adsorption. Catalytic activity of the catalyst was determined by using microwave assisted reaction. Study on the effect of ruthenium complex intercalation to physicochemical character as well as catalytic activity results was studied. The results indicated that ruthenium content affects significantly to the physicochemical character of the catalysts and the intercalation process contributes to increasing catalytic activity. The catalyst was regenerable catalyst respect to green catalysis.

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CALCINED DAM SEDIMENTS AS SUPPLEMENTARY CEMENTITIOUS MATERIALS: CHARACTERIZATION AND POZZOLANIC REACTIVITY

Antoine Faure (1,2)*, Agnes Smith (2), Coryse coudray (1), Baptiste Anger (1), Horacio Colina (3), Isabelle Moulin (4), François Thery (1)

(1) EDF R&D, EDF Lab Les Renardières, F-77818 Moret-sur-Loing Cedex, France, (2) Univ. Limoges, CNRS, ENSCI, SPCTS, UMR 7315, F-87068 Limoges Cedex, France, (3) ATILH, F-92974 Paris-la-Défense, France, (4) LERM, F-13631 Arles, France
*antoine.faure@etu.unilim.fr

The accumulation of fine-grained sediments is a phenomenon that occurs in different contexts: harbours, waterways and hydroelectric reservoirs as well. To ensure good operation, this solid material should be managed in a sustainable way. Extraction from the reservoir bed by dredging may be required. Then, sediment must be considered as waste according to European and French regulations.

As fine-grained sediments contain a substantial amount of clay minerals, a recovery solution could be a beneficial reuse as pozzolanic addition in composite-Portland cement after thermal activation. A reduced number of references can be found in literature, mainly on marine sediments. Both fixed-bed [1] and flash calcinations [2] were used. This study aims to characterize dredged materials from dams on mineralogical and physico-chemical properties and to optimize the thermal activation temperature.

Three raw sediments sampled in different French reservoirs and labelled “SF”, “SR” and “SS”, in accordance with their geographical origin, are investigated. Physico-chemical properties are analysed by different techniques: PSD by laser diffraction, density by He-pycnometry, specific surface area by both BET and Blaine methods and chemical composition by ICP-AES. Mineral compositions are assessed by XRD and thermal analyses (simultaneous TGA-DTA) are performed. The evolution of sediment characteristics is followed between 550 and 1000 °C, using ten different firing temperatures. In parallel, Frattini and saturated lime tests are performed. At selected firing temperatures, mechanical tests are performed on cement pastes using calcined sediments as Portland cement replacement (6, 20 and 35 wt%). Hydrated products obtained by reaction between the tested supplementary cementitious material (SCM) and $Ca(OH)_2$ are identified using TGA-DTA and XRD. At each step, sediments are compared to two other usual SCM: a limestone filler (LF - poorly reactive) and a silico-aluminous fly ash (FA - pozzolanic activity).

According to the sampling dam, sediment characteristics vary: clay and calcite contents, nature of clay minerals, major oxides compositions and physical properties. Optimum firing temperatures are found to be 850 °C for SF and SR and 900 °C for SS. Chemical pozzolanicity assessments show that SR and SS are more reactive than SF. Mechanical tests show better results when sediment is calcined at the optimized temperature rather than a lower temperature (600 °C) and raw material. Even if better strengths are obtained with FA as SCM, calcined sediments always give better performances than the LF. On lime-SCM blends, several hydrates are identified and, among them, carboaluminates.

As a conclusion, innovative and sustainable SCM can be suggested by dam fine-grained sediment calcination. However, reactivity after calcination vary from one sediment to another. Dredged materials require a detailed characterization to assess their potential.

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PREPARATION AND CHARACTERIZATION OF KAOLINITE-FE-TIO_2 NANOCOMPOSITES AS POTENTIAL PHOTOCATALYSTS FOR WASTEWATER TREATMENT

Maria Julia Fernandes (1), Larissa Bonfim (1), Katia J. Ciuffi (1), Miguel A. Vicente (2), Raquel Trujillano (2), Vicente Rives (2), Francisco Martín-Labajos (2), Antonio Gil (3)*, Sophia A. Korili (3), Emerson H. de Faria (1)

(1) Univ. Franca, Parque Universitário, 201, 14404-600, Franca, SP, Brazil, (2) GIR-QUESCAT, Dep. Química Inorgánica, Univ. Salamanca, 37008 Salamanca, Spain, (3) Dep. Química Aplicada, Univ. Pública de Navarra, 31006-Pamplona, Spain

Emerging Organic Pollutants (EOPs) exist in many commercial products and have been detected in various aquatic environments around the world. EOPs have become a matter of concern because they are potentially toxic and persistent and are prone to accumulate in human tissues [1-3].

In this work, a natural purified São Simão's (Brazil) kaolinite was used to synthesize a new nanocomposite with $FeCl_3$ and Ti(IV) isopropoxide *via* a non-hydrolytic sol-gel route; the final materials were obtained by thermal treatment at various temperatures. Kaolinite (10.0 g), ethanol (200 cm^3), acetic acid (1 cm^3), and Ti(IV) isopropoxide (2.0 cm^3) were mixed at room temperature in a beaker, and stirred for 24 h. The suspension was washed with distilled water and centrifuged several times, to remove the un-anchored alkoxide and other reagents from the surface of the clay. The solid was dried at 100 ºC for 24 h and split into four fractions: one was used as dried, and the other three were heated in air at 400, 700, and 1000 ºC, respectively, for 24 h. These temperatures were chosen based on the thermal analysis of the as-obtained solid.

The powder X-ray diffractogram and the infrared spectrum showed that kaolinite was very pure. The treatment with Ti(IV) isopropoxide and $FeCl_3$ did not produce any change in the basal spacing of kaolinite (7.14 Å); actually, due to the difficult swelling of this clay mineral, the direct insertion of the alkoxide into the interlayer region of kaolinite was not expected. This suggests that functionalization occurred at the lateral silanol and aluminol groups. On calcination, anatase was formed at 400 ºC; at higher temperatures anatase and rutile were formed and kaolinite was amorphized, and finally it transformed into metakaolinite. It may be remarked that the characteristic peaks of anatase are very close to those from kaolinite, which makes difficult the analysis.

Kaolinite promoted the dispersion of the active phase around the clay surface, which in turn promoted the fast degradation of ibuprofen, when applied to the degradation of this anti-inflammatory drug. This influence was confirmed by comparing the results when using separately the isolated components (TiO_2 and kaolinite) and the nanocomposite, finding that the formation of the nanocomposite played a fundamental role on the photodegradation pathways. It is proposed that formation of the kaolinite-Fe-TiO_2 nanocomposite promotes the interaction of ibuprofen molecules with the surface of the solid and TiO_2 dispersed in the matrix promotes the generation of highly reactive OH· radicals.

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MAGNESIAN CLAYS AS INDICATORS OF DEPOSITIONAL ENVIRONMENTS

Ana Mª. Fernández (1), Jose I. Escavy (2), Mª Josefa Herrero (3), J. J. Rey (1)*, J. Arribas (3), A. Melón (1), Luz Mª. Robredo (1), Dolores Mª. Sánchez (1), Miguel Sánchez (1), Miguel A. Labajo (1)

(1) CIEMAT, Dpto. Medio Ambiente, 28040 Madrid, Spain, (2) Dpto. Ingeniería y Morfología del Terreno. Escuela Técnica Superior de Ingenieros de Caminos, Canales y Puertos, Universidad Politécnica de Madrid, 28040 Madrid, Spain, (3) UCM, Dpto. de Petrología y Geoquímica, Facultad de Ciencias Geológicas, UCM, 28040, Madrid
*anamaria.fernandez@ciemat.es, ji.escavy@upm.es, mjherr@ucm.es

The research herein presented concerns the characterization of the depositional systems of the Miocene units found in the “Sinclinal de Villar de Cañas”, located within the Loranca Basin (westernmost part of the Tajo Basin, Spain). The Loranca basin was formed during the Eocene-Oligocente time span. The Altomira hight, to the east of the basin was uplifted during the Oligocene to lower Miocene dividing the Tajo basin into the Madrid and Loranca sub-basins. The Loranca sub-basin was filled by fluvial and lacustrine sedimentary sequences. The sedimentary infill is characterised by three main units called the Lower, Upper and Terminal units. Alluvian fan deposits characterise the edges of the basin, which show a basinal change into fluvial channel deposits and playa-lakes. Towards the center of the basin appear saline lakes, with saline mud flats and salt-pan deposits. The general vertical sequence indicates the higher aridity character of the basin climate towards the end of the succession.

The studied sequence has a total thickness of above 200 m that can be divided into four main units. The lowermost unit (UI) was deposited in an environment dominated by alluvial fans, inter-channel ponds, and flood plains. Higher up there is a retrogradation of the fan systems and the establishment of a palustrine and shallow lacustrine environment (LBI Unit), where deposits are characterized by dolomitic carbonates. Later on, saline lakes occupied the area, leaving a calcium sulfate-rich record in the sequence (YB Unit). This unit is formed by three subunits: i) the lower subunit (YB1) is composed by an alternation of shales, secondary gypsum after anhydrite, minor sodium sulphate minerals and anhydrite; ii) the second subunit (YB2) is mainly composed of primary gypsum deposits where several brine dilution-concentration sequences occur; iii) the uppermost YB subunit (YB3) is characterized by an alternation of shale and primary gypsum beds, and begins with the entrance into the basin of detritic materials transported by water that produced the dilution of the brine. The sequence ends with a progradation of the sedimentary systems, dominating a palustrine and shallow-lake environment, and the sedimentation of dolomitic and gypsiferous shales (LBS).

The materials are mainly composed of gypsum and carbonates (magnesite and dolomite, depending on the location), although they have variable amounts of illite and magnesium clay minerals. The characterisation of these clay minerals by using different techniques, such as XRD, FTIR, TG-DSC, and XRF of closely spaced samples from various cores, reveals a clear clay distribution related to different parts of the depositional environment. Once determined the different clay minerals content, their appearance has been related to the different lithologies and environmental interpretations of the different units. The main variations appear related to the content of palygorskite, illite and Mg-smectite, and minor amounts of kaolinite and/or chlorite. UI contains detrital clay-minerals, illite, dioctahedral smectite, I/Sm mixed-layers, and kaolinite and chlorite, being palygorskite almost absent. LBI is characterised by illite as the main clay mineral, and a rise in palygorskite content. Unit YB is characterised by having a trioctahedral Mg-smectite (saponite) as the main clay-mineral, although at some locations palygorskite and illite are also present. In the YB unit, the practical total absence of chlorite and kaolite is conspicuous.

This analysis has led to complete and understand the basinal distribution of the sedimentary environments and to determine more accurately their lateral and vertical distribution.

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STATE OF WATER UNDER CONFINEMENT AND TEMPERATURE THROUGH THE STUDY OF THE FEBEX BENTONITE PORE WATER

Ana Mª Fernández*, Jesús J. Rey, Sergio Fernández

CIEMAT, Dpto. Medio Ambiente, 28040 Madrid, Spain
*anamaria.fernandez@ciemat.es

Bentonites are foreseen fundamental in the retention of possible contaminants towards the biosphere because of their favourable properties. A main parameter to define the ionic transport and degree of water adsorption (swelling) in these materials is the chemical composition of the pore water, which is in equilibrium with the mineral surfaces of the clay minerals. This equilibrium could be modified by the degree of compaction/consolidation (porosity) of the material, salinity, type of clay minerals, type of exchangeable cation, and temperature; affecting to the amount of free water and interlamellar water in the system; and at the end to the accessible porosity for the diffusion of ions.

In different studies, it has been observed that, although the solute transport in bentonites is governed by diffusion, the porosity values derived from experimental data indicate that only part of the total water porosity is available for anion diffusion. Anion exclusion values between 5-8% in bentonites [1,2] and 50-70% in clayrocks [3] are illustrated in the literature. Most differences are related with the type and percentage of clay minerals involved (swelling, non-swelling), the pore water ionic strength, temperature, and the degree of compaction of the clayey material. These parameters directly impact on the amount water adsorbed in the interlamellar space; and hence, in the types of water and water distribution in the porous space and microstructure; as well as in the pore water composition through ions are transported through the environment. This is due to the compacted clay minerals are capable of acting as ion excluders, i.e., behave as semi-permeable membranes, because of the negative net charge on the clay mineral surfaces.

In this work, the interlayer and pore water composition relationship was analysed from the study of different compacted bentonite blocks obtained during dismantling of a large scale *in situ* test. The FEBEX *in situ* test was a non-isothermal test (100 ºC maximum) in which a compacted bentonite barrier was naturally hydrated along 18 years by groundwater from a granitic formation. Temperatures in the bentonite rings at sections surrounding the two heaters installed in the experiment, reached and maintained at steady state conditions over time (inner ring: 93-99 ºC; intermediate: 54-75 ºC and outer: 37-45 ºC). This test provided the opportunity to study the evolution of a real clay-water system under confined conditions, changes in salinity, different clay:water ratios and temperature variations, which affect the clay structure, types of water and its distribution, and porosity.

After dismantling of the FEBEX *in situ* test, bentonite blocks obtained at two different sections (heated and non-heated) along a radius were analysed. Squeezing tests for determining the chemical composition of the pore water as a function of the thermal and hydraulic gradient, XRD for analysing basal spacings, determinations of CEC and cation exchange population, layer charge, water adsorption isotherms and other physical and physico-chemical measurements were the main techniques used. Anion accessible porosity values obtained from comparison between squeezing and leaching tests were also obtained. For dry densities between 1.43 and 1.63 g/cm^3, the anion accessible porosity ranged between 0.43 and 0.25, decreasing when dry density increases.

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CHROMIUN AND COBALT SORPTION ON MODIFIED MONTMORILLONITE SYSTEMS

Facundo Barraqué (1), Cesar Fernández Morantes (2), Luciana Montes (3),
Mariela A. Fernández (1)*, Mercader Roberto Carlos (3), Rosa M. Torres Sánchez (1)

(1) CETMIC-CONICET CCT La Plata, LA Plata, Argentina, (2) Universidad Nacional de San Martín (UNSAM). Fac. De Ccia. Y Tecnología -Laboratorio 3ia. San Martín, Bs. As, Argentina, (3) IFLP- CONICET CCT-La Plata y Fac. De Ccias. Exactas, UNLP, La Plata, Argentina

Heavy metals pollution is an important environmental topic due to the potential health problems. In particular, Cr and Co are essential metals but in relatively high concentration are potentially toxics and they are mainly released from several industrial processes. Sorption of metals on clay systems is a frequently used methodology due to its simple application, high sorption capacity and sorbent material´s low cost. Actually, the development of magnetic clay systems allows the pollutant removal in continuous process, promoting the sorbent separation advantage by an external magnetic field.

This work analyse Cr and Co sorption on different montmorillonite sorbents: a raw from Argentina (Mt), an organic (OMt) and an organic-magnetic derivative (OMt-Mag), in batch conditions and with initial concentration from 10 to 60 mg/L; ratio solid/solution= 1 g/L, room temperature, contact time 24 h, and pH=6 and 3 for Co and Cr, respectively. Cr and Co in solution after sorption experiments was determined by colorimetric method [1,2]. Sorption isotherms were fitted to Langmuir, Freundlich and Sips mathematical models.

OMt sample was obtained after dispersing 2 g of Mt in 100 ml of distilled water containing 0.6 g of hexadecyl trimethyl ammonium bromide in order to achieve 100% of cationic exchange capacity. The suspension was stirred for 24 h at 60 °C. OMt-Mag sample was synthetized by co-precipitation method [3].

Sorbents were characterized by X-ray diffraction (XRD), zeta potential, Mössbauer spectroscopy and vibrating sample magnetometer (VSM) techniques, while solid resulted from maximal adsorption experiments (C_i = 50 ppm) were also analysed by XRD and zeta potential in order to determine changes in interlayer space (d001) and electric surface charge, respectively.

The experimental adsorption points fitted better to Freundlich than to Langmuir or Sips models, for all sorbents analysed. For Co, K_f values were 7.2, 3.0 and 3.0 for Mt, OMt and OMt-Mag, respectively. Although Mt sample showed the highest Co affinity, OMt-Mag sample presented a substantial sorption capacity between 81 to 75% when the initial concentration of Co ranged from 10 to 60 mg/L. For Cr, K_f values were 1.4, 0.4 and 0.2 for OMt-Mag, OMt and Mt sorbents, respectively. In this case, sorption percentage for OMt-Mag did not exceed 30%. The sorption percentage and K_f values obtained indicated that the sorbents studied were more efficient for Co than for Cr removal.

XRD results showed that after Cr and Co sorption the d001 value of Mt sample increased (0.30 and 0.32 nm) respect to raw Mt, while for OMt-Mag the d001 value remained constant (1.87 nm), indicating an entrance to the interlayer and surfactant screening, respectively. For OMt sample an increase and decrease of d001 values (0.11 and 0.06 nm) were found for Cr or Co sorption, respectively.

Zeta potential measurements showed the classical negative surface charge for Mt sample while OMt and OMt-Mag samples indicated a positive surface charge. After Cr and Co sorption, the negative charge of Mt decreased. While in OMt and OMt-Mag, after the heavy metals adsorption, a decrease the positive charge was found except for Cr sorption on OMt where the positive charge remained constant. This behaviour could be assigned to some contra-ion adsorption effect.

Mössbauer spectra from Mt and OMt were similar. They were fitted by 4 paramagnetic Fe sites, 3 corresponding to Fe^{3+} and one to Fe^{2+}. Mössbauer spectra of OMt-Mag showed, in addition to the same 4 paramagnetic sites, two magnetic Fe environments. The hyperfine parameters obtained for those sites were in agreement with that corresponding to magnetite, although the area ratio did not correspond to the expected for the magnetite ideal crystal. The obtained relative fraction of magnetic sites was 41±3%. Saturation magnetization value of OMt-Mag (5.43 Am^2/kg) was higher than those for Mt ($1.75\ 10^{-3}\ Am^2/kg$) and OMt samples ($2.63\ 10^{-3}\ Am^2/kg$).

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ARGENTINIAN SOILS/MONTMORILLINITE-CARBON SYSTEMS: ADSORPTION BEHAVIOUR AGAINST TWO PESTICIDES

Emilia Zelaya-Soule (1), Mariela A. Fernández (1)*, Maria L. Montes (2),
Fabián Suarez-García (3), Rosa M. Torres Sánchez (1), Juan M. Diez Tascón (3)

(1) CETMIC-CONICET CCT La Plata, LA Plata, Argentina, (2) IFLP-CONICET CCT La Plata, UNLP, Argentina, (3) Instituto Nacional del Carbon, INCAR-CSIC, Oviedo, España

The addition of pesticides to the soil to maintain the yield in the agricultural production generates concern about the soils and waters contamination. Among the remediation techniques, amendments with activated carbons have been used with success to restore soils contaminated [1]. The adsorption capacity of montmorillonite combined with that of carbon, can be considered as an economic and alternative system to activated carbon that can be used for same purpose. Among the pesticides utilized in Argentina, in fruit production, thiabendazole (TBZ) and chlorpyrifos (CPF) are applied in the greatest quantity and their behaviour in cultivated soils as well as in montmorillonite carbon systems (MCS) has not been evaluated.

In this work, thiabendazole and chlorpyrifos sorption on nine different surface soils and MCS were studied. Characterization of the product obtained by both pesticides and MCS was conducted in order to understand the sorption surface sites involved. The MCS synthesis was performed using a similar procedure to that reported by Martın-Jimeno et al. [2]. An Argentine montmorillonite from Rio Negro province was used as a carbon support (from 10 and 25 mg/L of dextrose). A suspension of 10 mg/L of montmorillonite was prepared and then 5, 10 or 25 mg/L of dextrose was added. The obtained suspension was sonicated by 3 h and then maintained at 180^{o}C during 16 h on hydrothermal reactor. The resultant material (MCS-5, MCS-10 and MCS-25) was washed and dried at 60^{o}C.

MCS sorbents were characterized by BET, XRD and SEM. Some soil characteristics, as clay content, surface area and organic carbon (OC) were also determined by conventional methods. MCS sorbents with the adsorbed pesticides were characterized by IR measurements.

Sorption studies were performed at room temperature in batch conditions, using 25 mg/L of TBZ or CPF, ratio solid-solution = 0.8 g/l, pH = 6 and 24 h of contact time. The TBZ or CPF adsorbed were determined as the difference between the initial concentration and that at equilibrium determined by HPLC.

Surface area for all MCS samples was around 1m^2/g. XRD showed that montmorillonite structure of all MCS samples was not modified, while SEM analysis indicated laminar structures without presence of free dextrose. Soils showed a clays range between 17 and 54%, specific surface area between 12 and 39 m^2/g, and OC between 1 and 5%.

TBZ sorption percentage on the different soils varied between 5 and 68% and the sorption capacity was positively correlated with the clay content (Pearson correlation coefficient = 0.88). Similar results were observed for CPF sorption, obtaining a Pearson correlation coefficient = 0.73). No correlation was observed between soil OC content and pesticides sorption capacity of the soils. Relatively high sorption percentages of TBZ on the MCS samples were obtained (around 95%).

The FTIR spectra of the adsorbed pesticides showed peaks corresponding to TBZ and CPF in the MCS.

These preliminary results indicated the capacity of MCS sorbents to retain the pesticides studied and their potential use as soil amendments.

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STABLE ISOTOPE COMPOSITION OF KAOLINITE FROM A LATERITIC PALEOWEATHERING PROFILE IN THE GUADALQUIVIR BASIN (SPAIN)

Juan Carlos Fernández-Caliani

Department of Earth Sciences, University of Huelva, 21071-Huelva, Spain
caliani@uhu.es

This study was undertaken to investigate a highly kaolinitic saprolite overlain by a ferruginous pisoliticduricrust formed by intense weathering of Pliocene arkosic sands at mid-latitude (~37º N), in the north-western margin of the Guadalquivir Basin (SW Spain). The geomorphological features and the mineralogical evolution of the weathering profile seem to be consistent with a lateritic paleosol evolved under humid subtropical conditions [1]. The hydrogen and oxygen stable isotope ratios of kaolinite were determined in order to further confirm this interpretation, providing the first estimates of the isotopic composition of meteoric water and temperature of the ancient weathering system.

Five kaolin samples representative of the white sandy clayey saprolite were selected for isotopic analysis. The <2 mm fraction was extracted from the bulk sample by wet sieving, settling in deionized water and centrifugation. The clay separates consist of more than 95% kaolinite with impurities of quartz and mica, as confirmed by XRD and SEM-EDS analyses. Isotope stable measurements were performed at Activation Laboratories (Canada)using a Thermo-Finnigan Delta Plus XP continuous-flow isotope-ratio mass spectrometer. The isotope values are reported in the standard delta notation relative to V-SMOW, with a precision of 0.1‰ for $\delta^{18}O$ and 3‰ for δD.

Kaolinite showed $d^{18}O$ values ranging from 17.3‰ to 20.0‰ and averaging 19.2±1.1‰, while the δD values varied between -71‰ and -60‰ with a mean value of -65±5‰. These isotope ratios match those of western European kaolins that formed at paleolatitudes of 35º to 40º N [2]. The intraprofile variation in the isotopic composition of kaolinite could be due to seasonal orannual changes in the isotopic composition of infiltrating rainfall. When plotted on a δD-$\delta^{18}O$ diagram, the samples fall on, or slightly to, the left of the kaolinite weathering line ($\delta D=7.5\delta^{18}O-220$), which delineates the composition of kaolinites in oxygen and hydrogen isotopic equilibrium with meteoric waters at Earth-surface temperatures.

Assuming that kaolinite formed in equilibrium with water slying on the global meteoric water line ($\delta D=8\delta^{18}O+10$), and was not subjected to significant isotope exchange after formation, the $\delta^{18}O$ and δD mean values indicate a crystallization temperature of 24±5 ºC, which is higher than the local present-day annual mean air temperature (~18 ºC). For this calculated temperature, the value of the oxygen isotope fractionation factor between kaolinite and water (a_{k-w}) is about 1.0248 [3], which implies that kaolinite formed in the presence of meteoric waters with an isotopic composition ($d^{18}O=$ -6.0‰ to -4.5‰, and $\delta D=$ -38‰ to -26‰) similar to that of modern precipitation water in the south-western of Iberia [4].

Although the climate prevailing at the time of kaolinization (Late Neogene) was comparatively warmer and wetter than today and would have favoured weathering processes, the unconsolidated sandy parent material provided a well-drained and easily leached substrate that played a determining role in the development of the deeply kaolinized saprolite at extratropical latitude location.

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LIME-METAKAOLIN BINDER: ALKALI ACTIVATION *VERSUS* POZZOLANIC REACTION

Ana Fernandez-Jimenez, Angel. Palomo

Instituto Eduardo Torroja (IETcc), CSIC, C/Serrano Galvache 4, 28033 Madrid, Spain

Metakaolin (MK-$2SiO_2.Al_2O_3$), obtained after the dehydroxylation of the kaolinite ($Al_4(SiO_4O_{10})(OH)_{10}$), is known for its high pozzolanic capacity. It reacts with calcium hydroxide to give rise to hydrated calcium silicates (C-S-H gel or C-(A)-S-H gel when Al is incorporated in the structure) which are X-ray amorphous phases responsible for the strength and durability of cementitious materials.

Metakaolin, traditionally used in mortars of lime-puzzolana or as an additive in Portland cement mortars [1-2], has been recently used in a third generation of binders [5], alkaline cements [3-4]. In a system with absence of CaO and an alkaline pH, MK reacts with the alkalis (Na or K) to give rise to N-A-S-H gels. This paper explores what happens when the system has CaO and an alkaline pH and which reactions prevail depending on the pH; the pozzolanic reaction or the alkaline activation. Further to these aims, the mechanical behavior and the reaction products of MK/$Ca(OH)_2$ (80/20) pastes mixed with water, a solution of NaOH of moderate alkalinity (5M) and high alkalinity (8M), were determined. The reaction products had been characterized by XRD and NMR. The results reveal that pH is decisive in controlling the type of reaction and gels formed.

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CONNECTING LENGTH AND TIME SCALES FOR THE ANALYSIS OF WATER DIFFUSION IN SWELLING CLAY POROUS MEDIA

Eric Ferrage (1)*, Fabien Hubert (1), Emmanuel Tertre (1), Pierre Levitz (2), Laurent J. Michot (2), Patrice Poirion (3), Alfred Delville (3)

(1) IC2MP-Hydrasa, UMR 7285 CNRS, Université de Poitiers, 86022 Poitiers, France, (2) PHENIX, UMR 82324 CNRS, Université Pierre & Marie Curie, 72522 Paris, France, (3) ICMN, UMR 7374 CNRS, Université d'Orléans, 45071 Orléans, France
*eric.ferrage@univ-poitiers.fr

The anisotropic properties of water migration in natural systems containing swelling clay minerals (smectite or vermiculite) is most often driven by [1] the bidimensional diffusion in interlayer space of the particles and [2] the mutual arrangements of these lamellar particles in the porous media, which induce additional pathways for water transfer.

At the crystal scale, combination of experimental diffraction/scattering techniques and molecular simulations can be used to unravel the details in the organizational and dynamical properties of the fluid confined in the interlayers of swelling clay minerals [1,2]. In addition, such a collation procedure provides key quantitative information about the validity of the semi-empirical atomic interaction parameters used in theoretical simulations.

In order to connect the diffusion of water obtained at the scale of the interlayer nanopore with macroscopic property of diffusion, representative porous media for swelling clay minerals are crucial. For montmorillonite, the determination of particle morphology is delicate due to its osmotic crystal swelling in water saturated conditions. To tackle this problem, our efforts have focused in the experimental characterization of swelling clay porous media composed of vermiculite minerals which display similar particle size and shape once immersed in water [3,4]. An algorithm, similar to the one proposed by Coelho et al. [5], was used to mimic the three-dimensional organization of swelling porous media for particles having elliptic disk morphology [6]. The obtained virtual porous media are used to perform Brownian Dynamics simulations. Based on the consideration of water diffusion in both interlayer and inter-particle porosity, the obtained results are found to be in fair agreement with experimental data. This allows getting additional insights onto the role played by particle organization on the overall macroscopic diffusion of water.

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TRACES OF PERMIAN TO JURASSIC BURIAL DISCRIMINATED FROM THE CRETACEOUS OROGENIC METAMORPHIC PATTERN (UPPER-AUSTROALPINE, GRAUBÜNDEN, SWITZERLAND)

Rafael Ferreiro Mählmann (1,2,4,5)*, Monika Wolf (3), Daniel Bernoulli (4), Rainer Petschick (5), Patrick Meister (4,6), Josef Mullis (2), Matthias Giger (7), Hans Krumm (5)

(1) Technische Universität Darmstadt, Institut für Angewandte Geowissenschaften, Technical and Low Temperature Petrology, D-64287 Darmstadt, Germany, (2) Universität Basel, Mineralogisch-Petrographisches Institut, CH-4056 Basel, Switzerland, (3) Mergelskull 29, D-47802 Krefeld, Germany, (4) ETH Zürich, CH-8092 Zürich, Switzerland, (5) Institut für Geowissenschaften, Goethe Universität Frankfurt am Main, D-60438 Frankfurt, Germany, (6) Department of Geodynamics and Sedimentology, University of Vienna, A-1090 Vienna, Austria, (7) Dammweg 27, CH-3604 Thun, Switzerland

In the Permian and Triassic sediments of the Upper Austroalpine nappes high coalification and illite aggradation gradients are related to pre-Alpine burial thermal pattern. An anthracite stage of rock maturity and epizonal illite Kübler-Index (KI) values in Scythian sediments were related to a post-volcanic heating [1]. The knowledge about the age of hyperthermal heating between the Variscan and the Alpine orogeny is limited. In the last decade fingerprints of a Permian to Triassic high-temperature/low-pressure metamorphism are also find out in Austroalpine basement nappes, but the influence of aborted rifting and graben tectonics in the Triassic and rifting and crustal thinning in the Jurassic on the diagenetic to metamorphic pattern is not well known. For a better understanding of the thermal conditions between the Upper Carboniferous (Variscan exhumation) and the Late Cretaceous (Alpine nappe stacking) the Silvretta nappe in Graubünden was selected. In this unit, basement and sedimentary rocks are in a stratigraphic succession. Graben structures are filled with Permian acid volcanoclastic and ignimbrite rocks. Also in the basement Upper Carboniferous diabase/dolerite dykes are giving evidences for volcanism. Alpine metamorphism did not overprint all traces of the retrograde path of the Carboniferous andalusite-facies metamorphic peak. During the Alpine orogeny the sedimentary rocks did not exceed diagenetic to low anchizonal conditions [2]. Therefore, the burial pattern can be used to reconstruct the paleo-geothermal evolution. Only Permian to Upper Triassic sediments shows epizone metamorphism. On the basis of petrologic and geochemical studies, followed by fluid inclusion thermo-barometry P-T conditions of the metamorphism were calculated. Radiometric mica-illite model-ages and fission-track ages determine the thermal evolution of post-Variscan cooling, Permian to Jurassic burial, and Alpine orogenic heating. Coalification gradients, clay mineral aggradation gradients, and illite-smectite relations are used to fit Arrhenius type time-temperature-pressure models based on empirical or kinetic based rate equations [3,4,5]. The results indicate an increase of diagenetic grade from the Jurassic to Upper Triassic in the sedimentary section and a steep increase of metamorphism in the Carnian to Permian part. The hypothermal gradient in the Jurassic sediments is the result of Alpine diagenetic to anchizone metamorphic heating. The increase to hyperthermal gradients in the Triassic section and at the contact with the volcanic rocks was inherited from a Permo-Triassic diasthathermal event prior to nappe stacking. Mica ages of 300 to 260 Ma from the basement are giving the upper and lower limits of the Permian metamorphism. A subsequent period of varying heat flow from Permian to Jurassic times is necessary to explain the metamorphic pattern for the best fit of modelling results in the Silvretta nappe. Part of the anchi- to epizone gradient (lower stratigraphic section) was formed under steady state heat flow conditions and shows typical burial correlations between different methods [6]. The stratigraphic younger section shows high disequilibrium conditions, thus different methods used to determine grade of diagenesis give different results on diagenesis of a short orogenic event complicated by hydrothermal patterns.

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INFLUENCE OF FINENESS OF RAW CLAY AND TEMPERATURE OF CALCINATION ON PERFORMANCE OF CALCINED CLAY-LIMESTONE BLENDED CEMENTS

Sergio Ferreiro (1)*, Mariana Canut (2), Jakob Lund (1), Duncan Herfort (1)

(1) Aalborg Portland A/S - Cementir Holding S.p.A., 9100 Aalborg, Denmark, (2) FLSmidth A/S, 2500 Valby, Denmark
*sergio.f.garzon@aalborgportland.com

Workability and strength performance of blended cements with 35% replacement level have been investigated for two calcined clays (mostly containing 2:1 clay minerals) and mixtures with limestone. Raw clays were flash calcined at different temperatures and with different raw meal fineness, but ground to similar 45 µm residues after calcination. The results show both temperature and fineness of the raw clay have a noticeable effect on the morphology and grindability of the resulting calcined particles, which results in different performance in terms of kinetics and long term reaction degree of the calcined clay, and workability and strength development of the blended cements in mortar. Workability is noticeably influenced by the calcined clay content in the cement and the fineness of the raw clay to a higher extend when calcined at low temperatures, due to higher specific surface areas and finer particle size distribution of the ground calcined products. In contrast, workability progressively improves with the increase of the calcination temperature due to resulting lower specific surface area, as a consequence of partial crystallization at the surface and a corresponding reduction in amorphous phase, which gives a round shape to some of the calcined clay particles. Strength performance improves at temperatures up to 900 °C, leveling off at up to 1000 °C for coarsely ground raw clays, whilst the best reactivity is found for the more finely ground raw clays calcined between 800 and 900 °C. Raw clays with higher contents of montmorillonite exhibit further formation of crystallized phase at a slightly higher temperature of calcination (925 °C), which reacts more slowly with $Ca(OH)_2$ on hydration of a cementitious system than the amorphous phase. This results in lower performance at 28 days than achieved at optimum calcination temperatures, but equivalent performance after 90 days of hydration.

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*Research and Development Center, Aalborg Portland, 9220 Aalborg, Denmark

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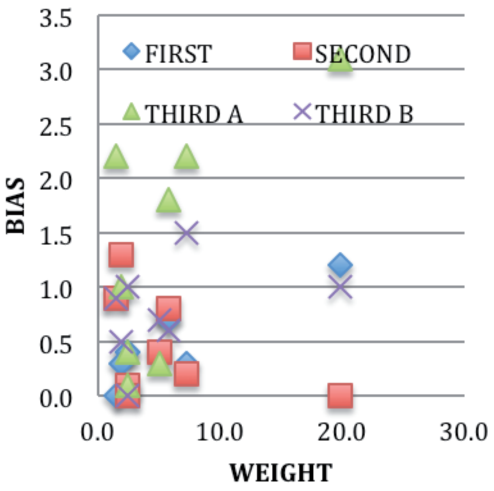
POST - REYNOLDS CUP QUANTITATIVE PHASE ANALYSIS

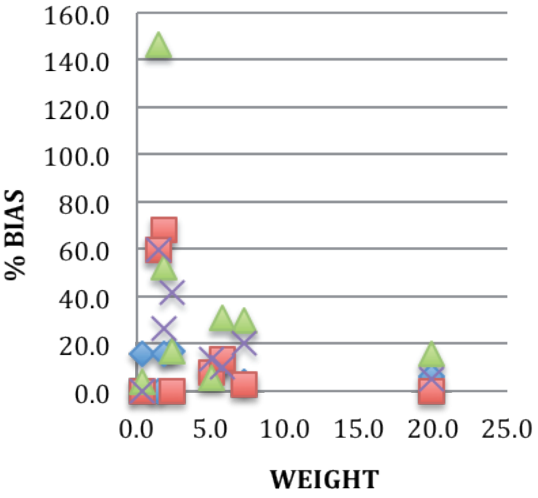
Ray E. Ferrell, Jr.

Professor Emeritus, Department of Geoscience, Louisiana State University, Baton Rouge, Louisiana, U.S.A. 70803

In the last decade, the Reynolds Cup competition has boosted interest and improved techniques for the quantitative determination of minerals by X-ray Powder Diffraction (www.clays.org/Reynold%27s.html). Participants were allowed to use any analysis method to provide abundance estimates of 12-20 minerals in three carefully prepared samples.

In the first six contests, approximately 20% of the entrants employed single peak methods, 20% employed whole pattern measurements, and 60% used Rietveld programs for quantification (Raven and Self, https://nist.gov/document-4954). Bias, the absolute value of the difference between the supplied weight % and the measured value, was used to assess the correctness of the results. The bias for the clay and other mineral estimates varied from 5 -10 for the winning analysts to more than 400 for less successful contestants. Bias and % Bias values obtained by the top four investigators for quartz, calcite and chlorite are shown below. Each point represents quartz, calcite or chlorite in one of the three RC-7 samples. Many of the determinations had a small bias and the % bias increased with smaller amounts of the mineral.





Quantitative estimates by the four groups were sometimes very different suggesting the results were often not very robust. This, plus the variable methods employed and the failure to assess repeatability indicate that the RC results have to be revisited if we want to improve quantification. A systematic evaluation of potential errors in sample preparation, intensity data collection, and calculation algorithms by a national society or AIPEA has the potential to produce a certifiable quantitative procedure that can be traced to standard reference materials. A handbook with a detailed protocol for each of the analysis steps is one potential product. This collective effort should result in improved documentation of quantitative methods that will benefit interlaboratory correlation.

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SQUEEZED INTERSTITIAL WATER AND CLAY SOIL PROPERTIES IN BRADANIC PLEISTOCENE BLUE CLAYS

Maria Dolores Fidelibus (1)*, Filomena Canora (2), Ilenia Argentiero (3), Roberta Pellicani (3), Giuseppe Spilotro (3)

(1) Department of Civil, Environmental, Land, Building Engineering and Chemistry (DICATECh), Politecnico di Bari, Bari, 70125, Italy, (2) School of Engineering, Università della Basilicata, Potenza, 85100, Italy, (3) Department of European and Mediterranean Cultures (DICEM), Università della Basilicata, Matera, 75100, Italy
*ilenia.argentiero@unibas.it

Basic statements of previous studies have already pointed out the close relation between the clayey soil geotechnical properties and concentration and chemical composition of interstitial fluids.

Present developments, besides adding new supports to these statements, remark the need to integrate the theory issues and the laboratory test results in the natural contexts.

This effort leads to identify as critical, in determining the behaviour of the clayey soils, the differences (naturally existing or human induced) between the chemical components and their concentration in pore waters and those of freely circulating water in discontinuities and on the border of clayey masses.

The extent and direction of related phenomena depend on a series of geomorphological and hydrogeological conditions, which define initial clay conditions, type and range of concerned differences and time limits of acting processes.

The study was performed on blue clays belonging to a wide region, geologically known as Bradanic Foretrough (Southern Italy). Sampling has been performed in different test sites, involved in engineering problems: building and building damages, tunnelling and landsliding. For each sample pore water has been extracted by squeezing in a special high pressure cell and subject to physico-chemical analysis. These pore water features have been related to those of free circulating waters and related to the main geotechnical characteristics of clay soils.

The interaction among different fluids, environmental or free circulating water and pore water of different chemical composition, involves the variation of various clay properties: suction, osmotic pressure, dielectric constant, composition of the diffuse double layer, field of the electrical forces inside the double layer.

Long term or seasonal variation of ionic concentrations in waters mainly circulating along clay fractures, cuts or excavations, caused by natural or human changes of environmental conditions, may determine unsteady state conditions and may cause disequilibrium between exchange complex and interstitial water.

The consequences are the change of both dielectric properties and electrical forces inside the diffuse double layer. Furthermore, a soil, of ancient geological origin, can exhibit, at present, a sudden work against the gravitative force due to overburden or a foundation by swelling or, most rarely, ensuing different border conditions, a big settlement under relatively insignificant heads.

These phenomena have been evaluated, up to now, in terms of swelling pressure, as geotechnical equipment allow. However, a better understanding can be gained using energetic terms: the energy balance is well correlated to the energy released by the soil volume when interacting with external water

The experimental results and in situ surveys allow concluding that a complete site characterization can be made only with the evaluation of both pore water and ambient water chemical composition, even if properly carried out geotechnical tests may correctly predict the expected behavior.

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NEW IRON-BASED LAYERED DOUBLE HYDROXIDES: SYNTHESIS, CHARACTERIZATION AND INSIGHTS UPON PHARMACOLOGICAL APPLICATIONS

Mariana P. Figueiredo*, Vera R. L. Constantino, Vanessa R. R. Cunha

Departamento de Química Fundamental, Universidade de São Paulo, São Paulo - SP, 05508-000, Brazil
*figueiredompires@usp.br

Inclusion compounds have been studied for pharmaceutical formulations in order to transcend adverse drug characteristics as low solubility, decomposition and side effects from administration. Layered double hydroxides (LDHs) possess great potential to act in drug storage and as delivery systems. This class of materials has the general formula $[M^{II}_{(1-x)}M^{III}_x(OH)_2](A^{n-})_{x/n}{\cdot}zH_2O$ (M^{II}: divalent metal, M^{III}: trivalent metal, A^{n-}: n-valent anion) with a structure based on brucite-like layers. The di and trivalent ions are distributed in the center of the octahedral which is formed by six hydroxyl groups, while the A^{n-} and water molecules occupy the interlayer region. The A^{n-} is an exchangeable anion as Cl^-, NO_3^-, CO_3^{2-} or organic anions. The biocompatibility of LDHs, an essential characteristic to allow pharmacological applications, is related to the layer contents [1]. The partial substitution of Al^{3+}, the most common trivalent cation present in the LDH compositions, for the endogenous Fe^{3+} ion tends to improve the biocompatibility but still maintaining the contribution of the high organization and crystallinity conferred by the aluminium. There are few papers reporting LDH hybrids composed only by iron or Fe/Al as trivalent cations. The intercalation of organic species and drugs have been challenging in the presence of iron, and for the Zn-LDH materials even the isolation of pure LDH phase is difficult.

This work presents the synthesis and characterization of new ternary LDHs with composition M2Fe0.5Al0.5-Cl (where M = Mg or Zn), as well as, insights of these phases applications in drug delivery systems, through the intercalation of the nonsteroidal anti-inflammatory drug (NSAID) naproxenate (NAP), used as a model species, and its in vitro release study. Up to the present time, the intercalation of NSAIDs into ternary LDHs was performed just in matrices with very low iron contents [1,2]. The LDH-Cl phases were obtained by coprecipitation method and applied as precursors for ion exchange reactions with NAP anions. X-ray patterns indicated the phase purity of the synthesized materials. For the Zn-LDH samples, the reflections are well defined, intense and narrow, suggesting an enhancement in the structural organization compared to the Mg-LDH materials. $Mg_2Fe_{0.5}Al_{0.5}$-Cl and $Zn_2Fe_{0.5}Al_{0.5}$-Cl materials presented the basal spacing related to (003) plane of 8.0 and 7.8 Å, respectively, and the three (00ℓ) harmonic reflections could be identified. The intercalation of NAP anion promoted the displacement of the (003) peak to 19.1 Å for $Mg_2Fe_{0.5}Al_{0.5}$-LDH and 22.2 Å for $Zn_2Fe_{0.5}Al_{0.5}$-LDH. It was proposed a bilayer arrangement of NAP ions between the LDH layers. Both ternary samples have appreciable amount of the drug: 35 wt% for $Mg_2Fe_{0.5}Al_{0.5}$-NAP and 28 wt% for $Zn_2Fe_{0.5}Al_{0.5}$-NAP. FT-IR and FT-Raman data endorse the integrity of the drug after the intercalation process. X-ray diffraction patterns of the materials after calcination at 1000 °C for 2 h in air revealed two different set of decomposition products: $Zn_2Fe_{0.5}Al_{0.5}$-Cl/NAP were converted to ZnO and $Zn(FeAl)O_4$ phases, while $Mg_2Fe_{0.5}Al_{0.5}$-Cl/NAP were transformed to MgO and the separated $MgFe_2O_4$ and $MgAl_2O_4$ spinels. The higher structural organization of the zinc based-LDHs in comparison to the Mg^{2+} analogous materials was also noticed by SEM images. The materials composed by Zn presented a pronounced aggregated of lamellar particles and a well-defined stacking of the sheets. However, even though were observed the usual LDH lamellar morphology for $Mg_2Fe_{0.5}Al_{0.5}$, the stacking seems to be in less extension compared to the $Zn_2Fe_{0.5}Al_{0.5}$ materials. This structural difference between them was reflected by the *in vitro* NAP release profile from LDHs pellets, performed in phosphate buffer (pH 7.4 and 37 °C). For LDH $Mg_2Fe_{0.5}Al_{0.5}$-NAP, the drug release was maintained for 2.5 days and for $Zn_2Fe_{0.5}Al_{0.5}$-NAP the release was sustained for over 4 days. In contrast, the total release of pristine NAP was observed after 30 minutes. Therefore, the high amount of NAP intercalated and the sustained release profile promoted by the LDHs evidenced their promising use for drug delivery. These results open opportunity to explore new LDHs phases constituted by high level of essential metals.

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EFFECTS OF CLAY WETTABILITY ON THE FLOW PROPERTIES IN OIL RESERVOIR ROCKS

Ingebret Fjelde (1), Aruoture voke Omekeh (2), Samuel Erzuah (3)

(1) University of Stavanger, National IOR Centre of Norway and IRIS, Stavanger, Norway, (2) IRIS, Stavanger, Norway, (3) University of Stavanger and National IOR Centre of Norway, Stavanger, Norway

Interactions between reservoir fluids and the minerals determine the wettability of the different minerals in oil reservoir rocks. In sandstone rocks, the clay minerals are contributing to most of the surface area. The concentration and distribution of these minerals and their wettability are therefore important for the flow properties of the fluid phases in the porous oil reservoir rocks. To determine reliable flow properties for the reservoir rock in laboratory experiments, it is important to establish conditions representative of the oil reservoirs. The objective for the presented studies has been to investigate the importance of clay minerals for wettability of oil reservoirs combining experiments and geochemical modelling.

Rock samples from oil reservoirs brought to the laboratory, can contain contaminations and precipitates from sampling and storage. These should be removed without affecting the original mineral composition and distribution. The challenges in cleaning of reservoir rock samples will be presented. Some components in the drilling fluid can alter the wettability of the original clay minerals by adsorption. Particles (e.g. clay minerals) from the drilling fluid can change the wettability because the surface area can be increased or other types of mineral surfaces can be introduced. Oxidation of mineral surfaces and precipitation of oxidation products during storage and experiments can also alter the surface properties of clay minerals and introduce new types of surfaces and thereby alter the flow properties. Actions that can be taken to reduce the oxidation will be discussed, including use of chemicals to establish anaerobic conditions.

The original wettability of the reservoir rock will determine the potential for different types of enhanced oil recovery processes, both for improving the microscopic sweep and the volumetric sweep. It is important to select the correct composition of the synthetic formation water in the laboratory experiments. This brine composition will determine the properties of the clay minerals and thereby the attraction between these minerals and crude oil-brine interfaces and then the established wettability. Alteration of wettability to more water-wet can have the potential to accelerate the oil production and reduce the water production. Since the clay is contributing to most of the surface area, alteration of the wettability of clay minerals is of interest. Methods to change the interactions between components in the crude oil - brine - rock system and thereby the wettability will be presented.

The paper will show examples of how combination of experimental work and geochemical simulations have been used to investigate the wettability of the original reservoir rock, effects of oxidation on the wettability of clay, selection of the composition of synthetic formation water and the potential for improving the oil recovery by changing the composition of the injection water.

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PYRIMETHANIL ADSORPTION ON MONTMORILLONITE AND ORGANO-MONTMORILLONITE. KINETIC AND EQUILIBRIUM STUDY

Federico Manuel Flores (1), Tomás Undabeytia (2)*, Esmeralda Morillo (2),
Rosa M. Torres Sánchez (1)

(1) Technological Center of Mineral Resources and Ceramics (CETMIC, CONICET-CCT La Plata-CIC), Camino Centenario y 506, CC 49, (B1897ZCA) M.B. Gonnet, Provincia de Buenos Aires, Argentina, (2) Institute of Natural Resources and Agrobiology (IRNAS-CSIC), Reina Mercedes 10, 41012 Sevilla, Spain

In the post-harvest treatment of pears and apples in the Argentinean Patagonia, several pesticides are used [1], including pyrimethanil (PRM), for the storage of fruits. The effluents released by the packing plants originate point source of contamination that should be treated prior to its discharge to natural water-courses. Montmorillonites (Mt) and their exchange products with quaternary ammonium salts, organo-montmorillonites (OrMt), have been used to remove this kind of contaminant [2] as well as metals [3], antibiotics [4], etc. The objective of this work was to study the adsorption of pyrimethanil on Mt and OrMt as well as the adsorption kinetics that manages the process. The adsorption isotherms were fitted to Langmuir, Freundlich and Dubinin-Radushkevitch (D-R) models. For kinetic analysis, three mathematical models were employed: pseudo first order (PFO), pseudo second order (PSO) and intra-particle diffusion model (IDM). The adsorption products were characterized by XRD and FTIR. The OrMt were prepared from didodecyldimethylammonium (DDAB) and octadecyltrimethylammonium (ODTMA) bromides at 150% of the cation exchange capacity (CEC). These adsorbents were named DMt150 and OMt149 for DDAB and ODTMA exchanged raw montmorillonite (Mt), respectively, where the number indicated the surfactant amount exchanged determined by total carbon analysis.

The maximum adsorption of PRM was the following: 330, 240 and 156 μmol PRM/g clay, for DMt150, OMt149 and Mt, respectively. The large amount adsorbed by DMt150 sample was assigned to different conformational states of DDAB in the interlayer space [5], due to the presence of two hydrocarbon chains, allowing the entrance of PRM to the interlayer, and conferring greater hydrophobicity than that of OMt149. All adsorbents fitted well to the sorption models, except OMt149 sample that did not fit to Langmuir. The DMt150 sample attained the highest K_F value (obtained from the Freundlich model) within the studied samples. The high PRM affinity for DMt150 sample indicated the presence of hydrophobic interactions between the PRM and the organic fraction of the OrMt. The Q_{max} parameter obtained with D-R model were higher than that obtained with Langmuir model for all samples. The adsorption energy values found by D-R model indicated a physisorption process for PRM adsorption on OrMt samples, supporting the hypothesis of hydrophobic or Van der Waals type interactions. The kinetics experiments indicated that the adsorption process was governed by pseudo-second order kinetics.

The XRD analysis indicated an increase of the basal spacing from 1.25 to 1.39 nm for Mt sample after PRM adsorption, assigned to PRM molecules arrangement in a planar conformation. For OrMt, no changes were noticed in the interlayer space after PRM adsorption, which could indicated a shielding of PRM entrance by the presence of the surfactant. FTIR analysis showed that the secondary amino group of PRM was involved in the adsorption process. The appearance of a new band in the Mt-PRM spectra at 1579 cm^{-1} could indicate the formation of H-bonding through one of the pyrimidine ring nitrogen.

Summarizing these results, PRM adsorption increased by the use of DMt150 and OMt149 compared to Mt due mainly to hydrophobic interactions between the PRM and the organic fraction of the OrMt samples.

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RARE EARTH ELEMENTS IN CLAYS: A RESOURCE FOR THE FUTURE?

Nora Foley

United States Geological Survey, Reston, VA
nfoley@usgs.gov

Rare earth element (REE) ion adsorption clay (IAC) deposits, which form by deep weathering of granitic rocks, are of global economic importance because they currently supply virtually all global production of heavy REE, Y, and a large proportion of light REE [1]. REE deposits of this type are currently being mined only in South China. The search for REE IAC deposits outside of China has focused mainly on areas of the Earth where large regolith deposits are formed on deeply weathered igneous suites. Granitic rocks of the Southeastern United States have been subjected to a long history of chemical and physical weathering under subtropical to temperate conditions. This has resulted in areas of extensive, thick, and relatively undisturbed clay-rich regolith resting on igneous bedrock, an environment comparable to that of South China REE IAC deposits. Prospective source rocks for these deposits are mainly REE enriched, highly fractionated granitic rocks that have been partially to completely altered. Previous work [2] identified a group of Neoproterozoic granites (Stewartsville, Striped Rock, Suck Mountain, and Battle Mountain plutons, Virginia, USA) having regoliths with Al_2O_3 concentrations ranging from 11.6 to 19.02% Al_2O_3. The regoliths have enriched REE contents and chondrite-normalized patterns that are similar to REE IAC deposits of China [1]. For comparison, several igneous-related white clay deposits having Al_2O_3 in the range of 13.1 to 33.4% Al_2O_3 and consisting of mainly kaolinitic clays were examined. (Sparta, Georgia; Haile, South Carolina [3]; and St. Austell, UK). The Stewartsville regolith has REE_{total} concentrations for (La-Lu, ~500-2800 ppm) and fractions of extractable REE (La-Lu, 30-70%; av., ~900 ppm) that approximate grades of REE deposits at Heling and Guposhan, China [1]. White clay deposits at Haile and St. Austell have REE_{total} concentrations in the range 41 to 304 ppm, but contain much lower percentage of extractable REE ions (<<15%).

The Virginia regolith deposits contain a diverse suite of REE minerals, including refractory igneous phases, remnants of soluble minerals, adsorbed REE ions, and deuteric, secondary, and authigenic REE-bearing phases. The results of this study show that for these granites REE enrichment in the regoliths results from removal of alkalis and other mobile elements by weathering of igneous phases such as allanite, feldspar, biotite, and apatite. Released REE are fixed as hydroxide ions on edges and interlayer sites of neoformed clay minerals. In the presence of carbonate or phosphate ions, mobile REE convert to newly formed secondary minerals, including fluoro-carbonates (e.g., synchysite, doverite) and phosphates (e.g., monazite). Cerium is typically sequestered in cerianite as a result of redox reactions. The Stewartsville and Striped Rock regoliths highlight the importance of allanite weathering in generating light-middle-REE-enriched clays from metaluminous granite, whereas the Suck Mountain and Battle Mountain cases show the result of weathering of allanite plus a variety of REE-fluoro-carbonate minerals formed under peralkaline conditions in pegmatitic melt fractions [2,3]. The REE distributions in the kaolin deposits at the Haile and St. Austell clay pits mainly reflect the presence of monazite-(La), monazite-(Nd), and poorly crystalline xenotime (Y, Dy, Gd). The minerals and chemical processes producing the kaolin deposits are analogous to those that formed REE IAC deposits in altered granitic rocks of China and Southeast Asia; however, the environments did not support retention of REE as adsorbed ions on clay minerals.

Micro-chemical-scale REE redistribution processes appear to be key factors in the retention of REE as adsorbed ions on clay. Thus, the REE resource potential of clay deposits is a function of the relative proportions of light to heavy REE (La_N/Yb_N) in source rocks and the amount of readily extractable REE adsorbed to clay minerals and bound up in soluble minerals (such as fluorocarbonates, oxylates) compared to the quantity of REE locked up in insoluble secondary and residual minerals. These studies demonstrate potential in the Southeast U.S. for REE IAC deposits of the type containing light-middle REE. Establishing the extent of the resource potential will depend on identifying sufficient volumes of regolith with high concentrations of readily extractable, high-value REE (e.g., Nd, Dy).

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WEATHERING ON THE DEVONIAN SLATES AND CHARACTERIZATION OF A BENTONITE LAYER IN THE WESTERWALD (GERMANY)

Fontaine François (1)*, Hamaekers Helen (2), Hoffmann Andreas (3), Yans Johan (4), Fagel Nathalie (1)

(1) AGEs, Argiles, Géochimie et Environnement sédimentaires, Université de Liège, Belgium, (2) Sibelco Belgium, Dessel, Belgium, (3) Sibelco Deutschland GmbH, Ransbach-Baumbach, Germany, (4) Département de Géologie, ILEE, Université de Namur, Belgium
*f.fontaine@ulg.ac.be

The Westerwald region is one of the largest and oldest clay mining areas of Germany. Those deposits were formed during the Eocene and Oligocene as a result of the weathering, erosion and redeposition of Devonian rocks. During the Miocene, intense volcanic activities led to a large basalt cover, protecting the clays from the erosion.

The two main goals of this study are first to improve the knowledge on the weathering processes of the Devonian slates that led to the current setting of those clay deposits by studying the mineralogical and chemical composition of the clays with depth. The second goal is to characterize a bentonite layer underneath the Miocene basalt cover using quantitative X-ray diffraction, chemical analysis, BET, cation exchange capacity and scanning electron microscope.

A 20 meter deep quarry mining the Devonian bedrock in southern Westerwald has been sampled on its entire depth. The XRD results show no significant variations of the mineralogy with depth, except for the phyllosilicates. The minerals of the <2 µm fraction are illite, kaolinite, smectite and mixed-layers minerals (vermiculite-chlorite and illite-chlorite). The proportions of the minerals in the mixed-layers chlorite-vermiculite vary with depth. At the bottom of the quarry, the proportion of vermiculite is very low while in the top, the proportion of vermiculite is higher. This is explained by the degree of the weathering, logically more intense at the top of the quarry. Trace elements compositions are currently being investigated.

A 3 meter thick greenish to brownish bentonite layer has been found in the eastern part of the Westerwald region. The XRD performed on different samples of this bentonite shows a relatively heterogeneous composition: montmorillonite (60-80%), kaolinite (5-12%), illite (0-7%), goethite (2-15%), talc (0-10%), K-feldspars (0-7%), plagioclase (0-4%) and traces of amphibole and pyroxene. This bentonite is probably the result of the weathering of volcanic ashes. Since there are not many outcrops of this bentonite layer, its spatial distribution is studied by drilling.

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DESIGN AND KINETIC STUDY OF SUSTAINABLE POTENTIAL SLOW-RELEASE FERTILIZER OBTAINED BY MECHANOCHEMICAL ACTIVATION OF CLAY MINERALS AND POTASSIUM MONOHYDROGEN PHOSPHATE

Roger Borges (1,2), Fernando Wypych (1), Vanessa Prévot (2), Claude Forano (2)*

(1) Universidade Federal do Paraná, Departamento de Química, Curitiba, PR, Brazil, (2) Université Clermont Auvergne, Univ. Blaise Pascal, ICCF CNRS UMR 6296, BP 10448, F-63000 Clermont-Ferrand, France
*Claude.forano@uca.fr

Currently, most of the nutrients applied through inorganic fertilizers containing N, P and K are easily lost by leaching, run-off and in gaseous form. As a consequence of this, the nutrients pollute the atmosphere and water bodies, in the latter case the accumulation of nutritient elements cause eutrophication [1]. These characteristics require the use of huge amounts of fertilizers to ensure food production, and the negative effects of lost nutrients become worse. Moreover, the increasing scarcity of phosphate resources threatens food security and requires a chang in fertilizer management approach. In this context, research for environmentally friendly methods and products is important. One possible option is to develop sustainable slow-release fertilizers (SSRFs). The main advantages of SSRFs are that they dissolve and release nutrients into soils in a way that assures bioavailability of nutrients to plants over a long period of growth. In addition, novel formulations can reduce or eliminate environmental problems caused by excess losses of nutrients through the use of conventional fertilizers. Interestingly, the use of different clay minerals in the mechanochemical process has been reported to produce efficient SSRFs. Clay minerals are of particular interest, since they are abundant and environmentally friendly. Kaolinite, for instance, when milled with KH_2PO_4 or $NH_4H_2PO_4$, produces amorphous phases that release K, N, and P slowly [2,3].

In this study [4], the solid-state mechanochemical activation method was used to prepare potential fertilizers by milling montmorillonite (MMT), a 2:1 dioctahedral cationic exchanger, and talc, a 2:1 trioctahedral nonionic exchanger, with K_2HPO_4. The main objective was to form metastable partially soluble materials under various milling conditions. Combined XRD, FTIR and solid state NMR analysis give evidences for changes of the local and extended structures due to the milling process. All milled samples undergo a strong amorphization. The structures of all mineral precursors collapse. In the meantime, K_2HPO_4 reacts with the clay mineral surface while octahedral Al is totally converted to the tetrahedral form. Kinetic studies and modelling have evidenced promising phosphate release performances. The intraparticle diffusion kinetic model, (the Higuchi model) based on the combination of a fast and a slow P release processes better described the phosphorus (P) release for both systems eventhough the release rate (kd) were different for both mechanisms. The potassium release behaviour was similar for both systems. Since crystallized potassium struvite (K-struvite-$MgKPO_4 \cdot 6H_2O$) was formed during the release experiments, talc based potential slow-release fertilizers displayed slower release behaviour of P compared to MMT.

Based on various characterization data, it was possible to conclude that potential fertilizers with slow-release behavior over 31 days were successfully obtained from both clay mineral systems by this approach, leading to different release mechanisms and kinetic behaviors.

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POTENTIAL SUSTAINABLE SLOW-RELEASE FERTILIZERS OBTAINED BY MECHANOCHEMICAL ACTIVATION OF LAYERED DOUBLE HYDROXIDES AND K_2HPO_4

Roger Borges (1,2), Fernando Wypych (1), Vanessa Prévot (2), Claude Forano (2)*

(1) Universidade Federal do Paraná, Departamento de Química, Curitiba, PR, Brazil, (2) Université Clermont Auvergne, Univ. Blaise Pascal, ICCF CNRS UMR 6296, BP 10448, F-63000 Clermont-Ferrand, France

Because of increasing scarcity of raw materials (Phosphate rocks), worldwide growing demand for people feeding and pollution damages cause to the environment (eutrophication of water resources), nutrient sustainable management is a high impact societal challenge that imposes to design innovative fertilizers or to develop more efficient fertilizing processes. Actually, the use of large amounts of fertilizers to ensure the food production induces increasingly pronounced negative effects. Indeed, most inorganic fertilizers currently used in agriculture have a high-solubility or are volatiles, leading to excessive wastes and losses and a high dissemination in the Environment. In this scenario, economic losses are inserted with these non-sustainable nutrient supplies.

Based on these statements and considering that food production is an essential activity for human life, this study describes the development of potential sustainable slow-release fertilizer (SSRF), obtained by mechanochemical activation (using a high-energy balls mill) of mixtures of calcined layered double hydroxides (LDH), $Mg_2Al(OH)_6(CO_3).3H_2O$ and $Mg_2Fe(OH)_6(CO_3).2.5H_2O$), and K_2HPO_4.

Layered Double Hydroxides are natural and synthetic clay minerals with unique anion exchange properties that may generate anion release under controlled conditions. HPO_4^{2-} loaded LDH have already demonstrated a great ability for slow-release of phosphate nutrient [1]. Interestingly, mechanochemical treatments of LDH may activate sorption sites [2] and modify porosity architectures and molecular diffusion properties [3,4]. In this study, we investigated mecanochemical treatments of mixtures of LDH or calcined LDH with potassium orthophosphate in order to prepare mixed metal oxides or hydroxides (LDO) with P/K/Mg slow-release properties. LDH precursors with $Mg_2Al(OH)_6(NO_3).nH_2O$, prepared by coprecipitation [6] and K_2HPO_4 were used as sources of Mg^{2+}, K^+ and P. Reactivity of LDH precursors against K_2HPO_4 was varied by calcination pre-treatment at different temperatures (200 °C, 300 °C, 400 °C). A series of ball milling conditions were the applied to LDO/K_2HPO_4 for various LDH/KHPO4 mass ratio. Kinetic and thermodynamic studies of nutrient release were then performed in batch conditions. Optimized preparation conditions for SSRF have been determined for 200 °C and 9 h LDH thermal and mecanochemical activation respectively.

All solid samples were characterized by XRD, TGA, SEM and EDX.

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IMPACT OF COMBINED HEAVY METALS AND CLAY MINERALS ON THE BIODEGRADATION OF MESOTRIONE BY *BACILLUS MEGATERIUM* MES11

Wang Miao (1), Bouakline Abdesslam (1), Alekseeva Tatiana (2), Pinsky David (2),
Prevot Vanessa (1), Forano Claude (1)*, Sancelme Martine (1), Besse-Hoggan Pascale (1)

(1) Université Clermont Auvergne, CNRS, SIGMA Clermont, Institut de Chimie (ICCF), F-63000 Clermont-Ferrand, France,
(2) Institute of Physical Chemical and Biological Problems of Soil Science. Russian Academy of Sciences, Institutskaya ul., 2, 142290 Pushchino, Russia
*claude.forano@univ-bpclermont.fr

Triketones (sulcotrione, tembotrione, mesotrione) can be considered as a new generation of herbicides, inspired by natural molecules that are nowadays increasingly applied either as individual or in cocktail form [1]. Although triketones were considered as “eco-friendly” herbicides, there is a need to better understand their behaviors and their disseminations in soils in order to develop sustainable agricultural practices for maintaining a high level of soil quality. Moreover, the impact of heavy metals on the biodegradation of triketones has not yet been investigated while heavy metals can be found in non-negligible amounts in soils due to specific pesticide compositions, sewage and compost spreading or industrial waste dissemination.

This study focus on the combined impact of heavy metals and clay or organo-clay fractions of soils on the biodegradation of mesotrione (Fig. 1) by *Bacillus megaterium* Mes11. As clay and organo-clay fractions are known to strongly interact with herbicide molecules, bacteria and heavy metals, our objective is to address the joint effect of all components to the fate of mesotrione.

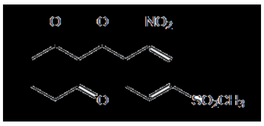

Fig. 1 : Mesotrione

Complexation reactions of heavy metals (Cu^{2+}, Cr^{3+}, Zn^{2+}, Pb^{2+}, Fe^{3+}) with mesotrione were first investigated using UV-Vis spectroscopy. The Cu^{2+} ions can form a complex with mesotrione (1/1 stoichiometric ratio), while no complexation was evidenced with other metallic cations. Adsorption isotherms of mesotrione and its main metabolite AMBA (2-amino-4-methylsulfonyl-benzoic acid) by Montmorillonite (Mont-Na^{+}, Mont-Ca^{2+}, Mont-Fe^{3+}) and Layered Double Hydroxides (Mg$_2$M(III)(OH)$_6$(NO$_3$).nH$_2$O with M(III) = Al, Fe) and related compounds loaded with 2.7% (w:w) of Humic acids were recorded. Partition coefficients (Kd) were found to vary in the series: MMT-Fe-AH$_{2,7\%}$ > MMT-Fe > Mg$_2$Al-AH$_{2,7\%}$ > MMT-Ca-AH$_{2,7\%}$ > MMT-Ca > Mg$_2$Al-NO$_3$ > Mg$_2$Fe-AH$_{2,7\%}$ > Mg$_2$Fe-NO$_3$ > MMT-Na.

Kinetics of mesotrione biodegradation by *Bacillus megaterium* Mes11 were studied in presence of model soil fractions (clay and organo-clay) and heavy metals separately or conjointly. As an example, in presence of Cu^{2+} and Cr^{3+}, the biodegradation of mesotrione (1 mM) by Mes11 is slowed down with a partial inhibition for the lowest concentration considered (0.2 mM) and a complete inhibition for the higher concentrations (2 and 10 mM) in metals. Combining the soil models (Mg$_2$AlNO$_3$-and-Mg$_2$AlAH$_{2,7\%}$) and Cu^{2+} or Cr^{3+} ions resulted in a complete inhibition of the mesotrione biodegradation. All these results will be presented and discussed.

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PICKERING EMUSLION STABILITY CONNECTED TO GLASS- OR GEL-LIKE STATES IN CLAY AT DROP INTERFACES

Azarmidokht Gholamipour-Shirazi (1), Marcio S. Carvalho (1), Manuel F. G. Huila (2),
Koiti Araki (2), Paul Dommersnes (3), Jon Otto Fossum (1,3)*

(1) Department of Mechanical Engineering, Pontificia Universidade Catolica do Rio de Janeiro, Rio de Janeiro, RJ, Brazil, (2) Institute of Chemistry, Universidade de São Paulo - USP, Sao Paulo, SP, Brazil, (3) Department of Physics, Norwegian University of Science and Technology - NTNU, Trondheim, Norway

Colloidal clay in water suspensions are known to exhibit a multitude of bulk phases depending on initial colloidal concentration and ionic strength, and examples of this include repulsive Wigner colloidal glasses at low ionic strength and attractive gels at higher ionic strength due to screened electrostatic forces by the electrolyte [1]. From confocal Raman microscopy combined with elasticity measurements, we infer that clay trapped at quasi two-dimensional interfaces between oil and water also exhibit confined glass-like or gel-like states [2]. Furthermore we have demonstrated that the results are important for the preparation of particles stabilized colloidal emulsions [3]. The results can be important for preparations of colloidal clay capsules and clay based colloidosomes, and a better understanding of this phenomenon may lead to new or improved emulsion or encapsulation technologies.

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LAPONITE CLAY AS SUPPORT FOR CHIRAL CATALYSTS: SURFACE EFFECTS ON STEREOSELECTIVITIES

José M. Fraile*, José I. García, Clara I. Herrerías, José A. Mayoral, Elísabet Pires

Instituto de Síntesis Química y Catálisis Homogénea (ISQCH), Facultad de Ciencias, Universidad de Zaragoza-CSIC, C/ Pedro Cerbuna 12, E-50009 Zaragoza, Spain
*jmfraile@unizar.es

Clays are well-known cation exchangers that have been used as supports for cationic catalytic complexes, in particular for chiral catalysts, for a long time [1]. As an immobilization method, cation exchange is very convenient given that it does not require the chemical modification of the chiral ligand, reducing in this way the cost associated to the immobilization process [2]. In particular, our group has been working in the use of clays, mainly the synthetic laponite, as support for chiral bis(oxazoline)-copper complexes [3]. The layered structure of clays, that places the chiral complex onto a two-dimensional environment, produces deep effects on the stereochemical course of the catalytic reaction [4], which are different depending on the reaction studied and the role of the catalyst.

In the copper(I) catalyzed cyclopropanation reaction, the first important effect is the formation of *cis* cyclopropanes as major products, instead of the *trans* obtained in solution. The trend to approach both carbene and alkene with the bulky groups far from the laponite surface drives this effect, as shown by the use of non-symmetrical bis(oxazolines), that allow a closer disposition of the complex to the surface with an improvement in the *cis* selectivity [5]. More importantly, the presence of the laponite surface provokes a change in the preferential attack of the alkene to one or another face of the carbene, with a reversal in the sense of the asymmetric induction and hence the major enantiomer is that with absolute configuration opposite to the one obtained in solution. Then, the laponite surface acts like a bulky substituent of the chiral ligand, hindering one of the faces of the copper-carbene intermediate for the approach of the alkene reagent.

When copper(II) acts as a Lewis acid, for example in Mukaiyama-Michael reactions, the effects are different, depending on the nature of the Michael acceptor [6]. In one case (benzylidenemalonate), the clay produces a reversal of the enantioselectivity, a similar result as that observed in cyclopropanation. In another case (butenoyloxazolidinone), a total reversal of the diastereoselectivity is obtained, leading for the first time in this reaction to the syn diastereomer. Finally, when unsaturated ketones are used, the reaction in homogeneous phase does not produce enantioselectivity at all, whereas on the clay support moderate enantioselectivity values are obtained, depending on the substituents of the ketone. The lack of deep knowledge about the reaction mechanism, mainly regarding the structure of the substrate-copper-ligand intermediate complex, makes it difficult to explain those effects, that must be related to the geometry of the Michael acceptor upon coordination to the chiral complex.

In this communication, an overview of all these results will be presented, together with the hypothesis for the clay effect on the stereochemical course of the different enantioselective reactions.

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LAPONITE CLAY AS CARRIER FOR INTRAVITREAL DEXAMETHASONE RELEASE

José M. Fraile (1)*, Elena Garcia-Martin (2), Cristina Gil (1), José A. Mayoral (1), Luis E. Pablo (2), Vicente Polo (2), Esther Prieto (2), Eugenio Vispe (3)

(1) Instituto de Síntesis Química y Catálisis Homogénea (ISQCH), Facultad de Ciencias, Universidad de Zaragoza-CSIC, C/ Pedro Cerbuna 12, E-50009 Zaragoza, Spain, (2) Departamento de Oftalmología, Hospital Universitario Miguel Servet, and Instituto de Investigación Sanitaria Aragón (IIS-Aragón), Universidad de Zaragoza, Facultad de Medicina, C/ Domingo Miral s/n, E-50009 Zaragoza, Spain, (3) Laboratorio de Cromatografía y Espectroscopia, ISQCH, Facultad de Ciencias, Universidad de Zaragoza-CSIC, C/ Pedro Cerbuna 12, E-50009 Zaragoza, Spain
*jmfraile@unizar.es

Intravitreal injection is considered an effective approach for treatment of posterior segment ocular diseases, as it delivers the therapeutic agent directly into the eye, but it presents some potential risks associated to the need for repeated injections [1]. Alternative drug delivery systems are being developed to overcome this kind of limitations by reducing the frequency of injections, for example using biodegradable polymeric implants for slow release of dexamethasone (an anti-inflammatory steroid), but this methodology requires a surgical intervention to implant the material [2]. Clays have been recently envisaged as carriers for drug delivery [3], but they had never been used for ophthalmic treatment.

Laponite (LAP) is a white synthetic smectite clay, able to form transparent colloidal dispersions in water [4]. We have demonstrated that dexamethasone (DEX), in spite of being a neutral molecule, is retained on laponite through weak interactions, mainly hydrogen bonds, as shown by solid state NMR. In vitro studies have shown that dexamethasone is released below its solubility in saline solution or in a model of vitreous humor, under equilibrium conditions [5].

The in vivo ocular biocompatibility of laponite has been assessed by eye examination (slit lamp and indirect ophthalmoscopy) after intravitreal administration to rabbits. The clay did not elicit any inflammatory response even if the clay could be observed floating into the vitreous body as a transparent gel from day 1 through week 14 postadministration. The small amount of eyes with cataract were probably due to a traumatic effect associated with the injection technique because the histological examination did not show any change in eye´s lens structure. Thus, laponite could be considered as a vehicle for potential clinical use in ocular drug administration due to its proved ocular biocompatibility and its transparency in the gel state. Moreover, Mg content in vitreous humor showed a decrease along the 14 weeks. About 33% of total initial LAP-dose administered could be detected in vitreous humor for up to 14 weeks postadministration, indicating some kind of degradation and/or elimination of the clay through an unknown mechanism.

Intravitreal injections of 100 µL dexamethasone/laponite dispersion (10 mg solid/mL, 1:10 DEX/LAP w/w) were performed in albino rabbits (New Zealand) and DEX concentrations in vitreous humor were monitored over 24 weeks. Vitreous dexamethasone levels remained relatively stable from 7th day postadministration, and showed an elimination rate significantly lower than that found after intravitreal injection of dexamethasone in solution (1 mg/mL) (C_L= 0.49 vs 315.29 g/day). The administration of DEX loading to laponite can lengthen the half-life of the drug ($T_{½\text{-el}}$= 132.75 vs 0.13 days) and enhance its clinical uses.

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ORGANOBENTONITES OBTAINED BY MICROWAVE SILYLATION IN DIFFERENT SOLVENTS AND THEIR USES FOR DYE REMOVAL

Líbia N. F. França (1), Ieda M. G. Santos (1), Edson C. Silva Filho (2), Josy A. Osajima (2), Maguy Jaber (3), Maria G. Fonseca (1)*

(1) Department of Chemistry, Universidade Federal da Paraíba, João Pessoa, 58051-970, Brazil, (2) Department of Materials Science, Universidade Federal do Piauí, Teresina, Brazil, (3) Sorbonne Universités, UPMC Univ Paris 06, CNRS, UMR 8220, Paris, 75005, France
*mgardennia@quimica.ufpb.br

Organofunctionalization of clay minerals is a current topic due the vast applications of resulted hybrid materials. Silylation of clay mineral surface is an effective procedure to obtain organic-inorganic hybrid layered materials. Successful silylation of clay mineral surfaces depends strongly on the reactivity of clay mineral surfaces, including all internal surfaces, external surfaces and broken edges [1]. Silylated products are very dependent of the nature of the clay minerals (swelling or non-swelling clay minerals), of the silane (nature and quantity of functional group and hydrolyzed groups) and of the experimental conditions, ie, polar and non-polar solvents, anhydrous conditions, temperature, time, silane concentration, among others [1,2]. This work aimed to prepare organobentonites through microwave silylation with 3-aminopropyltrimethoxysilane (APTMS, 97%, Sigma-Aldrich). The influence of different solvents on organofunctionalization was evaluated. The resulting aminopropyl bentonites (BentN) were used as adsorbents to dye from aqueous solution. The solids were characterized by elemental analysis of carbon hydrogen and nitrogen, infrared spectroscopy, X-ray diffraction, thermogravimetry, transmission electron microscopy and solid state UV-Vis spectroscopy. An Argentine bentonite sample with a cation exchange capacity (CEC) of 88.2 cmol(+) Kg^{-1} was provided by Bentonise S.A and was used as-received. The chemicals ethanol and ethylene glycol (EG) were used as solvents and the raw sample was activated under vacuum to eliminate physically adsorbed water. The reaction of APTMS with 3.0 g of the activated bentonite (Bent) was performed in a microwave reactor IS-TEC microwave RMW-1. After the previous suspension of solid in 50 mL of solvent, 10.0 mL of APTMS was added to reactor vessel. The solvents ethanol, isopropyl alcohol, hexane (hex), toluene and ethylene glycol (EG) were obtained from Sigma-Aldrich and used without further purification. The suspension was heated for 5 min at 323 K. The solid was then recovered by centrifugation and washing with ethanol and distilled water and dried at 323 K for 12 h. A control reaction was performed to verify the solvent/bentonite interaction at the same conditions without silane. Powder X-ray diffraction patterns of pristine bentonite showed different reflections attributed to three main phases consistent of montmorillonite (Mt), quartz and muscovite. After silylation, the basal spacings (d_{001}) increased to reach 1.51-1.82 nm indicating the intercalation or grafting of the APTMS in the interlayer space of the Mt. The *d* values were near for the samples prepared with both nonpolar and polar solvents, excepted to sample BentN/EG which value was higher (1.82 nm). An increase in the degree of immobilization was observed for synthesis with nonpolar solvents, where the maximum immobilization was 1.05 $mmolg^{-1}$, referring to the silanized sample in hexane. The samples with higher immobilized silane were used to 5R violet reactive dye removal. The influence of the contact time for adsorption of dye on BentN/Hex and BentN/EG in aqueous solution at pH 3 and 500 mg L^{-1} initial concentration dye demonstrated that the dye removal increased during the initial stages of adsorption where the obtained value was 13 mg g^{-1} in 5 minutes. After 40 minutes, the dye removal became 22-25 mg g^{-1}, corresponding to an increase of 50% over the initial five minutes and reached equilibrium after 90 and 38 minutes for BentN/HEX and BentN/EG, respectively. The combination of the experimental data stressed on the success of the microwave silylation of sodium bentonite. The silylated solids obtained by microwave irradiation behaved as good sorbents for the 5R violet reactive dye removal from aqueous solution.

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INFLUENCE OF THE STRUCTURE AND EXPERIMENTAL MODIFICATIONS OF MAGNESIUM-RICH CLAY MINERALS ON THE METHYLENE-BLUE ADSORPTION PROCESS

Francisco Franco (1), Juan Antonio Cecilia (1), Meena Heredia (1), Cristina López Moreno (2), Victor Hernandez (2), Manuel Pozo (3) Maria Bentabol (1)*

(1) Departamento de Química Inorgánica, Cristalografía y Mineralogía, Facultad de Ciencias Universidad de Málaga, Campus de Teatinos s/n 29071, Málaga, Spain, (2) Departamento de Química Física, Facultad de Ciencias, Universidad de Málaga, 29071 Málaga, Spain, (3) Departamento de Geología y Geoquímica, Facultad de Ciencias, Universidad Autónoma de Madrid, Cantoblanco, 28049 Madrid, Spain

Structural influence of two minerals, namely stevensite and sepiolite, that have very similar chemical compositions, was determined on the adsorption of methylene blue.. In addition, the structure and chemical composition of both magnesian clay minerals was experimentally modified to determine the influence of these modifications on the adsorption characteristics.

The clay mineral structure is the main factor controlling the adsorption process of methylene blue. Natural stevensite has a laminar structure with interlayer cations that are readily exchangeable with methylene blue cations. In this way, besides adsorption of methylene blue on the on the external surface of the stevensite particles, a large portion of these organic cations are retained in the interlayer positions through the cation exchange mechanism. On the other hand, natural sepiolite has a structure with channels of dimensions 10.6 Å × 3.6 Å where contaminants, with appropriate size, can be retained. In this case, the molecular size of the methylene blue (17 Å × 7.6 Å × 3.25 Å) is larger than that of the inlet section of the sepiolite channels. For this reason, sepiolite is unable to adsorb methylene blue inside their structure. In natural sepiolite, adsorption occurs on the outer surface of the individual fibers or on the surfaces and micropores of fiber bundles.

In the present work, it has been verified that the effect of microwave assisted acid treatment on the methylene blue adsorption was opposite in the two magnesian clay minerals. In the case of stevensite, due to the partial destruction of its lamellar structure and consequent loss of exchange centres and the release of amorphous silica a remarkable decrease occurred in the capacity of methylene blue adsorption. In contrast, the acid treatment increased the methylene blue adsorption capacity of sepiolite, possibly due to a greater dispersion of fibrous particles which increased the exposed external surface available to the adsorption.

Iron oxide supported materials obtained with both natural and acid-activated clay minerals show a remarkable increase in the capacities of methylene blue adsorption when compared with that of the starting materials. These improvements are related to the generation of new adsorption centres due to deposition of iron oxides on the external surfaces of natural and acid-activated clay particles. Nevertheless, this improvement was not observed with natural stevensite. This different behaviour was caused by a structural change. The treatment with $FeCl_3$ and subsequent calcination of the stevensite causes the appearance of iron oxides strongly bonding the 2:1 stevensite layers and preventing the swelling behaviour and, consequently, losing the exchangeable sites in the interlayer positions. On the contrary, in the case of acid-activated stevensite, the increase of the adsorption centres by the addition of iron oxides compensates, to a great extent, the loss of swelling behaviour.

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DETERMINATION AND VALIDATION OF THE GRAIN SIZE OF BOOM CLAY

Lander Frederickx (1,2), Mieke De Craen (1), Miroslav Honty (1), Reiner Dohrmann (3), Jan Elsen (2)

(1) SCK•CEN, Mol, Belgium, (2) KU Leuven, Leuven, Belgium, (3) BGR, Hannover, Germany

In the context of a study into the mineralogy of the clay fractions of the Boom Clay of northern Belgium, a detailed examination of the grain size distribution is vital. Over the last years, the laser diffraction technique has become a standard technique for determining the grain size distribution. It is often favoured due to its high precision and fast measurement time. However, serious concerns have been expressed regarding the accuracy of the technique when it comes to measuring non-spherical particles such as clay minerals (e.g. [1] and [2]). To address this problem, a sample set covering the entire Boom Clay stratigraphy was analysed using the laser diffraction technique (Malvern Mastersizer) and a sedimentation technique (Micromeritics SediGraph 5100), which is considered to be more accurate for non-spherical particles. Additionally, the bulk mineralogy of the entire sample set was determined using X-ray diffraction and certain size fractions were separated from a number of samples by centrifugation.

Upon comparing the mass fraction <2 μm as determined by both grain size techniques to the total clay content as determined by X-ray diffraction, it becomes clear that the laser diffraction technique severely underestimates the clay content, while the SediGraph data seem to be a reasonable proxy for the total clay content. Additionally, the mass proportions of the fraction <2 μm separated by centrifugation compare better to the SediGraph data than to the laser diffraction data. In order to further investigate the correct partitioning of the size classes by centrifugation, the different fractions will be examined by SEM and/or TEM. This should provide independent evidence of the SediGraph technique as a valid tool for the determination of the grain size distribution of clay-rich sediments.

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SMECTITE ILLITIZATION PROBED BY FORCE-FIELD MOLECULAR DYNAMICS AND DENSITY FUNCTIONAL THEORY

Francesco Frigerio (1)*, Luigi abbondanza (2), Claudio Geloni (1), Elisabetta Previde Massara (1)

(1) Eni S.p.A. Upstream and Technical Services, San Donato Milanese I-20097, Italy, (2) Eni S.p.A. Upstream and Technical Services, Novara I-28100, Italy

There is a need to clarify the mechanisms and processes involved in the illitization of smectite that is one of the dominant diagenetic mineral transformations in a clay rich sediment during burial history. This reaction influences greatly the chemical and physical evolution of the sediments by controlling porosity and permeability, water release, overpressure and mechanical properties.

Therefore our interest in this mineral transformation suggested the development of a series of Molecular Dynamics simulations and Quantum Chemistry calculations, applied to a carefully selected set of three-dimensional clay models (for the smectite and illite end members) on the nanoscopic/mesoscopic scale. Our goal was the feasibility assessment of a quantitative description of the mobility of structural ions/interlayer water and of the elastic properties of the model structures undergoing external stresses due to compaction. A stepwise approach allowed testing this twofold task.

Thermochemical and crystallographic database searches, coupled with Density Functional Theory (DFT) energetic/geometric relaxations, allowed the production of a detailed model for each mineral end member along the smectite to illite transition. For the purpose we decided to adopt Na-beidellite as smectite and, because of its structure similarity, muscovite as representative of illite.

The dimensional expansion of the two original structures into a series of larger and more complex models (from 42 to 420000 atoms for muscovite - from 210 to 2100000 atoms for Na-beidellite) preceded the assignment of the CLAYFF [1] force-field parameters to all atoms and the collection of MD trajectories produced by LAMMPS [2].

The alternative implementation into our MD calculations of a few different force-field parameters available in the literature for water molecules led to the comparison of their performances, in the specific context of restrained water diffusion in contact with mineral surface and within interlayer domains.

Clearly differing elastic properties and atomic mobility values in the two model series resulted from the analysis of performed MD simulations. Moreover, the diffusion coefficients calculated for water included into our models clearly illustrate a very different behaviour from bulk water solutions. Such difference has an impact on ion transport phenomena and can possibly have a role in the smectite to illite transformation process.

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CONTROLLED ENERGY TRANSFER AND SUBSEQUENT ELECTRON TRANSFER ACROSS THREE MOLECULES ASSEMBLED ON SAPONITE SURFACE

Takuya Fujimura (1)*, Elamparuthi Ramasamy (2), Yohei Ishida (3), Tetsuya Shimada (4,5), Shinsuke Takagi (4,5), Vaidhyanathan Ramamurthy (2)

(1) Department of Physics and Materials Science, Interdisciplinary Graduate School of Science and Engineering, Shimane University, Matsue, Shimane 690-8504, Japan, (2) Department of Chemistry, University of Miami, Florida 33146-0431, United States, (3) Division of Material Science and Engineering, Faculty of Engineering, Hokkaido University, Sapporo, Hokkaido 060-0808, Japan, (4) Department of Applied Chemistry, Graduate School of Urban Environmental Sciences, Tokyo Metropolitan University, Hachioji, Tokyo 192-0397, Japan, (5) Tokyo Metropolitan University, Center for Artificial Photosynthesis, Hachioji, Tokyo 192-0397, Japan
*murthy1@miami.edu

Clay minerals have attracted great interest as a host material for photofunctional organic-inorganic hybrid systems as well as photochemical reaction fields over the past decade [1,2]. Several reports demonstrated the excited energy transfer reaction between co-adsorbed dyes on clay surfaces [3]. These results should promise that artificial light harvesting system can be construct by dyes assemblies on clay surfaces. However, there have been few reports about energy transfer and subsequent photoinduced electron transfer reaction, which were performed in initial process of photosynthesis. In this research, we demonstrated the energy transfer and subsequent electron transfer across three molecules adsorbed on clay surfaces. To realize this sequential reaction, three kinds of the dyes, which are energy donor (EnD), energy acceptor (EnA) (as well as electron donor (elD)) and electron acceptor (elA) would be necessary, and unfavorable electron transfer between EnD and others have to be suppressed. In our novel strategy, EnD was encapsulated by organic cavitand molecule to suppress the unfavorable electron transfer. Synthetic saponite clay was used as host material and dispersed in water to obtain exfoliated nano-sheets. Energy donor (2-acetylanthracene) was encapsulated in cationic organic cavitand. Tetrakis(1-methylpyridinium-4-yl) porphyrinato zinc and 1,10-bis(2,4-dinitrophenyl)-4,40-bipyridinium were used as EnA (as well as elD) and elA, respectively. These molecules were anchored on exfoliated saponite clay surfaces by electrostatic interaction. Judging from UV-Vis. absorption spectra and fluorescence studies, anchored dyes on saponite surfaces were not aggregated even at high dye loadings [4]. Occurrence of energy transfer reaction was observed by steady-state and time-resolved fluorescence measurements. Fluorescence of EnD was quenched by addition of EnA instead of fluorescence enhancement of EnA insteady-state fluorescence spectra. It indicated that occurrence of excited energy transfer reaction from EnD to EnA. Furthermore, appearance of rise component observed by time-resolved fluorescence decay of EnA was also indicates the occurrence of energy transfer reaction. Electron transfer from EnD or EnA(as well as elD) was confirmed by fluorescence quenching reaction. When encapsulated EnD and elA were adsorbed on saponite surface, fluorescence intensity of EnD was almost kept. It indicated that electron transfer from encapsulated EnD to elA, which is unfavorable electron transfer, was suppressed. On the other hand, when EnA and elA was co-adsorbed on saponite surface, fluorescence of EnA was strongly quenched. It suggests occurrence of electron transfer from excited EnA to elD. To demonstrate sequential energy and electron transfer, EnD, EnA and elA were adsorbed on saponite surface and steady-state fluorescence spectra were measured. The reduced fluorescence intensity of EnD indicated the occurrence of energy transfer reactionfrom EnD to EnAeven in presence of elAbecause fluorescence of EnD was not quenched by elA. Then fluorescence intensity of EnA was decreased with increased loading level of elA. It indicated that electron transfer reaction proceeded between excited EnA and elA. Occurrence of energy transfer reaction was also confirmed by time-resolved fluorescence from EnA. Judging from these results, sequential energy and electron transfer reaction proceeds across three molecules assembled on saponite. The efficiency of energy and electron transfer were calculated as 71% and 81%, respectively. In addition, energy loss (fluorescence quenching of EnD without quenching via energy transfer) was suppressed under 5%.

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DYNAMIC OF ORGANIC SPECIES IN ORGANO-CLAY / POLYPROPYLENE COMPOSITE BY QUESI-ELASTIC NEUTRON SCATTERING

Yoshiaki Fukushima (1)*, Takeshi Yamada (1), Kenji Tamura (2), Kaoru Shibata (3)

(1) Neutron Sci. & Tech. Center, Comprehensive Res. Org. for Sci.& Soc. (CROSS), Tokai, Japan, (2) Functional Clay Materials Group, Res. Center for Functional Materials, National Institute for Materials Science, Tsukuba, Japan, (3) J-PARC Center, Japan Atomic Energy Agency, Japan

Polymer-clay mineral nano-composite, in which the silicate layers are dispersed in an organic polymer matrix, have been widely studied. Although the properties of the hybrids should be controlled by interactions between the organic molecules and the silicate surface, there have been only a few approaches to study the interaction.

In this study, we tried to derive a molecular movement of organic molecules on the clay surfaces bya quesi-elastic neutron scattering (QENS). When the surfactants and organic polymer was co-existed on the silicate surface, they should get any freedom to moving at the temperature higher than their melting points. A backscattering QENS instrument [1] installed at Materials and Life Science Experimental Facility (MLF) in Japan Proton Accelerator Research Complex (J-PARC) was designed for measuring the dynamics of several tens MeV; corresponding nanosecond, order in nanometre order spaces, which should be suitable for study the surfactants and polymer chain movements in composites.

An organic clay was prepared by using the synthetic expandable fluoromica; ME100, cation exchanged for dioctadecyl dimethyl ammonium. An atactic polypropylene (a-PP)and 33 wt% of the organic clay were kneaded at 170 °C to get the exfoliation type [2] a-PP/Clay nanocomposite, followed by hot-press plates forming with about 70 mm x 70 mm x 0.2~0.3 mmt. The composite and two reference samples; organic clay and a-PP, were checked by DSC in advance of the QENS measurements. The QENS spectra for the samples in aluminium containers were collected using BL02 installed in J-PARC with $0.28 Å^{-1}<Q<1.7 Å^{-1}$, that is corresponding $3.7 Å<r<22.4 Å$ in real space, -40 MeV < energy transfer (ΔE) < 100 MeV and 3.7 MeV of energy resolution. As the incoherent scattering length of H for the neutron used in this experiment (λ=6.26 Å) is $80.26x10^{-24} cm^2$ that is great larger than those of Si ($0.04 x10^{-24} cm^2$), Mg ($0.04 x10^{-24} cm^2$), O ($0.008 x10^{-24} cm^2$), F ($0.008 x10^{-24} cm^2$) and C($0.0035 x10^{-24} cm^2$), information obtained by neutron incoherent scattering are mostly that from molecules containing hydrogen. The scattering properties and the Q- ΔE space range of the spectrometer are suitable to study the rotation or slow translational movement of organic molecules in the interlayer or on the surface of silicate layers.

The results temperature dependence of elastic scattering intensity (elastic scan) were well corresponded to those of the DSC. The obtained QENS spectra at 273K, 373 K and 453 K, where surfactant is change from being severely impaired to being fairly mobile at 373 K and a-PP was also changed at 463 K, reflected the motions of surfactants in interlayer spacing and polymer chains surrounding silicate layers. However, we could a little but non-negligible difference from those obtained for reference samples, organic clay and a-PP at the same temperatures, that is expecting a signal from the interaction between the surfactants and polymer chains on the surface of the silicate layers. The movement of surfactant in the interlayer region was also interesting that is obviously different from that of a bilayer membrane of a resemble surfactant [3].

We are expecting this method to be one of the useful tools to distinguish between hybrids and composites.

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INHIBITION OF *E. COLI* GROWTH BY ADHERENCE TO SAPONITE PARTICLES

Gaálová Barbora (1)*, Kikhney Judith (2), Moter Annette (2), Bujdáková Helena (1)

(1) Comenius University in Bratislava, Faculty of Natural Sciences, Department of Microbiology and Virology, Ilkovičova 6, 84215, Bratislava, (2) Biofilmcenter, German Heart Center Berlin, Hindenburgdamm 30, 12203, Berlin, Germany
*gaalova@fns.uniba.sk

Research on clay minerals has received considerable attention in recent years, mainly for wide range of application, negligible environmental pollution and low price. In medicine, they are used as an alternative therapy for gastrointestinal and skin disorders. Although, the exact mechanisms of action are not fully known, adsorption of different substances or cells to negative charged clay surface plays the key role in this process, because of high exchange capacity of cations. This property can be used in a preparation of hybrid nanomaterials and nanocomposites, where the clay particles are carriers for biological active substances. Up to now, it has not been recorded any cases of resistance of microorganisms to clays, so it could be one of the promising alternative ways for eradication of microorganisms. Despite of intensive studies, there are a lot of unresolved questions related to the toxicity, immune response of host organism, or potential changes of gene expressions using clay nanoparticles. There is a need for analyse all of aspects of usage clay minerals to microorganisms, in pure form, as well as combined hybrid materials.

In *E. coli* model, we tested adhesion of cells to saponite particles, associated with inhibition of cell growth. The isolates are from different uro-infections and other sources from environment. All of isolates used in this study were identified biochemically (Enterotest 24, Coli test, Erba Lachema, Czech Republic) and confirmed by molecular analyses (restriction of 16S rDNA PCR products using enzymes BstBI and HaeIII or sequencing 16S rDNA). Our preliminary outcomes confirmed antimicrobial effect of saponite to reference strain *E. coli* CCM 3954 and some *E. coli* isolates in a scale of tested concentrations (from 0.5 mg/ml to 0.0125 mg/ml). The 0.5 mg/ml was evaluated as the concentration of saponite, which inhibited 50% of colony forming units CFU/ml of susceptible strains by plating samples on Mueller-Hinton agar, but 60% cells stayed metabolically active, evaluated by the viability assay by MTT reduction (3-[4,5-dimethylthiazol-2-yl]-2,5-diphenyl tetrazolium bromide), against the control without saponite. Using the technique of confocal laser scanning microscopy (CLSM) with the resazurine based viability staining (Almar Blue, 0.02% w/v) and FISH method we visualised the attachment of cells of different strains of *E. coli* to clay particles and their ability to form aggregates. In addition, we microscopically monitored the proportion of active (ribsosome containing) versus inactive cells after their adhesion to saponite particles in different time periods (4 h, 12 h and 24 h) *via* Fluorescence in situ hybridization (FISH). We hypothesized that a discrimination in behaviour of *E. coli* strains after their interaction with saponite could be associated with an expression of adhesins that is, generally, the *E. coli* strain-dependent characteristic. From the group of 4 tested genes for adhesins (fimA, pap, afa, aaf), the gene for FimA adhesin was proved by PCR and its presence was correlated with an increased adherence of 2 *E. coli* strains.

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NEMATIC *VS* LAMELLAR ORDER IN COLLOIDAL AQUEOUS SUSPENSIONS OF NANOSHEETS

Patrick Davidson (1), Christophe Penisson (2), Jean-Christophe P. Gabriel (2)*

(1) CNRS, Université Paris-Sud, Orsay, France, (2) CEA/INAC, Grenoble, France
*Jean-Christophe.Gabriel@cea.fr

Ordering 2D colloidal particles at the nanometer length-scale is currently a challenging and active research area in materials science [1]. Such ordering can spontaneously appear when anisotropic objects form liquid-crystalline phases. Well known for organic species, this tendency also exists for disk-like mineral particles [2,3], thus leading to nematic, lamellar and columnar mesophases [4,5]. In the case of nanosheets (defined as two-dimensional crystallites of sub-micronic diameter and of well-defined, small, thickness comparable to the unit-cell size) [6], nematic and lamellar phases were reported for clay particles [7,8], graphene and graphene oxide [9,10], titanates [11] or niobates [12,13] but so far, no columnar phase was ever described for such objects. Among nanosheets, phosphatoantimonate single layers ($H_3Sb_3P_2O_{14}$) were shown to display a liquid-crystalline lamellar phase [14] comprised of planar solid-like sheets (i.e. in which all atoms involved in a layer are covalently bonded) dispersed in water. Upon dilution, the lamellar spacing could be increased 100 fold, leading to 1D periodicities tunable from 1.5 to 225 nm. For such systems, significant differences were observed for two compounds of the same family, $H_3Sb_3P_2O_{14}$ and $HSbP_2O_8$, as the former leads to a lamellar phase whereas the latter only shows a nematic phase. Likewise, clay and graphene nanosheets self-assemble into nematic phases whereas niobates and phosphates sometimes display lamellar phases. The physical origin of such a difference in behavior remains largely unknown so far but might be ascribed to differences in sheet size, rigidity, polydispersity, and/or interaction potentials.

In this context, we will present the results of our recent detailed structural investigation by polarized-light optical microscopy and x-ray scattering of both lamellar and nematic phases in the system of phosphatoantimonates.

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NEW METHODOLOGY TO DISCRIMINATE ILLITE POLYTYPE BY ELECTRON DIFFRACTION

Anne-Claire Gaillot (1)*, Victor A. Drits (2), Bruno Lanson (3)

(1) Institut des Matériaux Jean Rouxel (IMN), Université de Nantes, CNRS, 2 rue de la Houssinière, BP 32229, 44322 Nantes Cedex 3, France, (2) Geological Institute, Russian Academy of Sciences, 7 Pyzhevsky street, 12 109017 Moscow, Russia, (3) ISTerre, Maison des Géosciences, CNRS & Univ. Grenoble Alpes, 38041 Grenoble Cedex 9, France
*Anne-Claire.Gaillot@cnrs-imn.fr

Illite is a widespread 2:1 phyllosilicate in soils and rocks, and its occurrence is for example known to have a direct impact on the permeability of sandstones and thus their oil reservoir potential. Several morphologies as well as different structural polytypes can be found within the same location. Statistical occurrence of different polytypes can be access by characterization using powder X-ray diffraction. However, concomitant analysis of both morphology and crystal structure of individual particles requires the use of transmission electron microscopy (TEM).

Recent work allowed us to develop a methodology to identify the illite polytypic variety using selected area electron diffraction (SAED) based on the qualitative analysis of the intensity distribution within the SAED pattern observed along the [001] zone axis [1]. However, this orientation is experimentally challenging to access, and observation along several zone axes is often needed to confirm the polytypic identification.

With technological progress of TEM instruments, a more advanced electron diffraction technique is recently developing to explore a large portion of the reciprocal space and perform 3D crystallographic analysis as done widely with x-rays. Insight on the precession electron diffraction technique and new possibilities for illite polytype discrimination will be presented.

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SPANISH CLAYS ENRICHED WITH NUTRIENTS AS COATING SEED MATERIALS

Antonia Gálvez, José Antonio Rodríguez-Liébana, Concepción Jiménez de Cisneros, Alberto López Galindo, César Viseras, Emilia Caballero, Aránzazu Peña*

Instituto Andaluz de Ciencias de la Tierra (CSIC-UGR), Avda. de las Palmeras 4, 18100 Armilla, Granada, Spain

Clays have been proposed for many industrial applications mainly because of their wide-ranging properties, high resistance to atmospheric conditions, geochemical purity, easy access to their deposits near the earth's surface and low price. In the seed agroindustrial market, coating seeds with nutrients is seen as an effective way of supplying starter fertilizer for the establishment and early growth of the seedlings. Thus, with the ultimate goal of designing enriched seed coatings, nine natural clay minerals (R1-R9) were collected fromthe eastern Andalusian region (south of Spain). The clays were evaluated for the retention of P, Mn and Zn, soil deficiencies of these nutrient elements have been reported [1]. The clays, characterized by X-ray powder diffraction and X-ray fluorescence, showed different mineralogical composition, consisting mainly of phyllosylicates (40-70%), quartz (13-25%)and calcite (up to 34%) and low organic carbon content (≤0.8%) [2]. The retention ability of the clays for the selected elements was established by batch adsorption studies and the experimental kinetic and adsorption data were fitted to various mathematical equations. Adsorption isotherms indicated that the maximum adsorption capacity on the analyzed clays was ranged as Zn>Mn>> P, as expected, because clays are hydrophilic and negatively charged and are therefore better adsorbents for cations than for anions. The highest amount of retained micronutrients, Zn and Mn, was found with R6 clay, possibly as a consequence of its highest amount of swelling clay minerals [2]. Meanwhile, amorphous aluminum oxides and iron compounds, higher inR7 and R9 [2], may be responsible for the larger capacity of these clays to adsorb P. Adsorption rates depended on the nutrient and the clay:the most rapid kinetics corresponded to R2 for Mn, to R6 for Zn and to R7 for P. In all cases Zn showed slower adsorption rates. The pseudo-second order model adequately explained the experimental kinetic data of Mn, Zn and P on the different adsorbents. Clays were able to retain nutrients for long periods of time (up to 96 days) and desorption was inversely related with adsorption. Simultaneous addition on selected clays of Zn and Mn led to significantly largernutrient desorption. The co-presence in clays of various elementsaffected their release, so this aspect deserves special attention in coating design. Results obtained suggest the feasibility of using these clay materials enriched with nutrients for seed coating.

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APPRAISING SOIL COMPONENTS GOVERNING THE SORPTION OF THE MONOTERPENE CARVONE IN AGRICULTURAL SOILS

Beatriz Gámiz*, M. Carmen Hermosín, Rafael Celis

Instituto de Recursos Naturales y Agrobiología de Sevilla (IRNAS), CSIC, Avenida Reina Mercedes 10, 41012 Sevilla, Spain
*bgamiz@irnase.csic.es

There is a worldwide trend to decrease the application of synthetic chemicals against pests. This trend is a consequence of the manifested environmental contamination and gradual pest resistance problems associated with the application of traditional pesticides. In this regard, the use of new pesticide active ingredients based on natural products has been proposed to increase the sustainability of agricultural activity [1]. For instance, some secondary metabolites in plants can be the source of inspiration to formulate new biopesticides. Such is the case of several monoterpenes, including carvone. Carvone exists in nature as two enantiomers, *R*-carvone and *S*-carvone, both with pesticidal properties. *R*-carvone has been proposed for use as an insect repellent and *S*-carvone as a plant growth regulator. Herbicidal properties have also been attributed to *R*-carvone [2]. In this work, the sorption of carvone enantiomers in six agricultural soils was assessed to determine the relationship between sorption and soil properties. Several model sorbents were also used to establish the role of mineral and organic colloidal components in carvone sorption. The results for this preliminary study could help to elucidate the behavior of these natural compounds in soil and could also be valuable to design new carvone-based pesticide formulations by supporting the active ingredient on clay minerals.

The batch sorption technique was used as a conventional method to assess the sorption of *RS*-carvone on the different agricultural soils selected, mainly characterized by their relatively low organic carbon content and different clay content and mineralogy. The model sorbents chosen to correlate the sorption observed in soils were three reference phyllosilicates (kaolinite, illite, and montmorillonite), a lab-synthesized Fe-oxide (ferrihydrite) and an olive-mill waste (OMW), the latter as representative of natural organic matter. The analysis of carvone was conducted using chiral high performance liquid chromatography (HPLC) to assess the individual sorptive behavior of the *R*- and *S*-carvone enantiomers. Distribution coefficients, K_d (L kg^{-1}), were calculated to express carvone sorption.

Overall, the sorption of carvone was relatively low, with K_d values ranging between 0.23 and 1.26 L kg^{-1}, and was non-enantioselective, meaning that both enantiomers were sorbed equally on the soils. Correlations showed that organic matter was the most important component determining the sorption of carvone on the soils ($r = 0.917$, $p < 0.05$), which was supported by the higher sorption of carvone on OMW ($K_d = 26$ L kg^{-1}) compared to the mineral model sorbents ($K_d < 6.3$ L kg^{-1}). There was no positive correlation ($p > 0.05$) between carvone sorption on soils and the clay content, our results showed that the extent of sorption was affected by the mineralogy of the clay fraction. Thereby, relevant affinity of carvone towards expandable montmorillonite in contrast to kaolinite and illite was observed. Ferrihydrite exhibited similar sorption properties respect to montmorillonite. The sorption followed the order: montmorillonite > ferrihydrite > illite > kaolinite.

Our results indicated that the organic carbon content can be a good predictor for carvone sorption in the soil. However, clay mineralogy, specifically the presence of (expandable) smectites, could also be significant for the sorption of this organic compound in soils with low organic carbon content. Furthermore, the affinity of carvone towards smectitic minerals suggests the possibility of using these materials for the preparation of carvone formulations based on natural or modified clays as carriers.

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MIXED OXIDES DERIVED FROM HYDROTALCITE FOR DRY REFORMING OF METHANE

Siby I. Garcés Polo (1,2)*, Antonio Gil (1), Sophia A. Korili (1)

(1) Universidad Pública de Navarra, Pamplona, 31006 Spain, (2) Current address: Universidad Libre, Bogotá D.C., 111071, Colombia

Use of CO_2 as a chemical feedstock represents an effective route to reduce emissions of this agent of climate change. In Dry Reforming of Methane, DRM, ($CO_2 + CH_4 \leftrightarrow 2H_2 + 2CO$; $\Delta H^0 = 247\ kJ \cdot mol^{-1}$) two greenhouse gases are catalytically converted to syngas, a key intermediate in important chemical processes, such as the production of light hydrocarbons by Fischer-Tropsch synthesis. One of the main problems in DRM is the formation of carbonaceous deposits on the surface of the catalyst. A possible solution for reducing carbon formation is the use of selective active phases and suitable supports. In this respect, the use of hydrotalcite-based supports is a challenging option due to the presence of basic centers which adsorb CO_2 species capable of reaction with the formed carbon.

In this work, Co, Fe and Ni mixed oxides (from 1 to 20% nominal content) were prepared by impregnation of a commercial hydrotalcite with metal salts. The materials were characterized by N_2 adsorption-desorption experiments, X-ray diffraction (XRD), temperature-programmed reduction in H_2 (TPR) and determination of acidity by NH_3 adsorption. According to the characterization results, mixed oxides and spinels with high crystallinity were present in the samples. Several degrees of interactions between the metal phases and the support were observed, especially in the case of iron and cobalt. All solids had a meso-macroporous texture and a NH_3 acidity that decreased with the incorporation of the metals. The catalytic behavior in DRM was studied at the temperature range 500 - 700 ºC, at atmospheric pressure. The reactivity in the reforming reaction followed the order Ni>Co>Fe. Iron catalysts had a low activity under the studied conditions. Cobalt and nickel catalysts, especially the ones with metal content higher than 5%, had a considerable activity in the DRM reaction. The sample containing 10% Ni was the most active and stable catalyst. In order to better explain the behavior of the samples and the possible effect of the support on the reaction, high temperature (300 ºC) CO_2 adsorption experiments were performed with the samples containing 5% metal. A similar tendency (Ni>Co>Fe) was found.

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COMPARATIVE STABILITY STUDY (MLS) OF REFERENCE CLAY MINERAL SUSPENSIONS

Fernando García (1)*, Marek kojdecki (2), Pablo Pardo (3), Rafael Ibañez (4), Joaquín Bastida (1)

(1) UD Geología. Universidad de Valencia, Burjasot, Valencia, Spain, (2) Instytut Matematyki i Kryptologii, Wojskowa Akademia Techniczna, Warszawa, Poland, (3) Departamento Química Inorgánica, Universidad de Valencia, Burjasot, Valencia, Spain, (4) Centro Nacional de Investigación sobre la Evolución Humana (CENIEH), Burgos, Spain
*fer.garciatomas@gmail.com

The present work deals with a set of different clay minerals including three reference clays - kaolinite (KGa1, Georgia kaolins), dioctahedral smectite (SWy-1, Wyoming Bentonite), dioctahedral calcium smectite (SAz-1, Cheto Bentonite)- and two industrial clays: trioctahedral saponite (saponite Yunclillos supplied by Tolsa) and trioctahedral hectorite (Bentone HC, supplied by Elementis). The studied set includes clay minerals with two different structures: kaolinite, with dioctahedral 1:1 layer type without layer charge and smectite, presenting dioctahedral 2:1 layer type with low layer charge [1]. The aim of the work was to characterize the XRD microstructural characteristics and the behaviour of suspensions of that materials.

The particle size distributions (obtained by laser diffraction) and chemical compositions (obtained by ICP, INAA, ICP/MS and XRF techniques) of the samples are provided. XRD microstructural powder difraction analysis (performed by the Voigt function method [2]) and multiple scattered light analysis of diluted aqueous suspensions (2% volume fraction) were obtained for <0.5 µm and <20 µm fractions of each sample.

Values of crystallite size by the Voigt function method [2] (Dv of 001*) were determined for both, ethylenglycolated and untreated materials, with ranges 61-77 nm for kaolinites and 3-9 nm for smectites. XRD microstructural characteristics of the minerals allowed the interpretation of the behaviour of the aqueous suspensions of the materials.

MLS analyzer gave different kinds of sedimentation (individual, compression, in mass, heterogeneous and by agglomeration) [3] and flocculation rates (0%/d -14%/d) of aqueous suspensions, and their sequence was found to be in agreement with the increasing sequence of measured XRD sizes

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ACTIVATION EFFECTS OF PHYLLOSILICATES IN CLAY MINERAL BASED WASTE FOR USE AS SUPPLEMENTARY CEMENTITIOUS MATERIALS

Raquel Vigil De La Villa (1), Rosario García (1)*, Moisés Frías (2),
Sagrario Martínez-Ramírez (3), Lucía Fernández-Carrasco (4), Iñigo Vegas (5)

(1) UAM, Departamento de Geología y Geoquímica. Associated Unit CSIC-UAM, raquel.vigil@uam.es, 28049 Madrid, Spain, (2) IETcc-CSIC, Eduardo Torroja Institute for Construction Sciences, mfrias@ietcc.csic.es; 28033Madrid, Spain, (3) IEM.CSIC, Institute for the Structure of Matter, sagrario@iem.cfmac.csic.es, Madrid, Spain, (4) UPB, Universidad Politécnica de Barcelona, lucia.fernandez@upc.edu; Barcelona, Spain, (5) Tecnalia, Área de Materiales, inigo.vegas@tecnalia.es; 48160 Derio, Spain
*rosario.garcia@uam.es

The manufacture of cements and concretes calls for new sources of products with high pozzolanic activity, which can help to improve the mechanical performance and the durability of the resulting matrix. These products will also reduce production costs and environmental impact.

The environmental impact of the accumulation of coal waste because of mining activity creates a need to study eco-innovative solutions for the exploitation of these waste products, aimed at recovering the mineral and energetic resources in a systematic way at the lowest cost to the environment.

Coal waste is formed of phylosillicates, illite, and kaolinite among other minerals. Controlled thermal activation of these phyllosilicates yields materials with high pozzolanic properties. Previous research exists on the addition of a chemical agent (ZnO) to natural kaolinite before the thermal activation treatment, in order to increase the chemical reactivity of the metakaolinite.

However, there is nothing in relation to kaolinite based industrial waste. For this reason, in this paper, the combined effects of temperature (600 °C / 2h) and a chemical agent (3% wt. of ZnO) on the mineralogy and pozzolanic properties of the coal waste are studied at 1 and 7 days of hydration time, through different techniques of characterization (XRF, XRD, SEM/EDX, TG/DTG, Raman, FT-IR).

The results are compared with those obtained for 100% coal waste under the same test conditions. The initial scientific results in this work on the effect of ZnOas a possible activator of recycled phyllosilicates obtained from industrial waste were not promising.

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FORMATION OF LDH (PHYLLOSILICATE/CARBONATE) TYPE COMPOUNDS IN THE POZZOLANIC REACTION OF INDUSTRIAL WASTE CONTAINING PHYLLOSILICATES

Isabel Sánchez (1), Marío Ramírez (2)*, Raquel Vigil De La Villa (2), Rosario García (2), Antonio Zapardiel (1)

(1) UNED, Departamento de Ciencias Analíticas; azapardiel@ccia.uned.es, 28040 Madrid, Spain, (2) UAM, Departamento de Geología y Geoquímica, 28049 Madrid, Spain
*mario.ramirez@uam.es, raquel.vigil@uam.es, rosario.garcia@uam.es

The exploitation of any sub-product or waste generated during an industrial process has, at present, great importance from various perspectives: scientific, technical, economic, energetic and environmental. One avenue open to the construction sector, for the exploitation of these solid industrial waste products, is their incorporation as active additions to cement.

Mineralogically, some industrial wastes are formed of an organic fraction and inorganic compounds among which the phyllosilicates are prominent. Controlled thermal activation of phyllosilicates yields dehydroxylated products with high pozzolanic properties. Hydrated crystalline phases and amorphous phases appearing during the pozzolanic reaction in a dehydroxylated phyllosilicate/lime system.

Layered Double Hydroxides (LDHs) are laminar layers of hydroxides with a positive laminar charge in the interlaminar region that is compensated by the presence of anions. In this structural group, both hydrotalcite (defined as the superimposition of octahedric layers of magnesium and aluminium hydroxides) and carboaluminate (superimposition of octahedric layers of magnesium and aluminium), are found. This process generate an excess positive charge in the interlaminar region that is compensated by anions; when the anion that neutralizes that charge is the carbonate anion, the spacing measured by X-Ray diffraction is 7.57 Å. The material formed in the pozzolanic reaction of industrial waste comprising the phyllosilicates could be included in this structural group.

In this study, the LDH (phyllosilicate/carbonate) phase, formed after 28 days of pozzolanic reaction in a metakaolin/lime system, is characterized using FRX, DRX, SEM-EDX, TG/ATD, FTIR, BET, RMN-MAS and Raman spectroscopy. The metakaolin was obtained from a mix of 50% kaolinite and 50% calcite, thermically activated at 600 ºC and 750 ºC, respectively for 2 hours.

The LDH (phyllosilicate/carbonate) type compound may be considered the superposition of tetrahedric layers of silica and octahedric layers of aluminium, dehydroxylated type 1:1 kaolinite/phyllosilicate, generating a positive charge in the interlaminar region that is compensated by carbonate anions, increasing the spectrographic spacing to 7.57 Å.

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MINERALOGY AND SPECTRAL RESPONSE OF TERTIARY - QUATERNARY SEDIMENTS FROM THE ESQUIVIAS AREA (TAJO BASIN, SPAIN)

Javier García-Rivas (1,2)*, Mercedes Suárez (1), Emilia García-Romero (2, 3), Eduardo García-Meléndez (4), Arturo Báscones (4), Manuel Sánchez Del Rio (5)

(1) Departament of Geología. University of Salamanca. Plaza de la Merced s/n. 37008. Salamanca. Spain, (2) Instituto de Geociencias (IGEO). Universidad Complutense de Madrid - Consejo Superior de Investigaciones Científicas. Avd. José Antonio Novais s/n. 28040. Madrid. Spain, (3) Departament of Crystalography and Mineralogy. Universidad Complutense de Madrid. Avd. José Antonio Novais s/n. 28040. Madrid. Spain, (4) Department of Geography and Geology. University of León. Campus de Vegazana s/n. 24007. León. Spain, (5) European Synchrotron Radiation Facility

The Tajo Basin is an intracratonic basin located in the centre of the Iberian Peninsula, originated by the alpine deformation and with its evolution was conditioned by the late variscan deformation. It was filled during the Tertiary by materials coming from the surrounding mountain ranges (Cordillera Ibérica, Sierra de Altomira, Sistema Central and Montes de Toledo). This basin is one of the most important deposits of the world of sepiolite and saponite, being particularly rare due to the high content in magnesic clays and to the lack of potential source rocks with high content in Mg. The spectral response of these magnesic clays in the NIR is discriminating, which enables their identification and mapping on the land surface by remote sensing. This work presents the preliminary results, concerning to the mineralogical composition and its relation with the spectral response in the NIR spectra, as a base for the study by remote sensing of this rich in Mg clays area. For this work, we have collected 48 superficial ground samples (~15 first centimetres) from an area of the Tajo Basin, at the south of Madrid, sampling the surface of formations both from the Tertiary (mainly Miocene) and from the Quaternary. Samples TES1 - TES7 were collected to the south of the locality of Borox (Toledo, Spain),. Samples TES8 - TES23 were collected along a pathway between the localities of Borox and Numancia de la Sagra, while samples TES24 - TES48 were collected along a different pathway between the same localities, approximately 1.5km to the south of the previous one.

The mineralogical composition of the samples were obtained by X-Ray Diffraction (XRD) using a diffractometer with CuKα radiation, both powder and oriented aggregates and their treatments to study the clay fraction. A semi-quantification of these mineral phases was performed through the reflective power method. We obtained the spectral response, both with the original texture as well as powdered sample, using a spectroradiometer with artificial light at the laboratory. Statistic treatment was performed by using the SPSS software.

The minerals identified in these samples were quartz, calcite, dolomite, gypsum, k-feldspar and plagioclase, along with several phyllosilicates such as smectite, illite, chlorite and kaolinite. Sepiolite was identified only in a sample close to Numancia de la Sagra. Regarding to the mineralogical composition, different associations have been defined: illitic, quart-feldspar, gypsum, and carbonatic associations. On the other way, the recorded spectra have been also classified in several groups according to the position and depth of the absorption bands and the maximum reflectance. A statistic treatment of mineralogical composition (proportion of each mineral and association type) and grouping of spectra had been made. The obtained results indicate that the spectra groping made could be extrapolate and help to identify and mapping the area in terms of mineralogical composition.

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CONVENTIONAL HYDROTHERMAL SYNTHESIS OF ZEOLITES BY USING SANITARY WARE WASTES AS RAW MATERIAL

Fátima Garcia-Villen (1,2)*, Eduardo Flores-Ruiz (2), Cristóbal Verdugo-escamilla (2), F. Javier Huertas (2)

(1) Department of Pharmacy and Pharmaceutical Technology (University of Granada), Granada, Spain, (2) Instituto Andaluz de Ciencias de la Tierra (CSIC-University of Granada), Armilla (Granada), Spain
*fgarvillen@ugr.es

Zeolites are extensively produced by hydrothermal treatment of different raw materials, as kaolin, metakaolin, or fly ash among others. The use of waste materials, by products of energy production or ceramic industry, in zeolites synthesis give them an added value as well as routes for their recycling.

Sanitary ware (SW) is a ceramic ware usually found in sinks, urinals and bathtubs whose production is led by Spanish domestic clay product industry. SW manufacture involves the use of kaolin, white clay and feldspar. The industrial production of SW generates approximately 8% of solid wastes in Spain, which increases landfills sizes and pose economic, social and technical problems [1,2].

This study aims to evaluate the feasibility of SW to produce zeolites once subjected to a conventional hydrothermal treatment during different times (1-30 days) and temperatures (100 - 200 ºC). Ground SW (2 g) were added to 10 mL of NaOH (5 M) inside a Teflon-lined stainless steel reactor (Parr 4744). Hydrothermal treatment was quenched with cold water. Solution was discarded and solid phases were washed 10 times with purified water, dried at 50 ºC and then manually ground. No special precautions were taken to prevent atmospheric CO_2 taking up during the process.

X-ray powder diffraction (XRD), Fourier-transform infrared spectroscopy (FT-IR) and scanning electron microscopy (SEM) were used to characterise both the raw material and resultant minerals phases. Additionally, chemical composition, major and trace elements, of SW was obtained by X-ray fluorescence (XRF).

Quartz and mullite present in SW transform into zeolites, as temperature and time increase, whereas zircon remains unreacted. Cancrinite (CAN), analcime (ANA) and sodalite (SOD) were the main zeolitic phases identified. Cancrinite crystallization is favoured by high temperatures, from 150 ºC to 200 ºC, while sodalite is formed preferentially at temperatures lower than 150 ºC; analcime behaves as a metastable phase, that crystallizes at short time (e.g., 1-7 days, 150 ºC) and disappear at longer reaction time.

We can conclude conventional SW wastes are an optimal raw material for zeolites synthesis under high alkaline hydrothermal conditions. Combining time and temperature it is possible to drive crystallization towards a particular phase.

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ANDALUSIAN PEATS IN HEALTH CARE FORMULATIONS. I. COMPOSITION OF THE RAW MATERIALS

García-Villén Fátima (1)*, Sánchez-Espejo Rita (2), Carazo Esperanza (1), Borrego-Sánchez Ana (2), Aguzzi Carola (1), Cerezo Pilar (1), Viseras César (1,3)

(1) Department of Pharmacy and Pharmaceutical Technology, University of Granada, Campus of Cartuja, 18071 s/n. (Granada), Spain, (2) Aguas Termales de Graena, S.A. C/San Antonio, 5 18517 Cortes y Graena (Granada), (3) Andalusian Institute of Earth Sciences, CSIC-University of Granada, Avda. de Las Palmeras 4, 18100. (Granada), Spain
*fgarvillen@ugr.es

Peats are natural materials with dark-brown colour resulting from transformation of vegetable wastes under anaerobic conditions in humid ambient. They are mainly composed of water and organic molecules (humic acids, humin and fulvic acids, lignin, cellulose, pectins). Peats also contain minor amounts of minerals, including clay minerals. Organic peat compounds have demonstrated biologic activities which make them potentially useful in topical health care [1]. Inorganic components, and in particular clay minerals, may greatly influence the technological and biopharmaceutical properties of peats, as for example, stability and rheology of the solid/water systems or bioavailability of the organic actives when topically applied, as happens with similar clay/organic systems [2]. Consequently, detailed identification of the mineral phases associated with organic substances in peat deposits must be considered in the design of semisolid health care formulations with these materials [3].

With these premises, three consecutive strata (P1, P2 and P3 from top to bottom) from a peat deposit in El Padul, (Granada, Spain) were characterised by X-ray powder diffraction (XRPD), thermogravimetric analysis (TGA) and elemental analysis (EAN). XRPD were done by using a Philips® X-Pert diffractometer with Cu Kα radiation. TGA analysis were carried out using a METTLER TOLEDO mod. TGA/DSC1 with FRS5 sensor and a microbalance (precision 0.1 µg) (Mettler-Toledo GMBH) under aerobic conditions in the interval 30-950 °C at 10 °C/min. EAN analysis of the samples were carried out with a CHNS/O analyser, FLASH 2000 model (Thermo Scientific).

P1 was mainly composed of chlorite and appeared as brownish-grey colour material whereas P2 showed an intense black colour and was composed mainly of organic matter and P3, with a grey tonality, was formed mainly by carbonates. TGA curves showed a first weight loss at around 100ºC attributed to water loss with values of 24% w/w (P1), 76% w/w (P2) and 35% w/w (P3). Total weight loss of the samples achieved 32% w/w (P1), 92% w/w (P2) and 64% w/w (P3), including loss of organic matter and carbonates. EAN results confirmed P2 (with 37% of C) as the stratum with highest amount of organic matter, while P1 only possessed 2% w/w of C; the higher amount of C in P3 stratum (13% w/w) was due to carbonates since N only accounted 0.12% w/w in this sample. Design of topical formulations with different proportions of P1, P2 and P3 would be necessary to obtain systems with optimal technological and biopharmaceutical properties.

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ANDALUSIAN PEATS IN HEALTH CARE FORMULATIONS. II. DEVELOPMENT OF SEMISOLID TOPICAL SYSTEMS

García-Villén Fátima (1)*, Sánchez-espejo Rita (2), Carazo Esperanza (1), Borrego-Sánchez Ana (2), Aguzzi Carola (1), Cerezo Pilar (1), Viseras César (1,3)

(1) Department of Pharmacy and Pharmaceutical Technology, University of Granada, Campus of Cartuja, 18071 s/n. (Granada), Spain, (2) Aguas Termales de Graena, S.A. C/San Antonio, 5 18517 Cortes y Graena (Granada), (3) Andalusian Institute of Earth Sciences, CSIC-University of Granada, Avda. de Las Palmeras 4, 18100. (Granada), Spain
*fgarvillen@ugr.es

Peat baths are semisolid systems used in Medical Hydrology and cosmetic treatments on the basis of chemical and physical mechanisms [1,2]. Classical use of these materials in the spa centres does not imply any manipulation or improvement of the solid/water system. However, it is well known that performance of semisolid topical formulations is strongly affected by their composition and preparation conditions. It has been fully demonstrated that rheology of solid/liquid systems determines their physical stability and applications [3]. The presence of clay minerals greatly influences technical and pharmaceutical parameters making necessary a systematic design of formulations with a view to optimize these topical systems [4]. In a previous work, composition of three different strata of an Andalusian peat deposit has been studied [5]. In detail, three consecutive strata (P1, P2 and P3 from top to bottom) from a peat deposit in El Padul, (Granada, Spain) were characterised by X-ray powder diffraction, thermogravimetry and elemental analyses. Compositional differences in the three strata allowed to conclude the necessity of formulate semisolid systems composed with different proportions of each stratum to obtain optimized baths. With these premises, in this work, dispersed system produced by mixing different proportions of P1, P2 and P3 were prepared and the resultant technological properties were determined including extensibility, cooling kinetics, pH and water retention. The results were then used to define the feasibility as semisolid health care formulations.

Extensibility was measured following the normalized method of Spanish National Formulary [6]. Cooling of the systems was measured following Cara et al., 2000 [7]. Crison 25+ pH-meter, equipped with a solid electrode (pH 2-11, Code 5053T), was used to determine pH of all the systems. Water retention capacity was evaluated by adding known volumes of purified water to the systems.

Extensibility, pH and water retention greatly depended on the composition of the systems, making necessary combination of the different stratum to obtain optimized peat baths. In particular, medium-high amount of P2 resulted in higher extensible systems, but presence of P1 and P3 was necessary to control final pH and water retention. Cooling kinetics depended on the solid/liquid proportion and secondarily on the solid composition.

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REGENERABLE STIMULI RESPONSIVE PVP-CLAY GRAFT COMPOSITES FOR THE REMOVAL OF HERBICIDES AND OXYANIONS FROM WATER

Ido Gardi*, Yael G. Mishael

Dept. Soil and Water Sci., The Faculty of Agri., Food and Environ., The Hebrew University of Jerusalem, P.O. Box 12, Rehovot 7610001, Israel
*Ido.Gardi@mail.huji.ac.il

In recent years, many studies have reported the development of polymer-clay composite sorbents for specific and high pollutant removal. High affinity of the pollutants to these sorbents frequently causes regeneration and reuse to be extremely challenging, due to irreversible binding and/or due to polymer loss during regeneration. In the current study, we aimed to develop new regenerable polymer-clay sorbents based on covalently grafted poly vinylpyridine (PVP) to montmorillonite. PVP grafted chains extends or collapses upon pH decrease and increase, respectively, due to gaining or losing monomer charge. The sorbents were prepared in four stages: 1. Acid activating the clay 2. Covalently grafting 3-aminopropyltriethoxysilane (APS) to the clay (determines grafting density) 3. Surface initiation with 2-bromoisobutyryl bromide and 4. Surface initiated atom transfer radical polymerization (SI-ATRP) of PVP. The sorbents were characterized by zeta potential, XRD, FTIR, TGA and XPS measurements. The colloidal size of the new composites can reversibly shrink to nearly a quarter of its original size, upon pH change from 2.5 to 8. Finally, the removal of herbicides and oxyanions by the sorbents and their recovery was explored. Adsorption of selenium to the composites depended mainly on the surface zeta potential, which increases with PVP chain length, while the adsorption of atrazine did not depended on polymer loading. Selenium and atrazine adsorption and desorption was demonstrated as a function of pH. Selenium filtration by composite columns presented a high capacity of 22.4 mg Se per g and column regeneration was achieved by increasing pH with 90% selenium desorption. Re-activation of the regenerated sorbent was performed by washing it with an acidic solution. Re-adsorption of selenium was as high as the first cycle and no polymer desorption was observed.

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NEW INSIGHTS IN THE MECHANISM OF FORMATION OF ORGANIC-INORGANIC HYBRIDS HAVING A TALC-LIKE STRUCTURE

Audrey Garnier (1,2), Jocelyne Brendle (1)*, Veronique Bounor-Legare (2), Fernande Da Cruz Boisson (3), Severinne Rigolet (1)

(1) Institut de Science des Matériaux de Mulhouse, UMR CNRS 7361, ENSCMu, Université de Haute Alsace, Mulhouse, 68093, France, (2) Ingénierie des Matériaux Polymères, IMP, UMR CNRS 5223, Université Lyon 1, Villeurbanne, 69622, France, (3) INSA Lyon, Service commun de RMN, Ingénierie des Matériaux Polymères, IMP, UMR CNRS 5223, Université Lyon 1, Villeurbanne, 69622, France
*Jocelyne.Brendle@uha.fr

The sol-gel process, involving hydrolysis and condensation reactions is an attractive way to form siloxane based hybrid materials since it is a one-step method performed under mild conditions. Organic-inorganic talc-like hybrids (TLH) can be obtained by this procedure starting from organotrialkoxysilanes with different functionalities, an ethanolic solution of magnesium salts, and in some case, an aqueous solution of sodium hydroxide. By this way, organic moieties are covalently bonding to the silicon of the tetrahedral sheets and pending in the interlayer space. The interesting feature in this case is that as many organotrialcoxysilanes are on the market, a wide range of organic moieties can be introduced as pending groups in the interlayer space leading to applications in various fields such as heavy metal cations chelation or fillers for polymers.

In this context, the purpose of our work was to study the mechanism of formation of these attractive compounds by using an innovative approach, i.e. by investigating the hydrolysis and condensation reactions occuring during the formation of TLH by high resolution ^{1}H, ^{29}Si and ^{31}P liquid nuclear magnetic resonance (NMR) and then characterize the obtained solids by ^{29}Si and ^{31}P solid state NMR and powder X-Ray diffraction. Diethylphosphatoethyltriethoxisilane (SiP) and magnesium nitrate were used as silicon and magnesium sources respectively. The influence of the magnesium nitrate on the hydrolysis and condensation of SiP as well as the relative concentration of NaOH aqueous solution used for the synthesis and the pH value of the reaction media were carefully studied. ^{29}Si liquid nuclear magnetic resonance (NMR) results indicated that magnesium nitrate increases dramatically the hydrolysis rate of SiP. The obtained results suggest also a scission of Si-O-Si or Si-O-Mg bonds for pH values up to 10 and whatever the NaOH concentration, a modification of the phosphorous local environment.

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ORGANIC-INORGANIC HYBRIDS HAVING A TALC LIKE STRUCTURE AS POTENTIAL FLAME RETARDANT FOR PA6

Audrey Garnier (1,2), Jocelyne Brendle (1)*, Veronique Bounor-Legare (2), Fabienne Samyn (3), Sophie Duquesne (3), Serge Bourbigot (3), Fernande Da Cruz Boisson (4), Severinne Rigolet (1)

(1) Institut de Science des Matériaux de Mulhouse, UMR CNRS 7361, ENSCMu, Université de Haute Alsace, Mulhouse, 68093, France, (2) Ingénierie des Matériaux Polymères, IMP, UMR CNRS 5223, Université Lyon 1, Villeurbanne, 69622, France, (3) UMET, CNRS, UMR 8207, ENSCL, Université de Lille, F-59000 Lille, France, (4) INSA Lyon, Service commun de RMN, Ingénierie des Matériaux Polymères, IMP, UMR CNRS 5223, Université Lyon 1, Villeurbanne, 69622, France
*Jocelyne.Brendle@uha.fr

The development of fire retardant polymer nanocomposites containing montmorillonite or lamellar double hydroxides has been extensively investigated. Particular attention has been paid to the modification of the inorganic filler with organic surfactant or to the modification of the processing technology in order to evenly disperse the nanofiller in the matrix. However, even if success has been achieved on the dispersion of the filler at a nanoscale, these materials by themselves are unable to pass some fire tests of interest such as for example UL-94. This is generally explained by the fact that upon burning, the accumulation on the sample surface of the initially well dispersed platelets forms a protective barrier that delay the release of combustible gases to feed the flame [1]. However, the presence of the filler does not affect the composition and the quantity of gases. With such organo-modified nanofiller, the combustion cycle is thus not interrupted but the combustion is delayed [2].

In that frame, the aim of this presentation is to investigate the use of new hybrid organic-inorganic systems including organic moieties covalently bonded to the tetrahedral sheets of the talc-like structure. With such an approach, it is expected to form of a highly cohesive structure when the material burns that will allow to interrupt the combustion of the polymer leading to improved fire retardant performance.

Talc like hybrids (TLH) having the chemical formula $Mg_3(RSi)_4O_8(OH)_2$ where R stands for an organic moiety containing phosphorous have been incorporated in polyamide-6 (PA6). Two approaches were followed to prepare the PA6/TLH composites. The TLH synthesized using a sol-gel process have been either prepared prior to their incorporation in PA6 (ex situ route) or were formed by reactive extrusion in PA6 (in situ route). A set of analyses performed on the TLH prepared ex situ indicate the formation of a lamellar structure (XRD, IRTF, solid state ^{29}Si NMR) whereas the formation of a layered structure was not proven in the case of the in situ synthesis. Regarding the TLH prepared ex situ, this filler was not nanodispersed in the PA6 according to the SEM observations. In terms of fire performances, improvements have been observed for both materials in mass loss cone calorimeter and LOI.

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CATALYTIC ACTIVITY OF COPPER-DOPED TITANIA-PILLARED CLAY CATALYST TOWARDS BIGINELLI REACTION

Smitha George (1), Sneha Sreekumar (2), Nikhil Mohan (3), Kannan Vellayan (4), Beatriz González (5)*

(1) Cochin University of Science and Technology, Kerala 682022, India, (2) University of Hyderabad, Telangana, 500046, India, (3) Central University of Tamil Nadu, 610101, India, (4) Department of Chemistry, Government College, Kattappana, Kerala, India, (5) Dep. Química Inorgánica, Univ. Salamanca, 37008 Salamanca, Spain

Development of clean and environmentally benign chemical processes using less harmful catalysts has become a primary goal in synthetic organic chemistry. Reactions carried out under heterogeneous conditions are more promising as they involve the facile recovery and reuse of the catalysts. In this sense, clays are suitable catalysts for carrying out organic reactions. Clays can accommodate ligands in their layered structure or change their natural cations by transition metal cations. Clays can function as Brønsted and/or Lewis acids, or as bases. Clays with combined acidic and basic properties have been developed by simple procedures of modification. Such clays are employed to catalyze a sequence of acid and base-catalyzed reactions in one pot.

Multicomponent condensations (MCC) are of great importance in organic and medicinal chemistry, where three or more reactants combine to afford a new core structure possessing the molecular features of the composite building blocks, being a powerful method for the preparation of molecular diversity. One of the many examples of a three MCC, Biginelli reaction, brings together ureas, aldehydes and β-ketoesters to afford functionalized pyrimidinones as the core structure. The present communication discusses the investigation of the catalytic activity of a Cu-doped Ti-pillared clay catalyst towards Biginelli reaction.

Biginelli reaction was carried out by mixing equimolar amounts (8.33 mmol) of diketone (acetylacetone, ethylacetoacetate), aldehyde (benzaldehyde, p-nitrobenzaldehyde, 4-chlorobenzaldehyde, anisaldehyde, furfuraldehyde, cinnamaldehyde) and urea in a round bottom flask containing Cu-doped Ti-pillared clay catalyst. Ethanol was added as solvent. Under room temperature, no reaction was found. At 70 ºC, 25 mg of catalyst for a time period of 6 h showed good yield. But to facilitate the use of the valuable catalyst, the reaction conditions were optimized as 70 ºC with 10 mg catalyst for overnight. Among different aldehyde tried, 4-chlorobenzaldehyde was found to give maximum yield of 90% with both the diketones. Benzaldehyde gives 88% product yield with acetylacetone and 86% yield with ethylacetoacetate. The catalyst was found to be 100% selective towards 3,4-dihydropyrimidin-2(1H)-one derivative. After the reaction, reaction mixture was cooled to room temperature, filtered and poured into crushed ice and stirred for 5-10 min and recrystallized from hot ethanol to afford pure product. The products were analyzed with GCMS, and comparison of the spectral data (FT-IR, ^{1}H NMR) and melting point with those reported. The yield of the products correlated well with the expected electronic effects of the substituents. Reusability of Cu-doped Ti-pillared clay catalyst towards Biginelli reaction was tested for three reaction cycles without loss of significant catalytic activity.

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GEOPOLYMER MATERIALS BASED ON DIFFERENT ALUMINOSILICATE SOURCES

Ameni Gharzouni*, Sylvie Rossignol

Science des Procédés Céramiques et de Traitements de Surface (SPCTS), 12 rue Atlantis, 87068, Limoges Cedex, France

Over the last decades, geopolymers have gained tremendous interest as promising new binders, environmentally friendly and with good working properties. These ecomaterials result from the activation of an aluminosilicate source by an alkaline solution at room temperature. Metakaolin is one of the most used aluminosilicate precursor due to its high purity and reactivity. Nevertheless, research of low-cost and more available materials has encouraged many investigators to turn to the use of common clays and industrial co-products. In this topic, the objective of this work is to compare various geopolymer materials based on different aluminosilicate sources such as two metakaolins with different characteristics, dredged sediment and argillite (host rock for nuclear waste disposal) which are rich in calcite. At first, the reactivity of the different studied aluminosilicate sources was estimated using chemical characterization and structural investigations by XR diffraction and ^{27}Al NMR spectroscopy. Then, the feasibility of geopolymer materials based on the different precursors was evaluated. The structural evolution of the reactive mixtures during the formation was investigated using FTIR spectroscopy. Finally, the measurement of mechanical strength was tested by compression.

Whatever the aluminosilicate source, the reactivity increases essentially with the increase of purity degree, amorphous phase and wettability value. Further structural informations were given by ^{27}Al NMR concerning the effect of heat treatment on the conversion rate of $Al^{(VI)}$ and $Al^{(V)}$ species to $Al^{(IV)}$ one. For example, a heat treatment of argillite at 800 °C induces a total transformation of $Al^{(VI)}$ to $Al^{(IV)}$. Moreover, the feasibility study evidences the suitability of the different sources after heat treatment to produce geopolymer materials. Then, the investigation of geopolymer formation using in situ FTIR spectroscopy revealed that the presence of impurities is responsible of the generation of several networks. Indeed, the presence of calcium in sediment and argillite samples leads to the competition between Si-O-Al and Si-O-Ca bonds. The formed networks influence the mechanical properties of the resulting materials. Better compressive strengths were obtained for metakaolin based geopolymers.

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HALLOYSITE NANOTUBES AS DRUG DELIVERY SYSTEMS FOR THE TREATMENT OF COLON CANCER

Eleni Gianni (1), Dimitrios Papoulis (1)*, Konstantinos Avgoustakis (2)

(1) Department of Geology, University of Patras, Rio 26 504, Patras, Greece, (2) Department of Pharmacy, University of Patras, Rio 26 504, Patras, Greece

Halloysite is a 1:1 aluminosilicate clay mineral. Usually it has a tubular crystal shape, a unique structure and significant solute entrapment properties. As a result halloysite can retain a variety of substances inside its lumen for different purposes and uses. In this study, halloysite nanotubes were investigated as possible drug delivery systems for colon cancer. Halloysite from the Dragon mine (Utah, USA) was used and in order to remove the impurities the clay fraction was extracted. The drug that was loaded within the lumen of halloysite nanotubes was irinotecan. In order to provide enteric release properties to the drug-loaded nanotubes, they were coated with the polymer Eudragit S 100. The reproducibility of the above procedures was tested by performing the experiments in triplicate and the results of the three different samples for each case were similar showing that in every case irinotecan as well the polymer reacts with halloysite following the same pattern.

The samples were characterized by many techniques including XRD, TEM, FTIR, TGA and DSL. It was found that irinotecan was successfully loaded within the lumen of halloysite with a loading capacity of 4.5%. Additionally, the samples that were treated with polymer found to be well coated. The release of irinotecan in simulated gastric and intestinal liquids was also tested. Sustained drug release was observed, which was slower with the polymer-coated samples. The results show that halloysite nanotubes are promising irinotecan delivery systems for colon cancer treatment.

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TWO-PHASE POROSITY-PRESERVING CHLORITE CEMENTS IN SHALLOW-MARINE VOLCANICLASTIC SANDSTONES: EVIDENCE FROM CRETACEOUS SANDSTONES OF THE SAWAN GAS FIELD, PAKISTAN

Anna Berger (1), Susanne Gier (1)*, Peter Krois (2)

(1) Department of Geodynamics and Sedimentology, University of Vienna, Althanstrasse 14, 1090 Vienna, Austria, (2) OMV AG, Trabrennstrasse 6-8, 1020 Vienna
*susanne.gier@univie.ac.at

Sandstones with high porosity and permeability at great burial depth and high temperatures are of economic importance, as a significant amount of hydrocarbons have been discovered in such reservoirs. The Sawan gas field, with an expected ultimate recovery of more than 1 Tcf lies in the Middle Indus basin. The reservoir rocks, Cretaceous volcaniclastic sandstones of the lower Goru Formation, show very high porosities at a reservoir temperature of 175° C and depths of 3000 to 3500 m. The sandstones are mostly feldspathic litharenites. Strongly altered volcanic rock fragments are the most important lithic component. The clay fraction consists of Fe-rich chlorite (chamosite) and illite.

Diagenetic features such as compaction, quartz overgrowths, carbonate cements and feldspar dissolution are observed. The most distinguishing feature is a double layer of authigenic chlorite, lining the pores of the sandstones. Chlorite additionally occurs as pore-filling cement and as chloritized detrital components, all having similar chemical composition. The pore-lining cement clearly developed in two stages; an earlier, poorly crystallized and a later better crystallized growth. Missing rims at grain contacts show that precipitation occurred after an initial stage of compaction but early relative to other diagenetic phases. Both chlorite rims grew by direct precipitation from pore waters, using products derived from volcanic rock fragments. In areas with no, thin, or discontinuous chlorite rims, quartz cementation is common. Well-developed chlorite rims inhibited quartz cementation, preserved porosities of up to 20% and good permeabilities. Porosity-preserving chlorite cementation in Sawan is restricted to sediments of a shallow-marine environment. While reported examples from shallow marine environment have formed through clay mineral precursor phases, the chlorites in the volcaniclastic sandstones of the lower Goru Formation can be traced back to the dissolution of detrital grains.

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LAPONITE FUNCTIONALIZED WITH BIURET AND MELAMINE - APPLICATION TO ADSORPTION OF TRIMETHOPRIM ANTIBIOTIC

Beatriz González (1), Tiago H. Da Silva (2), Katia J. Ciuffi (2), Miguel A. Vicente (1), Raquel Trujillano (1), Vicente Rives (1), Elena Pérez-Bernal (1)*, Emerson H. De Faria (2)

(1) GIR-QUESCAT, Departamento de Química Inorgánica, Universidad de Salamanca, 37008 Salamanca, Spain, (2) Universidade de Franca, Av. Dr. Armando Salles Oliveira, Parque Universitário, 201, 14404-600, Franca, SP, Brazil

Clay minerals are hydrophilic substances. However, for several uses, it is preferred, even mandatory, to confer their surface an organophilic nature by the incorporation of organic species. In all these uses, the organophilic nature of the clay mineral surfaces favours their interaction with other organic species (polymers, pollutants, etc.) [1,2]. Laponite (Lap) is a commercial synthetic hectorite. It exfoliates very easily in aqueous dispersion, and solid samples do not show a long order in their basal reflection. It has exchangeable cations that can be substituted by cationic species, but without intercalation. Functionalization of laponite has been scarcely studied [3], but it occurs by grafting on the external surface of the layers. Trimethoprim [5-(3,4,5-trimethoxybenzyl) pyrimidine-2,4-diamine] (TMP) is a drug used to treat infections, and may inhibit a variety of gram-positive and gram-negative bacteria [4], being used in various processes of antibacterial treatment. However, TMP is incompletely metabolized by the human body during the therapeutic process, and about 80% is excreted in the pharmacologically active form [4].

In the present work, results are presented on the adsorption of TMP using laponite/(3-chloropropyl) triethoxysilane (ClPTES)/(biuret (BIU) or melamine (MEL)) hybrids obtained by different routes, aqueous (H) and non-aqueous. Powder X-ray diffraction demonstrated the incorporation of the aminosilanes to the clay and that the reaction did not give rise to changes in the laponite layers. Characteristic IR bands of BIU or MEL evidenced the functionalization of Lap with the aminosilanes. The nitrogen adsorption isotherms can be classified as Type IV, with hysteresis H2, in the case of Lap, Lap-BiuH and Lap-MelH, and as Type IIb, with hysteresis H3, for samples Lap-Biu and Lap-Mel. Thermal analysis demonstrated that the organic matter immobilized on the laponite is burned off in the 150-650 °C range, and that the loss in both materials occurred in a similar manner. Kinetics studies (50 mg of material suspended in 5 mL of a 50 mg/L TMP solution with reaction times between 1 and 150 min) and equilibrium (50 mg of material suspended in 5 mL of solution ranging from 1 to 1000 mg/L, for a period of 20 min) were carried out to insight in the adsorption of TMP. The kinetics parameters were calculated using mathematical models and the data fitted better to the pseudo-first order model, showing that the adsorption process happened through a physisorption mechanism. The solids prepared by the non-hydrolytic route showed a higher adsorption capacity, as concluded from the data on the amounts of adsorbed TMP: q_t = 4.32 mg/g for Lap-Biu against q_t = 0.0043 mg/g for Lap-BiuH, and q_t = 4.87 mg/g for Lap-Mel versus q_t = 0.0050 mg/g for Lap-MelH.

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SOL-GEL Fe,Si/CLAY COMPOSITES AS CATALYSTS FOR THE SYNTHESIS OF 1,5-BENZODIAZEPINE FROM 1,2 PHENYLENEDIAMINE AND ACETONE

Beatriz González (1)*, Raquel Trujillano (1), Maria Timofeeva (2), Miguel A. Vicente (1), Antonio Gil (3)

(1) Dep. Química Inorgánica, Universidad de Salamanca, Salamanca, Spain, (2) Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia, (3) Dep. Química Aplicada, Universidad Pública de Navarra, Pamplona, Spain
*bei@usal.es

The intercalation chemistry of smectite clays is one of the main fields for preparation of catalysts or catalyst supports as alternatives to zeolites and zeotype materials. Materials prepared via layer intercalation show high thermal resistance and stability, development of microporosity, great surface area and presence of Brønsted and Lewis acid sites. Pillared clays (PILCs), such as Al-PILCs, Fe-PILCs, mixed Fe,Al-PILCs etc., synthesized via exchange of interlayer cations and subsequent calcination of the intercalated solids, are widely studied. Nowadays, a sol-gel approach to modifying clay surfaces has attracted attention as an alternative way for synthesis of porous clay-nanocomposites. However, information on physicochemical and catalytic properties of these materials is limited in the literature.

In this work, we report for the first time on the synthesis of mixed Fe/Si/clay composites (Fe/Si-CC) by sol-gel method and their physicochemical and catalytic behaviour in acid catalysis. Fe/Si-CC materials were prepared from purified montmorillonite (Cheto, Arizona, USA) through sol-gel polymerization technique using APTES (3-aminopropyltriethoxysilane) and $FeCl_3.6H_2O$ as sources of Si and Fe, in aqueous medium. The amount of Fe in the solids was varied in the interval of 1.9-3.8 wt.%. Fe/Si-CC materials were calcined at 400 or 500 °C (Fe/Si-CC-400, Fe/Si-CC-500).

The physicochemical characterization pointed out the effectiveness of the incorporation of Fe and Si in the interlayer space of the clay. Specific surface area of Fe/Si-CC-500 samples rose from 80 to 171 m^2/g with increasing of Fe content from 1.9 to 3.8 wt.%. The interlayer space also depended on the Fe content, the insertion of 1.9 wt.% Fe to the framework of the clay increased the interlayer space from 9.57 to 13.89 Å, but the further increase of Fe content led to the decrease in the interlayer distance to 13.69 Å. Probably, this phenomenon is related to the increase of Fe content with respect to Si content in the solids. According to DR-UV-vis spectroscopy, oligomeric state of Fe in Fe/Si-CC-400 depended on Fe content; the larger Fe content, the larger particle size of Fe_2O_3.

Catalytic properties of Fe/Si-CC materials were studied in cyclocondensation of o-phenylenediamine (DA) with acetone to 1,5-benzodiazepine. Benzadiazepines and their derivatives are very important class of nitrogen-containing heterocyclic compounds with biological activity, widely used in medicine as antidepressants, analgesic, sedative compounds, etc. Reaction of DA with acetone was investigated AT 50 °C, WITH ACETONE/1,5-benzodiazepine MOL/MOL RATIO OF 2.5 IN methanol as the major reaction medium. Fe content affected the reaction rate and yield of 1,5-benzodiazepine. The larger Fe content, the higher reaction rate and yield of 1,5-benzodiazepine. The maximum yield of 1,5-benzodiazepine under the investigated conditions was 86-88% in the presence of 3.8%Fe/Si-CC-500 for 180 min. The catalytic behaviour of 3.8%Fe/Si-CC-500 was compared with that of 3.2%Fe/Al-PILC-500 prepared by pillaring method using Keggin type mixed Fe,Al polycation. The activity of 3.2%Fe/Al-PILC-500 was higher than that of 3.8%Fe/Si-CC-500 for the first 30 min, in accord to the amount of Lewis acid sites. Then, their catalytic behaviours became similar due to the blocking of active sites by the reaction products.

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ULTRASOUND-ASSISTED PREPARATION OF CELLULOSE NANOCRYSTALS-SEPIOLITE BIONANOCOMPOSITES

Borja Caja, M. Mar González del Campo*, Margarita Darder, Pilar Aranda, Luis Vázquez, Eduardo Ruiz-Hitzky

Instituto de Ciencia de Materiales de Madrid, CSIC, 28049 Madrid, Spain
*mmar.gonzalezcampo@csic.es

Bionanocomposites are a group of hybrid materials resulting from the combination of naturally occurring polymers and inorganic nanoparticles, which show interesting properties such as non-toxicity, biocompatibility and biodegradability [1]. Cellulose, the most abundant biopolymer on earth, is being widely applied in diverse areas (paper industry, food and pharmaceutical sectors…) and also used in the development of bionanocomposites, in some cases based on its assembly to clay minerals [2-5]. Cellulose is a linear polysaccharide consisting of β(1→4) linked D-glucose units, present as a structural component of the cell wall mainly in higher plants. These individual polysaccharide chains are arranged in crystalline and amorphous regions in elementary fibrils that assemble into cellulose fibers [6]. Several methodologies are applied for defibrillation of wood pulp in order to give the so-called microcrystalline cellulose (50-10 µm length and 10-50 µm diameter) or nanocelluloses, including microfibrillated cellulose (0.5-1 µm length and 10-100 nm diameter) as well as cellulose nanofibers (CNF, 0.5-2 µm length and 4-20 nm diameter) or nanocrystals (CNC, 50-500 nm length and 3-5 nm diameter) [6], which are suitable for preparation of bionanocomposite materials.

The current work explores the development of bionanocomposites based on the assembly of two dissimilar fibrous components: sepiolite (Pangel® S9 from Vallecas-Vicálvaro, Tolsa SA) as inorganic component, and CNC obtained from commercial microcrystalline cellulose as the biological counterpart. The methodology used for the preparation of these materials involves the application of shear force and ultrasound energy to aqueous suspensions of microcrystalline cellulose in the presence of sepiolite [5]. CNC are produced during the sonication process [7], as confirmed by FE-SEM and AFM, avoiding the use of concentrated sulfuric acid commonly employed to obtain these nanomaterials. During the sonication process, the interaction of the sepiolite fibers with the produced CNC may help to reduce their re-aggregation, in a similar way than that reported for carbon nanotubes-sepiolite systems prepared under analogous conditions [8]. Thus, the resulting gels are stable and homogeneous, and can be conformed as self-standing films by solvent casting or vacuum filtration. Their characterization by FTIR confirms the good interaction between both types of organic and inorganic fibers, revealing the establishment of hydrogen bonding interactions between the hydroxyl groups in the CNC and the silanol groups in the external surface of sepiolite. The films show improved water resistance as determined from water sorption isotherms. In addition, multifunctional materials can be easily produced by incorporating other components during the preparation step, as for instance carbon nanotubes, or by grafting or adsorbing organic molecules with the desired properties. The CNC-sepiolite films can be promising materials in diverse fields such as environmental remediation, food packaging or biomedicine.

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ARCHAEOMETRIC CHARACTERIZATION OF CERAMIC MATERIALS FROM CUATROVITAS (SEVILLE, SPAIN). IMPORTANCE IN THE PATRIMONIAL RESTORATION

Isabel González, Adolfo Miras, Paloma Campos, Antonio Romero

Departamento de Cristalografia Mineralogía y Química Agrícola, Seville, Spain

Presently the archaeological hypotheses in the study of any site that contains heritage remains of historical importance must be based on the scientific data that provide the material analysis. The systematic study of the archeological pieces found in a particular site can lead to settle the origin of the materials used for the making of artefacts, the work temperature for ceramic bodies, the manufacture, the age, etc. In the case of the Cuatrovitas (Seville, Spain) archaeological site, the archeometric study of the different remains found (ceramics) can contribute to the knowledge of the European culture occurred in the early medieval times.

In the present work, four samples from the Neogene clay deposits close to the Cuatrovitas archeological have been studied, as possible raw materials for the medieval ceramics. In addition, 13 ceramic pieces have been collected from the Cuatrovitas site and two structural elements (brick and tile) from the mosque.

For the raw materials, the mineralogy of the whole sample has been performed by X-ray diffraction (XDR). The mineralogical composition of the <2 μm fraction has been studied on oriented aggregates using standard methods, involving drying at room temperature, solvation with ethylene glycol and heating to 350 and 550 °C for 2 h. The quantification of mineral phases in ceramic pieces has been determined using Rietveld method and internal standard for an amorphous phase approach. In order not to destroy the archaeological pieces, the characterization of these materials has been carried out by microdiffraction and X-ray microfluorescence.

In addition, the mineralogical and petrographical study has been completed with the optical microscopy in thin section of the ceramic pieces. Moreover, the fabric of those materials has been observed by scanning electron microscopy. Those observations provide data on the almohade ceramic manufacture.

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APPLICATION OF BIOENGINEERING TO STABILIZE EROSION OF CLAY SOILS: RESEARCH EXPERIENCES ON SLOPES IN SELECTED GROUNDS AT GUATEMALA

F. M. González-Miranda (1), Eduardo Garzón-Garzón (2), J. Reca (2), Pedro José Sánchez-Soto (3), Luis Pérez-Villarejo (4), Sergio Martínez-Martínez (4)*

(1) School of Industrial Mechanical Engineering, Faculty of Engineering. University of San Carlos, Guatemala, (2) Department of Engineering. University of Almería, 04120 Almería, Spain, (3) Materials Science Institute of Sevilla (ICMS), Joint Center Spanish National Research Council (CSIC)-University of Sevilla, 41092 Sevilla, Spain (4) Department of Chemical, Environmental, and Materials Engineering. University of Jaen, 23071 Jaén, Spain

The objective of this research is the application of Bioengineering tools to stabilize erosion of clay soils using slopes. In this case, selected grounds at Guatemala were the subject of the present communication. The purpose is to decrease the erosion provoked by episodes of torrential rains. For this, the sowing has been performed on samples of clay soils previously characterized by X-Ray Diffraction (XRD), thermogravimetric analysis, particle size analysis, measures of pH, electrical conductivity, soluble salts, organic matter and capacity of exchangeable cations by standard methods. The pore size distribution and specific surface areas by nitrogen adsorption have been studied to characterize the soils. Other complementary determinations have been the liquid and plastic limits, plasticity index and shear strength. Cohesion and internal friction angles as Geotechnical properties have been also determined. Finally, it is presented the experimental results concerning the sowing of a plant, Vetiveria Zizanioides, using slopes of selected grounds in Guatemala.

The results suggested that the soil is fairly acid, with absence of calcium carbonate and worthless salinity. The levels of organic matter range from normal to very high, suggesting that it is a soil very fertile for the development of the plant. The mineralogy deduced by XRD allowed the identification of quartz, iron oxides (hematites and maghemite), feldspars and clay minerals, in particular metahalloysite, kaolinite, illite and chamosite with possible riebeckite. The particle size analysis of selected samples shows a predominate sand fraction (67.38 wt.%), followed by the clay fraction (25.16 wt.%), with a plasticity index of 7.9% and a liquid limit of 27.9%. These results allow classify this soil as sand-lime, mixtures of sand and lime, or sand-gravel-lime, according to the Unified Classification (Casagrande).

The specific surface area ranges from 11.68 to 15.5 m^2/g and the pore size ranges between 17.39-160 nm. Heating treatments of the sample produces an increase of the pore sizes. The accumulated specific surface area were higher in the desorption and the values were lower when the samples were heated. According to the characteristics of the soil, it was found the presence of cohesion (2.05 tn/m^2) and a internal friction angle of Ø= 31.69º. After the plantation of Vetiveria Zizanioides, it was observed an increase of the internal friction angle (38.03º, 40.63º), a decrease in the cohesion (1.29, 1.45 tn/m^2) and the predominant pore sizes in the range 17-160 µm. It is interesting to remark that the infiltration rate is lower at the first minutes because the rain waters are retained in the leaves of the plant. Consequently, the erosion provoked by episodes of torrential rains decreased, which is an interesting result from a point of view of Bioengineering.

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SURFACE REACTIVITY INTERFACE EXPERIMENTS STUDYING MICROSCALE CONCRETE-BENTONITE INTERACTION

Daniel González-Santamaría*, Raúl Fernández, Ana Isabel Ruiz, María Angulo, Almudena Ortega, Enrique Rodríguez, Jaime Cuevas

Universidad Autónoma de Madrid. Facultad de Ciencias. 28049 Madrid. Spain

Several small scale tests have been developed to help in the discrimination of the reaction processes and its kinetics for representative conditions of concrete/bentonite (C-B) interface within a real radioactive waste storage scenario. The overall objectives of the experiments are (1) the determination of the characteristic surface interface reactivity of FEBEX bentonite induced by different OPCs based concretes hydrated by granitic (Grimsel test site, Switzerland) groundwater; and (2) to integrate chemical interactions at µm-mm scale with physical properties; i.e. measured hydraulic conductivity and porosity changes indicators. The identification of new forming phases from the first stages of alteration and the comparison of results between low pH versus conventional OPC high pH concrete, are expected to bring useful and relevant data for the repository design.

A C-B interface was built by first curing a cement mortar (1cement paste+0.7H_2O+3quartz sand) in a methacrylate cylinder of 20 mm inner diameter, forming a 9 mm length column of pressed mortar which was capped by a PTFE porous membrane. After 30(high pH) or 90(low pH) days under water vapour atmosphere, a 9mm length compacted bentonite was pressed to 1.6 g/cm3 dry density above the PTFE. The composite column was then confined between two porous steel plates hermetically encased in a stainless steel body. This cells, operating at 20 ± 5 ºC, were designed to infiltrate water at 1MPa through C to B in the column experiment. The leached solution is collected at the bentonite end for major ions chemistry and silica determination by ion chromatography, titration and spectrophotometric analyses. The characterization of the column materials involved EDX-SEM analyses and XRD techniques. EDX-SEM was used to characterize fresh surfaces at the hydration of C, and the C or B sides of the interface. A polished longitudinal cut comprising the whole path length, including interfaces, was analysed for a chemical EDX (major elements) profile at µm scale.

Results obtained during first 90 days of barriers interaction have shown a higher hydraulic conductivity for low pH C material than high pH OPC (7E-13 to 8E-14 m/s). The leached water show virtually the same pH (8.1±2) with independence of time and C material. Regarding SEM-EDX studies, low pH C have shown an important loss of Ca at the interface with water (C-W). C-S-H gels with~<0.8 Ca/Si ratio were analysed both at the interfaces C-B and C-W. In contrast, C-S-H gels in high pH OPCs have shown higher ratio Ca/Si (>1.9) at both interfaces. These high values are overestimated by the presence of carbonates, calcite, substituting or coating C-S-H gels. Ettringite crystals have been better identified at low pH concrete side interface, filling open pores. These crystals may be produced in a secondary precipitation of sulfates in combination with Al dissolution from montmorillonite. Al depletion in the bentonite side at <20 µm thickness was observed in the EDX profiles. These profiles also reveal significant mass transfer at <100 µm scale characterized by Mg concentration at the bentonite side or in the interface contact. A Ca maximum is located in the middle of the low pH mortar column due to the Ca leaching from the hydration source.

Mg rich phases and carbonate rims (<5mm thickness) have been observed in FEBEX large scale C-B interfaces (>10 years and >5 cm B thickness) in situ and laboratory experiments [1,2]. These small scale experiments will contribute to up-scale the long-term impact of the alkaline perturbation of the studied EBS system.

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CLAY- AND CARBONATE BEARING LITHOLOGIES IN THE OUTER CARPATHIANS AND THEIR PALAEOGEOGRAPHIC IMPLICATION

Katarzyna Górniak

AGH-University of Science and Technology, Faculty of Geology, Geophysics and Environmental Protection, 30-059 Kraków, al. Mickiewicza 30, Poland
gorniak@agh.edu.pl

Discrete sequences of clay-bearing fine-grained carbonates intercalated within siliciclastic flysch deposits of the northern domain of the Tethys Ocean (Outer Carpathian Basin) were studied. These rocks, in field practice called marls, differ in age, location in the sedimentary basin, and lithology [2]. Starting sediments for these marls were deposited in a shelf-related environment and subsequently redeposited into deeper parts of the basin both unconsolidated as mud and lithified as olistoliths [3]. The following marls were examined: marls from the Vendryně Formation (Upper Jurassic, Silesian Unit), Siliceous-Fucoid Marls and Węgierka Marls (Upper Cretaceous, Skole Unit), Jasienica Marls, Żegocina Marls, Frydek Marls, and Węglówka Marls (Upper Cretaceous, Sub-Silesian Unit), Łącko Marls, Zembrzyce Marls, Budzów Marls, and marls from the Malcov Formation (Tertiary, Magura Unit), Sub-Cergowa Marls (Tertiary, Dukla Unit), Grybów Marls (Tertiary, Fore-Magura Unit), and Dynów Marls (Tertiary, Skole Unit).

Each clay-bearing fine grained carbonate layer that separates siliciclastic sediments represents an abrupt change in depositional conditions within the Outer Carpathian sedimentary basin. Therefore marls are important in understanding the geological history of the northern domain of the Tethys Ocean. Because both the clay and carbonate present in clay bearing carbonate rocks may have variable origins, this paper focuses on the grain-provenance study of components of the Outer Carpathian marls. The depositional and diagenetic controls of their variability have been discussed for integration of this kind of sediment into a basin-scale facies model.

Two imaging techniques: standard, i.e. optical microscopy, and high-resolution petrography, i.e. field emission gun electron microscopy (FEG-SEM), combined with X-ray diffraction, thermal analysis, and chemical analysis, have been applied. 117 bulk samples and fine clay fractions (<0.2um) isolated from selected marls were studied.

The results obtained are as follows: (1) the Outer Carpathian marls, which differ in age and location in the sedimentary basin, are similar in terms of mineral composition, but the contents of the main components are variable; (2) coccolith debris is the main carbonate constituent, so that the Outer Carpathian marls petrographically are a chalk-type deposits; (3) clay and silica minerals are also present in these rocks, for this reason the Outer Carpathian marls should be called an impure chalk; (4) silica minerals are mostly authigenic in the marls studied and consists of nanoquartz or opal CT; (5) illite-smectite-dominated clay assemblages [1] [3] [4] have been recognized in all samples studied; (6) smectite and silica minerals seem to be formed originally within the sediments owing to the alteration of volcanic material; (7) illite-smectite resulted from burial diagenesis (8) variable amounts of the main components in the marls studied (8-76% of carbonates, 3-79% of clay, 4-70% silica minerals) can be explain by episodic input of volcanic material into calcareous mud and by changing diagenetic conditions within the sediments.

Detailed petrographic analysis reveals that the Outer Carpathian marls studied represent an oceanic type of chalk, which was deposited within a periodically starved basin. Coccolithophore blooms in the basin were caused by volcanic activity, which fertilized the oceanic water. The Outer Carpathian marls are the sedimentary record of volcanic and tectonic activity that was related to the opening (Upper Jurassic), reconstitution (Upper Cretaceous) and closing stages (Tertiary) of the Outer Carpathian basin, i.e., the northern domain of the Tethys Ocean. This work was financially supported by AGH University of Science and Technology grant no.11.11.140.319.

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CHITOSAN/HALLOYSITE NANOFIBROUS MEMBRANES FOR BONE TISSUE ENGINEERING

Kavitha Govindasamy (1), Pooria Pasbakhsh (1)*, Sharaniza Ab. Rahim (2), Goh Kheng Lim (3)

(1) Mechanical Engineering Dicsipline, School of Engineering, Monash Univeristy, Selangor, Malaysia, (2) Faculty of Medicine, University Technology Mara, Selangor, Malaysia, (3) NewCastle University, School of Mechanical & Systems Engineering
*pooria.pasbakhsh@monash.edu

In this study feasibility of chitosan nanofibrous membranes reinforced by halloysite nanotubes (HNTs) has been investigated for the purpose of bone tissue engineering. 1, 3, 5, 7 and 10 wt% of HNTs added to the mixture of chitosan and polyethylene terephthalate (PET) to be used during the electrospinning process. Morphological analysis showed HNTs were attached along the chitosan/PEO nanofibers and agglomerated HNTs were found in chitosan/PEO at higher wt% of HNTs concentration. The average range of fiber diameter obtained across all concentration was from 72.073.30 nm to 154.876.77 nm and supports the values attained in the literature for being ideal for bone tissue scaffolding. Chitosan/PEO with 0, 1, 3, and 5 wt% of HNTs revealed to have larger pores and supported the successful NHOst cell culture. STEM micrographs revealed that the single tube and the hollowness of a typical HNTs structure was evidently expressed in fibers for chitosan/PEO membranes and resulted to larger fiber diameters. In chitosan/PEO with 5 wt% of HNTs, tubes were randomly distributed and agglomerated HNTs were evident through out the fibers only at higher HNT concentrations. Tensile test revealed that the membranes reinforced with 5 wt% HNTs yielded the highest σ (26.51 ± 1.38 MPa) and E (1.25 ± 0.19 GPa), respectively, due to the uniform dispersions of HNTs. TGA indicated increased in thermal stability with the addition of HNTs. Contact angle of chitosan/PEO with 0 to 5 wt% HNTs are compatible within the accepted standard for bone tissue scaffolding as they showed high surface energy (low contact angle) that falls within the range of 0° to 75°. This range assisted adsorption of nutrients from the culture media which promoted cell proliferation as revealed in the in vitro analysis. *In vitro* analysis revealed matured osteoblast cells in chitosan/PEO with 5 wt% HNTs and immature osteoblastic cells are observed for chitosan/PEO with 7 and 10 wt% HNTs as the pore size allowed cell aggregation and prohibited cell proliferatio. ALP activity test showed that chitosan/PEO with 5 wt% HNTs is the most suitable membrane for bone tissue engineering particular at day 14.

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THE ADSORPTION OF PHOSPHATE BY HALLOYSITE NANOTUBES

Nia Gray (1,3)*, Stephen Hillier (1,2), David Lumsdon (1), Chris Greenwell (3)

(1) The James Hutton Institute, Aberdeen, AB15 8QH, UK, (2) Department of Soil and Environment, Swedish University of Agricultural Sciences, Box 7014, Uppsala SE-750 07, Sweden, (3) Durham University, Department of Earth Sciences, Durham, DH1 3LE, UK

Halloysite nanotubes are increasingly being studied for their use in technologies such as medicine and plastics due to their tubular nature and available surface reaction sites. In agriculture the study of the transport of anionic phosphorus from fertilizersand glyphosate© containing herbicides in soil is of environmental relevance. Halloysite is found globally in soils [1] and research into the adsorption capacity of different halloysite nanotubes for phosphorus will be detailed here.

Two previously studied tubular halloysites were chosen [2,3], one cylindrical and one prismatic, on which the adsorption of phosphate over a pH range of 3-10 was studied using a batch equilibrium system. Previous work has indicated that the edge sites of halloysite are the only source of adsorption of phosphorus and that the degree of adsorption is dependent upon the number of these sites, pH and particle morphology [4]. The difference in adsorption behaviour of the halloysites over the pH range with different ionic strengths will be used to determine the phosphate adsorption of the two types of halloysite. A Constant Capacitance Model (CCM) will be employed describe the adsorption behaviour on the surface of the halloysite nanotubes where the greatest adsorption is expected at low pH.

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INVESTIGATION OF RETENTION MECHANISMS OF DYE BY LAYERED DOUBLE HYDROXIDES: A JOINT THEORETICAL AND EXPERIMENTAL STUDY

Brian Grégoire (1,2,3)*, Fabrice Salles (1), Géraldine Layrac (1), Didier Tichit (1), Rozenn Le Parc (2), Jean-Louis Bantignies (2), Gaelle Martin-Gassin (1)

(1) Institut Charles Gerhardt Montpellier, UMR5253 CNRS-UM-ENSCM, 1502 Place E. Bataillon, 34095 Montpellier Cedex 05, France, (2) Laboratoire Charles Coulomb, UMR 5221 CNRS-UM, Place E. Bataillon, 34095 Montpellier Cedex 05, France, (3) Institut de Chimie des Milieux et Matériaux de Poitiers - HydrASA, UMR 7285 CNRS-Université de Poitiers, 86073 Poitiers, France
*brian.gregoire@univ-poitiers.fr

Nowadays, environmental issues, especially those related to water pollution, have become a major concern for the whole population. Textiles industries are the main contributors of water contamination worldwide through the large volume of water they use in different processes. Dyes are certainly the main chemical contaminant of water from textile industry, since around 2% of the annual production is directly discharged in aqueous effluents and another 10% are systematically lost during the coloration process [1]. By changing the water acidity or salinity, dyes have harmful impacts on the photosynthesis of aquatic plants in addition to their inherent toxicity.

Most of the dyes are difficult to biodegrade and a specific treatment has to be adopted for dye removal [2]. Adsorption processes are gaining importance in this context with the use of very efficient low-cost adsorbents. For example, clays are very good candidates since they exhibit high exchange capacity and can be regenerated by appropriate treatment. However, in order to improve the efficiency of the catalysts, the mechanisms of retention have to be understood.

We have constrained our study to the capture of anionic dyes by anionic clays, namely layered double hydroxides (LDHs). LDHs are lamellar materials with important anionic exchange capacity due to the presence of positive layer charge. They can entirely be synthesised in laboratory with the possibility to tune the chemical composition, the crystallinity, or the particle size [3-4]. The aim of our project is therefore to understand how the structural parameters of the solid (particle sizes, crystallinity, atomic composition…) and the solution chemistry (nature of dyes, charges, ionic strength, solvent activity etc ...) impact the sorption capacity and the molecular organisation at the interface solid-solution.

To gain this molecular level of interface description, our methodology lies on the combined use of X-Ray diffraction techniques and vibrational spectroscopies (Infrared and Raman spectroscopies), aided by molecular simulations (DFT and Monte-Carlo simulations). Depending on the nature of the dye, surface and interlayer sites can be populated. In order to discriminate these two contributions to the overall dye uptake, topotactic exchange reactions were performed to prevent dye molecules to enter the interlayer domain so that adsorption only occurs on surface sites. It is observed that the surface of LDH catalyses the aggregation of dye, with a long range ordering as given by XRD analysis. However, the organisation of dye within the interlayer domain does not exhibit any periodic structure.

In addition to explain the high adsorption capacity of dyes by LDHs, these findings may also suggest that LDHs surfaces can catalysed the formation of ordered structures, depending on the nature of the molecules.

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MINERALOGICAL CHARACTERISTIC OF PELITIC ALLUVIAL PLEISTOCENE SEDIMENTS IN THE AREA OF SESVETE (ZAGREB, CROATIA)

Anita Grizelj

Croatian Geological Survey, Sachsova 2, 10 000 Zagreb, Croatia
grizelj.anita@hgi-cgs.hr

During the mapping for the Basic Geological Map of the Republic of Croatia 1:50.000 two boreholes (Badel-1 of 71.50 m and Badel-2 of 84.40 m) were studied in the area of Sesvete near Zagreb. Sediments from boreholes belong to the Pleistocene, informal Bistra Formation which is composed of silts, clays, sands and gravels. Within these sediments three different facies were interpreted [1]:

1) gravels and sands typical for alluvial environments
2) structureless beds of silts and clays deposited in oxbow lakes, marshes and floodplains
3) chaotic sediments deposited in the upper part of the alluvial fan.

Mineralogical analysis of pelitic sediments from structurless beds facies of oxbow lakes, marshes and floodplains included X-ray powder diffraction (XRPD) analyses on random mounts of bulk samples and oriented mounts of the <0.063 µm fraction. Oriented mounts of the <0.063 µm fraction were record after the following treatments: a) air drying, b) saturation with K^+ and Mg^{2+}, c) ethylene-glycol solvation, d) DMSO solvation, e) glycerol solvation, f) heating to 400 °C and 550 °C.

The main mineral components of these sediments are quartz, swelling clays and illite/muscovite. Among the swelling clays smectite and vermiculite are determinate in various ratios. Calcite, feldspar, kaolinite are present in a lesser quantity, while chlorite is present only in some samples.

According to [1] studied sediments from boreholes are a product of intensive weathering of different types of rocks from the Medvednica Mt. with the prevalence of green-schists. Smectite present in pelitic sediments probably originated from Miocenmarls. Absence of chlorite and presence of vermiculite are in accordance to intensive chemical weathering during the humid climate period in the Pleistocene.

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FRACTURE PROPERTIES OF NACRE-MIMETIC CLAY-BASED BIONANOCOMPOSITES

MARIA MORITS (1), TUUKKA VERHO (1), JUHANA SORVARI (1), VILLE LILJESTRÖM (1), ANDRÉ H. GRÖSCHEL (1,2)*, OLLI IKKALA (1)

(1) Molecular Materials, Department of Applied Physics, School of Science, Aalto University, 02150 Espoo, Finland, (2) Colloid and Polymer Science, Physical Chemistry and Centre for Nanointegration Duisburg-Essen (CENIDE), University of Duisburg-Essen, 45127 Essen, Germany
*andre.groeschel@uni-due.de

Nacre is the inner part of some seashells (e.g. oysters) and well known for its outstanding mechanical properties. The naturally occurring nanocomposite manages to combine mutually exclusive material properties including strength, stiffness, and toughness [1,2].n This is accomplished by clever arrangement of reinforcing calcium carbonate platelets intercalated by only about 5% of organic chitin/protein matrix. The interplay of nano-structural features (e.g., few nanometer inorganic asperities, platelet-platelet bridges, etc.) and energy dissipative soft matrix allows for unusually large deformations before critical failure, partly *via* crack deflection and arrest of non-propagating microcracks. In recent years several strategies were pursued to mimic these features and to harvest, and ultimately exceed, the mechanical properties of nacre [3]. Especially the toughness of bionanocomposites remains a design challenge and optimization requires more insight into the underlying failure mechanisms at the nanoscale.

Here, we present first measurements of the fracture properties of clay-based nanocomposites with high filler content and high alignment of the platelets [4]. Such measurements have been elusive, because specimens from clay (or other 2D nano-reinforcements) have so far been prepared mostly in thin films up to 100 µm and are not suitable for fracture toughness tests. Through a combination of evaporation-induced self-assembly and lamination we prepared macroscopic test beams for 3-point bending measurements. The test beams feature a clay filler content of about 38 vol%, are well-aligned with a Hermann's orientation parameter of 0.74, and a 1.6 nm intercalating poly(vinyl alcohol) gluing layer. In bending tests the material shows step-wise failure and pronounced crack deflection away from the process zone. Both of these observations are characteristic for anisotropic nanocomposites such as wood and bone. The fracture toughness was derived from the J-Integral resulting in a K_{IC}-value extrapolation to 3.5 MPa $m^{1/2}$. Surprisingly, when kept at high humid conditions for prolonged time (75% RH, 50 days) the nacre-mimetic nanocomposite retains much of its toughness, even though in form of a difference failure mechanism (larger plastic deformation before failure).

In more recent studies, we compared the fracture behaviour of the nacre-mimetic material with that of nacre *in-situ* using laser speckle imaging. We found that while the process zone in nacre is blunted and rather spherical, in the nacre-mimetic nanocomposite, the process zone is strongly anisotropic and deformed suggesting but also insufficient adhesion between the platelets.

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NANOCOMPOSITES OF THERMOPLASTIC STARCH REINFORCED WITH MODIFIED BENTONITE OBTAINED BY REACTIVE EXTRUSION FOR PACKAGING APPLICATIONS

María P. Guarás, Andrés Torres Nicolini, Romina Ollier*, Leandro Ludueña, Vera Alvarez

Composite Materials Group (CoMP), Institute of Materials Science and Technology (INTEMA), National University of Mar del Plata (UNMdP) - National Research Council (CONICET), Mar del Plata, Argentina

Conventional polymers derived from fossil fuels are not only non-renewable and finite resources, but also cause problems in post-consumer processing, as they are largely inert to microbial attack. The use of polymers capable of being degraded by the action of microorganisms and/or enzymes without causing harmful effects is a strategy in waste management. Starch is a natural, abundant and versatile biopolymer obtained from renewable plant resources such as maize, wheat and potato harvests. Moreover, starch is economically competitive with polymers derived from petroleum for manufacture of packaging materials. However, the structure of native starch must be modified since its degradation temperature is lower than the melting temperature. For this reason, natural starch cannot be processed by traditional polymer processing methods without being previously modified. Formation of thermoplastic starch (TPS) requires disruption of the crystalline regions of starch granules by processing them in the presence of a specific amount of plasticizer, under certain extrusion conditions [1].

Neat TPS is not suitable for use as packaging material due to its poor mechanical properties and high hydrophilicity. Different methods can be implemented in order to improve its competitiveness with a high cost/efficiency ratio. On the one hand, various physico-chemical modification methods of TPS have been developed in order to improve these aspects. Derivatization of starch is a type of chemical modification by which the hydroxyl groups are replaced by other groups with the desired functionality. On the other hand, nano-reinforcements can be incorporated into the mixtures. In this way, biopolymer-clay nanocomposites are a new class of materials with potentially improved mechanical and thermal properties [2]. These composites are prepared by addition of low amounts of clay to the biopolymer matrix. The main challenge for preparing nanocomposites with enhanced properties is the nanoscale dispersion of clay in the polymer matrix. Bentonite is one of the most commonly used natural clay and has been successfully applied in numerous nanocomposite systems. However, many starch-clay nanocomposites suffer from poor dispersion, which is a key factor for obtaining high performance materials. To improve the clay dispersion, organic cations such as alkylammonium cations can be used to exchange with the sodium ions residing in the interlayer of pristine clay [3]. The more the modifier is compatible with starch, the more it facilitates clay dispersion.

The objective of this work was to prepare biodegradable TPS/organobentonite nanocomposites by melt intercalation using reactive extrusion technique. For this purpose, pristine bentonite was firstly exchanged with benzalkonium chloride. The resulting organobentonite was used as nano-reinforcement of the thermoplastic starch matrix. The derivatization of starch was performed with maleic anhydride and once modified it was processed in the presence of a plasticizer in a twin screw extruder. The effect of clay modification on the morphology (X-ray diffractometry, XRD), thermal properties (differential scanning calorimetry, DSC, and thermogravimetry, TGA), water absorption, mechanical response and biodegradability of nanocomposites were studied and discussed in detail.

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ELABORATION OF CARMINIC ACID - SMECTITES HYBRIDS PIGMENTS: FOCUS ON CHEMICAL INTERACTIONS

D. Guillermin (1)*, B. Rigaud (2), P. Walter (1), L. de Viguerie (1), L. Michot (3), S. Balme (4), M. Jaber (1)

(1) Sorbonne Universités, Laboratoire d'Archéologie Moléculaire et Structurale, UMR 8220, Université Pierre-et-Marie-Curie, Paris, France, (2) Sorbonne Universités, Institut des Matériaux de Paris Centre, Université Pierre-et-Marie-Curie, Paris, France, (3) Sorbonne Universités, Physicochimie des Electrolytes et Nanosystèmes interfaciaux, UMR 8234, Université Pierre-et-Marie-Curie, Paris, France, (4) Institut Européen des Membranes, UMR 5635, Montpellier - France

Fading of dyes is a common phenomenon observed on painting. Many cases were reported as famous painting "L'Église d'Auvers sur Oise" from Vincent van Gogh (pink fading of Eosin [1]). Other painters, as Auguste Renoir with "Bal du Moulin de la Galette" 20 years later, were so surprised by the degradation of their painting that they did not recognized their own work.

Reasons of fading are various: exposition to light, wet atmosphere, temperature changes, pollution from human activities or urban area, and also the activity of pests and microorganisms as fungi and bacteria.

Meanwhile, a well-known example of organic-inorganic pigment called Maya blue crossed ages with its astonishing resistance [2]. Most of the painted walls from the 9th century was degraded but the Maya blue remained unspoiled.

This study aims to synthetize new hybrid materials with enhanced photo-chemical resistance, by using inorganic matrix to prevent the decomposition of unstable organic dyes. Carminic acid was used as natural red dye, and several smectite (mainly Montmorillonite) were employed as supporting mineral.

The clay mineral surface charge was inversed by a cationic polymer. Adsorption of the later and the carminic acid molecules was done by wet impregnation in presence of an excess of water. The free organic molecules were removed by washing with water. The cationic polymer is intercalated in the interlayer space as attested by XRD. The dye molecules are probably adsorbed on the edges. ^{13}C NMR spectroscopy stress on the presence of hydrogen bonds between the edges of the clay mineral and the carminic acid. The interactions involved between the inorganic and organic parts influence directly the release properties of the organic molecules in different solvent. The photo-stability of the new pigments was investigated under focused light. Color changes were followed using CIE L*a*b* parameters. The inversion of surface charge seems to increase the photo-stability of the new pigments compared to the one prepared without any cationic polymer.

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DIELECTRIC BEHAVIOUR OF POLYBISPHENOL A CARBONATE-PRISTINE BENTONITE COMPOSITES

Selahaddin Guner (1)*, Ahmet Ugur Kaya (2), Emine Can (3), Fatma Gozuak (3)

(1) Kocaeli, Turkey Kocaeli University Faculty of Art&Science, Department of Chemistry, Kocaeli, Turkey, (2) Kocaeli University Faculty of Art&Science, Department of Physic, Kocaeli, Turkey, (3) Istanbul Medeniyet University, Department of Physics Engineering, İstanbul, Turkey
*seguner@kocaeli.edu.tr

Aim of the study is to determine the dielectric behaviour of polybisphenol a carbonate (PC)-Pristine Bentonite as a function of Pc loading. The composites were prepared by adding PC solution of different masses dissolved in 20 mL of chloroform to a suspension of bentonite in 30 mL of chloroform. The resulting PVC-Pristine Bentonite mixture was filtered then the solid portion was dried at room temperature under vacuum condition. Dielectric measurements were carried out 1 Hz-1 MHz. The measurements show that reel permittivities (ε') of samples were increased with increase of PC loading. Loss factor (tanδ) was shifted to the low frequencies according to Pristine Bentonite. Infrared spectra of samples were measured and results were supported by infrared spectroscopy. As a result, at low PC loading, clay-PC interaction increased and dielectric permittivities of composites decreased relative to pure bentonite.

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BIOLOGICAL AVAILABILITY OF CUBAN MINERAL SOURCES FOR ANIMAL FEEDING

Odilia Gutiérrez*, Lourdes Savón, Juan Cairo, Moises Valera

Instituto de Ciencia Animal, San José de las Lajas (CP: 32700), Mayabeque, Cuba

Mineral supplementation is an expensive practice and in most cases it is necessary to import the main raw materials for premixes preparation according to nutritional requirements of each species. In the last few decades the Animal Science Institute in Cuba had evaluated national mineral sources for animal nutrition. Among these sources are rock phophates and aluminosilicates (zeolite and bentonite). For biological evaluation of rock phosphates several experiments were conducted under in vitro and in vivo conditions with broilers, pig, ovine and bovine cattle. The chemical composition of rock phosphates showed calcium and phosphorus levels ranging from 20-24% and 12-18%, respectively, which are similar to imported calcium phosphate but with relatively high level of fluorine between 1.30- 3%. In vitro evaluation in citric (2%) and hydrochloric (0.4%) acids was conducted, denoting high results of solubility and bioavailability of calcium and phosphorus in this source. In vitro availability of calcium and phosphorus in Cuban calcium phosphate were 80.4 and 94.6%, respectively and in vivo availability was 76.9 and 64.2%, respectively in calves, growing- fattening and fattening steers. Fluorine metabolism was studied and it was demonstrated that more than 50% is in calcium fluoride form with lower solubility than sodium fluoride which is used as international reference of toxic values for all species. The established metabolic pathway of flouride was blood, teeth, bone and urine, and the two last tissues being the best for fluorosis detection and prevention in farm animals. The content of other toxic trace elements such as Cu, Pb, As, Hg was very low. In all cases, phosphoric rocks substituted imported dicalcum phosphate with very good results. It was found that in digestive contents of cows consuming green forages and zeolite, the mineral exchanged their calcium mobile ions by similar ammonium equivalent, which was slowly released in the ruminal medium improving nitrogen utilization by rumen microorganisms and guarantying a best pH for their activity. Zeolite in ruminal medium provokes changes in VFA proportion and also in some bacteria and protozoa. Cuban sodium bentonite was evaluated as a regulator of internal medium and protector of ruminal proteolysis. Bentonite was able to maintain the pH in internal medium in calves and protect dietary protein of ruminal microorganism attack decreasing ammonium ruminal production. This mineral was utilized with some protein feeds and resulted in a good nitrogen protector in ruminal medium. Action mechanism of zeolites and bentonites are different. Zeolite is preferred when the ruminant are feeding on poor quality pastures and bentonite when pastures have higher biological values.

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TWO CASE STUDIES OF CLAY-BASED BIONANOCOMPOSITES

Chang-Sik Ha

Department of Polymer Science and Engineering, Pusan National University, Geumjeong-gu, Busan 46241, Republic of Korea
csha@pnu.edu

In this talk, I will present two case studies of clay-based bionanocomposites that have been done in my laboratory for years. First, I will touch on the biodegradable polymer/clay nanocomposites based on aliphatic polyester (APES) or thermoplastic starch (TPS). In the APES/clay bionanocomposites, we found that the biodegradability of bionanocomposites was not decreased with increasing contents of organoclays. For the TPS based bionanocomposites, we found the dramatic lowering of water vapor transmission rate in the bionanocomposites due to the presence of dispersed large aspect ratio silicate layers in the polymer matrix as seen in other PLS hybrid nanocomposites and that natural clay is more compatible than organoclays with a polymer in the case of hydrophilic polymer like TPS. Second, I will talk on the halloysite containing bionanocomposite hydrogels with sodium hyaluronate(SH) and poly(hydroxyethyl methacrylate). Owing to the presence of the SH content, the bionanocomposite hydrogel exhibited not only pH sensitivity, but also uniform stabilization ability of the Hal in the hydrogel networks. The release studies suggested that the new type of bionanocomposite hydrogels is promising controlled-release carriers for colon cancer delivery.

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SULFAMERAZINE SCHIFF-BASE COMPLEXES INTERCALATED LAYERED DOUBLE HYDROXIDE FOR ANTIBACTERIAL APPLICATIONS

Mary Jenisha Barnabas, Surendran Parambadath, Chang-Sik Ha*

Department of Polymer Science and Engineering, Pusan National University, Busan 46241, Republic of Korea
*csha@pnu.edu

This study is aimed to evaluate the potential application of an antimicrobial system consisting of Cu(II) and Co(II) complexes of sulfamrazine-salicylaldehyde (SS) intercalated Mg/Al-layered double hydroxide [Cu(II)-SS-Mg/Al-LDH and Co(II)-SS-Mg/Al-LDH]. The ligand was synthesized by reacting sulfamerazine and salicylaldehyde in methanol and further complexed with Cu(II) and Co(II) metal ions [Cu(II)-SS and Co(II)-SS]. The successful intercalation of Cu(II)-SS and Co(II)-SS into Mg/Al-LDH by delaminating/restacking method. The ligand SS, Cu(II)-SS, Co(II)-SS, Cu(II)-SS-Mg/Al-LDH and Co(II)-SS-Mg/Al-LDH were characterized by various physico-chemical and spectroscopic methods viz. IR, UV-Vis, ^{1}H and ^{13}C NMR spectroscopy as well as X-ray diffraction, TG analysis, SEM and TEM analysis. The synthesized Cu(II)-SS-Mg/Al-LDH and Co(II)-SS-Mg/Al-LDH were used to study their antibacterial activity by inhibition zone method, where the LDH materials exhibited good activity against both gram positive (Staphylococcus aureus) and gram negative (Escherichia coli) bacteria. The results indicated that the Cu(II)-SS-Mg/Al-LDH and Co(II)-SS-Mg/Al-LDH can be used effectively for antimicrobial applications.

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SYNTHESIS AND CARACTERISATION OF PALYGORSKITE FUNCTIONALIZED BY TIN DIOXIDE

Abderrahmane Habibi (1), Lala Setti Belaroui (1,2), Abdelkader Bengueddach (1), Alberto López Galindo (3), Aránzazu Peña Heras (3)

(1) Lab. of Chemistry of Materials (LCM), University of Oran 1, BP 1524 Oran El M'Naouer, Oran, Algeria, (2) Dep. of Pharmacy, Fac. of Medicine, University of Oran 1, BP 1510 Oran El M'Naouer, Oran, Algeria, (3) Instituto Andaluz de Ciencias de la Tierra (CSIC-UGR), Avda. de las Palmeras 4, 18100 Armilla, Granada, Spain

Palygorskite is a hydrated 2:1 aluminum - magnesium phyllosillicate, with fibrous morphology, it has a high specific surface area and negative lattice charges, which provide a high absorption capacity [1]. Algerian Pal material (Fig 1 a) is mainly composed of palygorskite (69%) and dolomite (19%), but also includes 6% of calcite, 3% of quartz, 3% illite, and traces of cristobalite [2]. The objective of this study is to synthesize nanocomposites by depositing SnO_2 oxides on the surface of palygorskiteby in situ sol-gel method. SnO_2-Pal was prepared by adding tin chloride ($SnCl_{2,}$ $2H_2O$)in an acid medium. This solution was added into the clay suspension Pal at 1% in weight. The mixture reaction was stirred at 60 °C for 24 hours; the resulting suspension was centrifuged, washed, dried at 80 °C and calcined at 300 °C for 4 hours. The resulting sample was characterized by mean of XRD, FTIR and SEM. The XRD pattern show the formation of cassiterite particles (SnO_2) identified by the peaks: d_{110} (3.31 Å)$_{;}$ d_{101} (2.62 Å); d_{211}(2.35 Å), d_{440} (1.75 Å). The SEM images (Fig 1b and 1c) confirmed that casiterite particles were formed and uniformly distributed onto the surface of palygorskite nanorods. The resulting nanocomposite of SnO_2-palygorskite is tested as an adsorbent for the removal of pharmaceuticals compounds from aqueous solution.

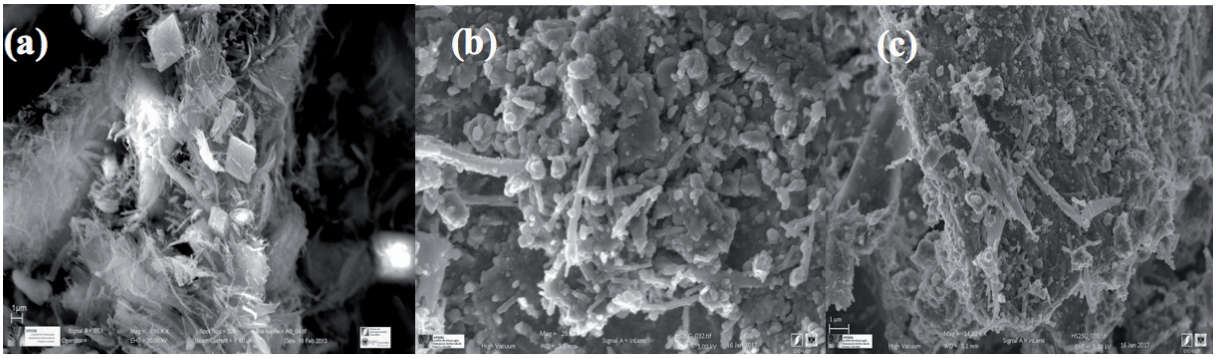

Fig.1. SEM images of samples: (a) Pal, (b) and (c) SnO_2- Pal.

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MINERALOGICAL AND GEOCHEMICAL CHARACTERIZATION OF THE GUENFOUDA KAOLIN DEPOSIT, EASTERN MOROCCO

Amal Hachimi*, Mostafa Berkhli, Hafsa Tourab, Hassan Mounach

University of Moulay Ismail, Faculty of sciences, Department of geology. PO. Box 11201 Zitoune, Meknès - Maroc.
m.berkhli@fs-umi.ac.ma

The Guenfouda kaolin deposit is located on the northern flank of the Carboniferous Jerada Basin. The mineralogical study showed that the source rock of this white clay is a volcanic rock with rhyolitic - rhyodacitic composition. The source rock was fractured after its emplacement and then was affected by hydrothermal alteration via circulation of paleofluids with a temperature lower than 300 °C [1]. The aim of this work is to characterize the clay of this deposit and determine its suitability for industrial applications. The characterization of the kaolin clay by different analytical methods, including X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy and scanning electron microscopy (SEM/EDS):

X-ray diffraction analyses of whole rock showed that the Guenfouda kaolin is composed of kaolinite, illite, pyrophyllite, chlorite, micas, apatite, jarosite, pyrrhotite and quartz. The qualitative and semi-quantitative analysis of the diffractograms of the clay fraction show that this clay consists essentially of illite, pyrophyllite, kaolinite, chlorite and quartz with a variable percentage at different zones of the quarry.

The FTIR spectrum of the clay is characterized by a band at 693 cm^{-1} corresponding to the Si-O bending of kaolinite, a band at 798 cm^{-1} indicating the presence of quartz and, a band at 3404 cm^{-1} corresponding to the interlayer water of halloysite. These results are in line with XRD results and confirm the presence of kaolinite, illite, chlorite, micas and quartz in the studied clay. The EDS analyses show that this clay contains oxygen, silicon, aluminum, titanium and potassium. The center of the Guenfouda quarry is rich in titanium and devoid of potassium and its periphery is rather rich in potassium and free of titanium.

The comparison of the geochemical and mineralogical composition of Guenfouda kaolin with the industrial standards of materials used in various products shows that Guenfouda kaolin might be used in ceramics, paints, paper or in refractories.

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MINERALOGICAL AND GEOCHEMICAL CHARACTERIZATION OF MATERIALS OF OULAD ALI AREA (NE MOROCCO): APPLICATION FOR THE MANUFACTURE OF BRICKS

Amal Hachimi*, Mostafa Berkhli, Hafsa Tourab, Hassan Mounach

University of Moulay Ismail, Faculty of sciences, Department of geology. PO. Box 11201 Zitoune, Meknès - Marocco
m.berkhli@fs-umi.ac.ma

The Oulad Ali area is located 25Km NNW of Taourirt city (NE Morocco). It belongs to the Tertiary Basin of Taourirt, being situated in an intermediate position between a marine domain to the west (Guercif basin) and a continental domain located to the South and the East. Its sedimentary filling consists of a Turtonian-Messinian marine facies (blue marl) and more sandy coastal facies, discordant on a Jurassic or Paleozoic substratum [1]. The aims of this work is to give the mineralogical and geochemical characterization of the materials of Oulad Ali and to test its application for the manufacture of bricks. Different techniques have been used to achieve these objectives.

The results of the calcimetry show three groups of materials according to their $CaCO_3$ content, corresponding to three types of rocks: limestone clays, marly-limestone clays and marls. These rocks belong to the plastic materials. X-ray fluorescence analysis shows that these materials are composed of SiO_2 (37.74%), Al_2O_3 (10.97%), Fe_2O_3 (4.75%), TiO_2 (0.59%), CaO (15.49%), MgO (4.03%), Na_2O (0.68%), K_2O (2.25%), MnO (0.06%), P_2O_5 (0.14%) and LOI is 19.98% [2]. The X-ray diffraction (XRD) results show the presence of palygorskite, smectite, chlorite, illite, kaolinite and vermiculite. The XRD also showed the presence of a smectite monocrystal, sample (G-OMR). IR spectra showed that this smectite is dioctahedral. Chemical analysis shows that it is composed of Si, O, Al, Fe, Mg, K, Ca, and Na. Thermal analysis (DTA) confirms these results and showed that the dioctahedral smectite is nontronite.

Technological tests were carried out on two types of briquettes. The first type was made of a marl without further additions. The raw material of the second type is a marl from Oulad Ali (90%) with 10% additio of sand from Machraâ Hamadi. The prepared briquettes were subjected to five technological tests: fire loss, shrinkage on firing, apparent porosity, bulk density flexural strength.

The comparison of the two groups of briquettes, shows that the shrinkage during firing of briquettes with additives is lower compared to that of briquettes without additives. This explains the higher porosity of the briquettes with additives compared to their counterparts without aditives. Also, the apparent density is inversely proportional to the porosity. The mechanical resistance to bending of briquettes with additives is lower than that of briquettes without additives [3]. These preliminary studies indicate that any modification of the compositions of the raw materials affects directly the technological properties of briquettes.

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TRADITIONAL EXPLOITATION OF POTTERY AT THE ADENDIM AND WANINA BASINS; AIT OURIR AREA (HIGH ATLAS OF MARRAKECH, MOROCCO)

Fatiha Hadach*, Ahmed Algouti, Abdellah Algouti, Zahra Mourabit, Zouhair Oughzif

Cadi Ayyad University, Faculty of Sciences Semlalia, Laboratory Geosciences, Geotourism, Natural Hazards and Remote Sensing"2GRNT", Geology Department. BP 2390, 40000, Marrakech, Morocco
*Fatiha.hadach@gmail.com

This contribution is to locate and characterize favorable layers for traditional pottery mining using geochemical analysis of clay samples in the High Atlas of Marrakech area. The macroscopic and microscopic descriptions of the different layers identified in the study area allow the interpretation of sedimentological and structural characteristics of each facies. At the outcrop, these facies are generally marked by abundant desiccation figures and the presence of traces of biological activity, reflecting a low layer of water depositional environment under a moderate to low hydrodynamic regime. The geochemical analysis of claysamples shows relatively similar results to that of the Ourika Douar Tafza region, known for its traditional pottery mining. As such, we are convinced that the results presented in this work provide a good basisfor future potential developmental projects in the High Atlas of Marrakech area.

Keywords: Traditional pottery mining, clay geochemical analysis, High Atlas.

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PALEOENVIRONMENTAL OF THE RED FORMATION IN AIT OURIR AREA (HIGH ATLAS OF MARRAKECH, MOROCCO)

Fatiha Hadach*, Ahmed Algouti, Abdellah Algouti

Cadi Ayyad University, Faculty of Sciences Semlalia, Laboratory Geosciences, Geotourism, Natural Hazards and Remote Sensing"2GRNT", Geology Department. BP 2390, 40000, Marrakech, Morocco
*Fatiha.hadach@gmail.com

The detailed sedimentological study of the Senonian in the Wanina basin of AïtOurir basins attached to the northern slope of the High Atlas Marrakech, gave the deposit silty carbonato-evaporite, which are carried out in an environment of type sebkha where alternate phases of detrital inputs, under a hot and arid climate and in conditions of bridging favoring the installation of evaporite deposition, and the phases of carbonate deposits more marine installed under the action of a slight increase in sea level degenerating quickly, in an upper intertidal temporarily emerged. In general these carbonate benches mark to their surfaces a rupture of the sedimentation that is materialized by ferruginous hardened surfaces.

Keywords: Marrakech High Atlas, Senonian, Sedimentation, Paleoenvironnement.

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TREATMENT OF PETROLEUM HYDROCARBONS-CONTAMINATED SOIL BY ADVANCED CHEMICAL OXIDATION

Ouriache Hadjer, Arrar Jazia

Laboratoire des Sciences et Techniques de l'Environnement (LSTE), Ecole Nationale Polytechnique, 10 Avenue Hassen Badi, Belfort, El-Harrach, 16110 Alger, Algeria
hadjer-ou@hotmail.fr, jazia.arrar@enp.edu.dz

Background: Remediation of soils polluted by petroleum hydrocarbons is a very interesting topic in environmental research, several techniques have been used and others are in development. Advanced oxidation technologies have received increasing attention recently, for their significant effectiveness on various recalcitrant organic pollutants destruction. Among these technologies, we are interested in Fenton-like oxidation because of its application at neutral pH favored for indigenous microorganisms' development for eventual biodegradation. *Objectives:* The present study aims to investigate the influence of hydrogen peroxide, iron zero-valent contents and chelating agent presence on petroleum hydrocarbons degradation efficiency by Fenton-like oxidation is evaluated. For this effect, we follow the temporal evolution of total petroleum hydrocarbons (TPH), the pH change, and the humidity was kept constant during the treatment period.

Methods: Our processing relates to abiotic systems, by varying hydrogen peroxide content and only based on the amount of iron that exists originally in soil, after choosing optimal hydrogen peroxide content, we set the hydrogen peroxide content and we varied the iron content, and finally the contents is fixed to hydrogen peroxide and iron and varying the content of the chelating agent (EDTA).

The reactors are under conditions of ambient temperature, neutral pH, protected from light to avoid photo- oxidation phenomenon and stirring of 150 rd/min throughout the treatment. *Conclusions:* Degradation rate of total petroleum hydrocarbons (TPH) in the case of Fenton-like treatment by varying iron content, consequently ratio molar H_2O_2:Fe are between 21 and 40%. The optimal efficiency is obtained for a molar ratio H_2O_2:Fe of 15:4. The introduction of chelating agent in Fenton-like process in different ratios improves significantly TPH degradation efficiency, which reached 73%. A priori, chelating agent played an important role in maximizing iron catalytic activity.

Keywords: Fenton-like, EDTA, petroleum hydrocarbon, soils remediation, advances oxidation.

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FISCHER-TROPSCH SYNTHESIS OVER COBALT SUPPORTED ON PILLARED MONTMORILLONITE

Qing-Qing Hao (1), Zhao-Tie Liu (2), Zhong-Wen Liu (2)*

(1) School of Chemical Engineering, Northwest University, Chemical Engineering Research Center of the Ministry of Education for Advanced Use Technology of Shanbei Energy, Xi'an 710069, China, (2) Key Laboratory of Applied Surface and Colloid Chemistry, MOE, School of Chemistry & Chemical Engineering, Shaanxi Normal University, Xi'an 710119, China

Fischer-Tropsch (FT) synthesis is an effective process for producing clean fuels from syngas originating from coal, natural gas, and biomass. However, the FT products, which are controlled by the Anderson-Schulz-Flory (ASF) polymerization kinetics, are very complicated mixtures and nonselective to any specific hydrocarbons. For selectively synthesizing liquid fuels, the best strategy is to make an efficient bifunctional catalyst, in which an FT active metal is integrated with a solid acid having suitable acidity and mesoporosity. Over the bifunctional catalyst, the reaction of hydrocracking and/or isomerization of FT heavier hydrocarbons to middle-distillate products will occur [1,2]. Pillared montmorillonite (PILM) is a solid acid characterized by high surface area, adjustable porosity and acidity, which make the Co/PILM a promising bifunctional catalyst for selectively synthesizing liquid fuels via the FT synthesis. In our previous work, Co supported on a series of PILMs (Al_2O_3-PILM, SiO_2-PILM, and ZrO_2-PILM) were investigated for controlling the product distribution of FT synthesis. Although the Co/PILMs can effectively narrow the product distribution of FT synthesis, the minimum selectivity of $C_{21}+$ hydrocarbons is still above 12% [3].

Thus, in order to further investigate the effect of basal spacing, surface area, porous structure, and acidity of PILM on the FT synthesis, and further decrease the selectivity of $C_{21}+$ hydrocarbons, herein, the hybrid PILMs, i.e. SiO_2-Al_2O_3-PILM, SiO_2/ZrO_2-PILM, SiO_2/TiO_2-PILM, Al_2O_3-ZrO_2-PILM were prepared, and the Co/PILMs were evaluated for catalyzing the FT synthesis. The results indicated that both the activity, selectivity of hydrocarbon, and the stability of the catalysts for FT synthesis were changed with the porous structure, acidity, and metal oxides in the clay interlayer, which are well correlated with the characterization results. Moreover, a high-performance catalyst for the FT synthesis was obtained. With a similar CO conversion and CH_4 selectivity to a typical FT catalyst of Co/SiO_2, the optimal catalyst of SiO_2/ZrO_2-PILM showed a high selectivity to C_5-C_{20} liquid fuels (>64%) and very low selectivity to $C_{21}+$ hydrocarbons (<5%).

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THE USAGE OF MODIFIED PUMICE WITH NANO ZERO-VALENT IRON IN REMOVING OF ZINC FROM WATER

B. Ilker Harman (1)*, Noorjan S. Ibrahim (2)

(1) Technical Science Vocational School, Suleyman Demirel University, Isparta 32260 Turkey, (2) Department of Environmental Engineering, Suleyman Demirel University, Isparta 32260, Turkey
*ilkerharman@sdu.edu.tr

The main objective of this research was to investigate the removal of a heavy metal through adsorption from water. Novel pumice supported nano zero-valent iron (P-nZVI) was tested as adsorbent for zinc. The nanoscale zero valent iron supported on pumice was synthesized by using conventional liquid-phase method, the reduction of $FeCl_3$ conducted using $NaBH_4$ as reducing agent and then supported on to the pumice with reference to Liu et al. [1,2]. Adsorbent dose, pH and temperature of solution and initial metal concentration on the rate of zinc removal were studied. All adsorption experiments were conducted employing the variable-dose completely mixed batch reactor bottle-point method. nZVI coating of natural pumice significantly increased its zinc uptake. More than 90% of zinc was removed by P-nZVI with a dosage of 1 g/L in 20 minutes. A strong linear correlation was observed between the nZVI surfaces of modified pumices and their Freundlich affinity parameters (K_F). Three different pH of solution (4.0, 5.0 and 7.0) were tested in this study. The removal of zinc was always more than 90% of the initial amount present. Our results indicate that zinc adsorption was independent of solution pH used in the experiments. Thermodynamic data ($\Delta G°$, $\Delta H°$ and $\Delta S°$) showed that the adsorption reactions between zinc and P-nZVI surfaces were spontaneous and the sorption process was endothermic. The overall results of this study showed that the P-nZVI exhibited a high efficiency for zinc removal from contaminated water andin this context P-nZVI may be a promising novel adsorbent for this purpose.

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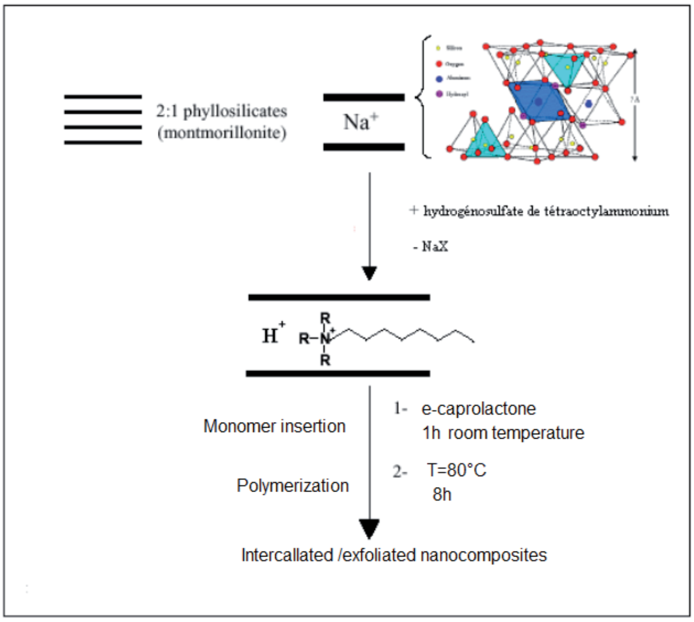
DIRECT *IN-SITU* POLYMERIZATION TO PRODUCE POLYCAPROLACTONE/MAGHNITE NANOCOMPOSITES

Amine Harrane*, Mahmoud Belalia, Ahmed Belhakem

Department of Chemistry, Faculty of Exact Sciences and Computer, University of Abdelhamid Ibnbadis Mostaganem
*amineharrane@yahoo.fr

Poly (e-caprolactone) (PCL)/Montmorillonite layered silicate nanocomposites have the advantage adding biocompatibility and biodegradability to the traditional properties of nanocomposites. They can be prepared by in-situ ring-opening polymerization of e-caprolactone using conventional initiator to induce polymerization in the presence of an organophilic clay, such as organomodified montmorillonite. In this work, we have used an alternative method to prepare poly(e-caprolactone)/montmorillonite nanocomposites. The cationic polymerization of e -caprolactone was initiated directly by Maghnite-TOA, organomodified montmorillonite clay, as a catalyst, to produce nanocomposites (Scheme 1). Resulted nanocomposites were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), force atomic microscopy (AFM) and thermogravimetry.



Preparation of nanocomposites PCL/ Maghnite-TOA

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EFFECT OF CLAY MINERALOGY ON POTASSIUM FORMS AND AVAILABILITY IN PADDY AND NON-PADDY SOILS

Soheila Sadat Hashemi (1)*, Hakime Abbaslou (2)

(1) Assistant professor of Soil Science Department, Agriculture College, Malayer University, Malayer, Iran, (2) Assistant professor in Environmental and Civil Engineering Department, Civil Engineering College, Sirjan University of Technology, Sirjan, Iran
*S.Hashemi@Malayeru.ac.ir

Potassium content in soils depends on the type of parent material and degree of soil and mineral weathering. Soil K exists in four forms that are in equilibrium, each differing in its availability to crops. These forms, in increasing order are: mineral, non-exchangeable (fixed or difficultly available), exchangeable, and solution (Havlin et al., 2004). Most of the K in soil is held in the primary minerals like micas and potassic feldspars (microcline) and secondary minerals. The soil silicate clay minerals (2:1) have a notable influence in soil potassium availability, and the presence of 2:1 clay minerals, even in subsidiary quantities, increases the effective K availability in soils. In general, soils that are rich in vermiculite and micas can have large amounts of non-exchangeable K, whereas soils containing much kaolinite, quartz and other siliceous minerals contain less available and exchangeable K (Martin and Sparks, 1985). Hashemi and Abbaslou (2016), a significant correlation was observed between non exchangeable potassium and illite mineral. Based on the previous soil survey and reports 9 pedons were investigated that five pedone were located in paddy rice cultivation and four pedons investigated in sugare beet and canola cutivations. Soil samples from all horizons were collected from paddy and non paddy cultivations and analyzed in laboratory. Some physical and chemical properties of the soil samples were determined according to standard method. Pedons were described and classified according to the Soil Survey Manual (2012) and Keys to Soil Taxonomy (Soil Survey Staff, 2014). All pedons classified to inceptisols order which were located in flood plains, alluvial and piedmont plains. Different potassium forms were determined by the method Helmeke and Sparks (1996). Mineralogical study was made with Moore and Reynolds (1997) method. The results revealed that potassium different forms reduced with increasing depth in all pedons. The results showed that the mean of solution, exchangeable, non-exchangeable and total potassium in canola cultivation (equal to 41.7, 135.7, 393.9 and 6075 mg/Kg, respectively) more than sugar beet cultivation (equal to 16.6, 107.3, 228.7 and 4900, respectively). Smectite were observed in two products (sugar beet and canola) frequency. The presence of this mineral has basic role on exchangeable potassium. Sugar beet is high nutrient requiring crop, however induced to removal potassium of soils. The results showed that mean of solution (44.2 mg/Kg), exchangeable (311 mg/Kg), non exchangeable (1585.4 mg/Kg) and total potassium (7251.1 mg/Kg) in paddy rice higher than upland products (sugar beet and canola). The clay content is major factor for high presence of solution, non exchangeable and total potassium in paddy rice. Smectite (20-30%) and vermiculite (30-50%) minerals in the surface soil and illite mineral (20-30%) in subsurface layer are other parameter, too. In paddy rice, high amount of clay particles induce to increasing of clay minerals and this factor affecting on total potassium. The presence of these minerals can be the reason of high levels of total K. In this research, concluded that potassium status of the soils is greatly influenced by the type of clay minerals, their abundance in soils and cultivation type.

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INHIBITION OF SHALES SWELLING USING INORGANIC SALTS AND NANOSCALE OXIDES

Mohamed Farage, Mervat S. Hassan*

Central Metallurgical R & D Institute, Cairo, Egypt
Hassan_mervat@yahoo.com

Problems caused by shales in petroleum activities are not new. At the beginning of the 1950s, many soil mechanics experts were interested in the swelling of clays, which are important for maintaining wellbore stability during drilling, especially in water-sensitive shale and clay formations. The rocks within these types of formations absorb the fluid used in drilling, which causes them and may lead to a wellbore collapse. In drilling fluids, the terms inhibit, inhibition and inhibitive mud system refer to arresting or slowing the hydration, swelling and disintegration of clays and shales.

Shale cuttings consist of different montmorillonite content collected from different core samples were evaluated using X-ray diffraction (XRD), X- ray Fluorescence (XRF), Cation Exchange Capacity (CEC) using Methylene Blue (MB). Swelling index of the shale measured using compressed disks of the shale in contact with OCMA bentonite for 20 hrs. using Linear Swelling Meter (LSM). Inorganic salt in term of Potassium chlorite (KCl) and nanoscale oxides in terms of ZnO, SiO_2 and TiO_2 used as inhibitor of swelling of shale cuttings. All these inhibitor are added to OCMA bentonite.

Shale core samples consist of Ca-montmorillonite followed by Kaolin in addition of trace of illite. Quartz considered as main non-clay minerals followed by Feldspar, calcite, Siderite and Pyrite. Shale C has the highest montmorillonite content followed by Shale B and finally shale A.

Swelling of the shale directly related to the montmorillonite content, more montmorillonite means more swelling in contact with OCMA bentonite. Swelling of Shale cuttings decreased in the direction A<B<C. However, shale A stop swell after 2 hours compared with that of shale B and C (3 hours).

The inhibition of swelling of these shale cuttings using 1-4% KCl achieved decreasing in swelling ranged from 17% at 2% (shale A), 22% at 3% (shale B) and 30% at 4% (shale C). This demonstrates that the addition of KCl to solutions of clay inhibitors improves their ability to reduce the absorption of aqueous fluid by shale. The variation in KCl% needs to exchange the interlayer cations of montmorillonite to K form (K -fixation) directly related to montmorillonite content.

Meanwhile, the effect of nanoscale oxides as inhibitor was great compared with KCl. These nanoscale oxides caused dramatic decreases in swelling of shales. Nanoscale SiO_2achieved almost 50% decrease in swelling of shales at 0.25% in contact with OCMA bentonite. Meanwhile ZnO and TiO2 caused less swelling decreaseing at the same concentration (0.25%) ranged between 25 and 38% for ZnO and TiO2 respectively. The mechanism of KCl and nanoscales oxides as inhibitors is different. Nanoscale oxide precipitate into pore spaces and onto the surfaces of shales and cuttings prevent adsorption of fluid and reduced swelling.

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RECENT ADVANCED IN LAYERED DOUBLE HYDROXIDES FOR GREEN CATALYSIS

Zhe An, Jing He*

State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Beijing 100029, P. R. China
*hejing@mail.buct.edu.cn

Layered double hydroxides (LDHs), also known as hydrotalcite-like materials, are a class of two-dimensional (2D) anionic clays consisting of positively charged host layers and exchangeable interlayer anions [1]. LDHs has found extensive applications in diverse areas such as biology and medicine, separation science, and optical materials, as a result of their versatility in chemical composition. Recently, considerable attention has been focused its application as precursor for supported metal catalysts and intercalated chiral catalysts for green catalysis [2]. Benefiting from the atomic-scale distribution of metal cations in the brucite-like layer of LDHs and the lattice confinement/inducement effects in the topotactic transformation, homogeneously dispersed metal particles in high-density or pseudo-single-atom metal sites have been afforded, which exhibit excellent catalytic activity, selectivity, and stability in the syngas conversion, nanotube carbon synthesis, paraffin isomerization, and etc. [3] Owing to the tunability of interlayer anions, diversified molecular catalytic sites, including chiral complex or amine segment, could be intercalated into the interlayer space as anions, affording intercalated chiral catalysts [4]. In virtue of confinement of interlayer space or the steric synergies of rigid LDH layers, remarkable enhancement of chiral induction has been achieved in asymmetric sulfoxidation or epoxidation. The ‘huge’ brucite-like layers make a stable ‘rigid’ environment around the chiral centre, and thus have significant impact on the enantiomeric selectivity by restricting or directing the access trajectory of reactant molecules. In virtue of the desired basicity afforded by the layers of LDHs, impressive enhancement of the catalytic activity in C-H activation has been achieved.

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MOLECULAR DETAILS OF PHOTORESPONSES OF SWITCHABLE AZOBEZENE DERIVATIVES AND ALKYLAMMONIUM SURFACTANTS IN CLAY INTERLAYER SPACES

Hendrik Heinz

Department of Chemical and Biological Engineering, University of Colorado Boulder, Boulder, Colorado 80309, USA

The molecular-level orientation and reorganization of model azobenzene derivatives in the interlayer space of layered silicates upon laser excitation was examined by molecular dynamics (MD) simulation in comparison with existing X-ray diffraction data and UV/vis absorption measurements. MD results show uniform reversible changes in basal plane spacing of montmorillonite up to 2.8 Å (14%) upon trans-cis isomerization of attached photoactive surfactants such as (4,4′-phenylazophenyl)-diammonium ions and (4-phenylazophenyl)ammonium ions. Uniform, significant responses are supported by the presence of cointercalate to compensate changes in interlayer density, by conformational rigidity and upright orientation of the azobenzene-containing surfactants on the mineral surface, and a medium-to-high packing density [1]. Experimentally, Okada et al. have shown nonuniform reversible optical switching of the gallery height for semiflexible surfactants up to 10 Å (41%) in the presence of phenol and uniform reversible optical switching of 0.9 Å (4%) without cointercalates [2]. Further experimental data also show the absence of changes in gallery spacing for azobenzene derivatives with attached flexible hydrocarbon chains at low packing density without cointercalates and are explained by simulation. From a methods viewpoint, an approach is introduced to simulate the photoisomerization reaction using classical molecular dynamics, taking quantitatively into account the input of photon energy, the time scale of the isomerization (~1 ps), and the relative energies of the trans and of the cis isomer, as well as the thermal conversion barrier. A temporary modification of the C-N=N-C torsion potential describes the input of photon (excitation) energy, which can be applied to common force fields (including PCFF, OPLS-AA, COMPASS, CVFF, AMBER, CHARMM) and facilitates the simulation of the photoisomerization reaction as a function of molecular environment, pressure, temperature, and excitation time [3].

We will also discuss the interlayer structure and cleavage energy of 50 different alkylammonium-modified montmorillonites of different cation exchange capacity (CECs of 91 meq/100 g and 143 meq/100 g), head group structure, and chain length by comparison of experimental data and molecular dynamics simulations [1]. The interlayer density and the cleavage energy are lower for partially packed, flat-on alkyl multilayers in the interlayer space and higher for densely packed, flat-on alkyl multilayers in the interlayer space, in agreement with trends in gallery spacing and molecular conformation. Particularly high cleavage energies, in excess of 60 mJ/m2, are found when charged head groups of surfactants are not vertically separated between the clay mineral layers at equilibrium distance due to strong contributions from Coulombic cohesion. A widely tunable range of cleavage energies between 25 and 210 mJ/m2 was identified. Alkylammonium-modified clay minerals with the lowest cleavage energy are of particular interest as additives for nanocomposites with increased potential for exfoliation and dispersion in nonpolar host media.

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CLAY/WATER INTERFACIAL MODELS (KAOLINITE, MICAS, MONTMORILLONITE) TO REPRODUCE HYDRATION ENERGIES, CONTACT ANGLES AND ORGANIC ADSORPTION

Tariq Jamil (1), Thomas Underwood (2), H. Christopher Greenwell (2), Hendrik Heinz (1)

(1) Department of Chemical and Biological Engineering, University of Colorado Boulder, Boulder, Colorado 80309, USA,
(2) Department of Earth Sciences, University of Durham, Durham, DH1 3LE, UK

In this lecture, clay/water interfacial models and adsorption of organic compounds will be discussed. Recent developments of clay models allow rather precise simulations of cell parameters and surface properties of clay minerals, including surface energies, interfacial energies with different solvents, and their electrostatic and van-der-Waals energy contributions. In particular, calculations of hydration energies, contact angles, and binding energies of organic and biological molecules will be discussed at hand of examples. Important aspects of clay surface chemistry and their inclusion in molecular models will be described, for example, composition, cation exchange capacity, the role of divalent versus monovalent ions and pH. Adsorption of organic molecules and polymers is influenced by factors such as the presence of cationic groups, ability for hydrogen bonding to superficial oxygen in silicate rings or AlOH groups, as well as hydrophobic depletion forces. A visible role is hereby also played by the hydration shells of ions on the surface of clay minerals, which simulations can visualize. The influence of ionic strength, concentration, and pH on conformations and adsorption energies of peptides and carbohydrate polymers on clay surfaces will discussed by means of simulations and comparisons to measurements.

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CLAY MINERALOGY AND GENESIS OF THE Ni-Co LATERITIC DEPOSIT IN THE ÇALDAĞ REGION (MANISA, WEST ANATOLIA), TURKEY

Cahit Helvaci (1), Selahattin Kadir (2)*, Necip Güven (3), Tolga Oyman (1), Him Gündoğan (1)

(1) Dokuz Eylül University, Department of Geological Engineering, TR-35160 İzmir, Turkey, (2)Eskişehir Osmangazi University, Department of Geological Engineering, TR-26480 Eskişehir, Turkey, (3)University of Texas at San Antonio, Department of Physics, San Antonio, Texas 78248, USA
*skadir.euroclay@gmail.com, cahit.helvaci@deu.edu.tr, guvenclay@gmail.com, tolga.oyman@deu.edu.tr, ibrahim.gundogan@deu.edu.tr

The Çaldağ Ni-Co deposit is characterized by a reddish-brown oxide laterite, containing residual Ni deposits formed by the intense tropical weathering (lateritization) of peridotites. Ni-Co ore is associated with allochthonous lateritization during the Upper Paleocene-Middle Eocene, represented by colloform Fe-oxyhydroxides and autochtonous lateritization during Oligocene. The lateritic units are developed over serpentinized dunitic ultramafic rocks and consist mainly of smectite, berthierite, kaolinite, gypsum, pyrite, takovite, and pecoraite. These units were examined by using polarized-light microscopy, X-ray diffraction, scanning and transmission electron microscopy (SEM and STEM) and geochemical methods. Mineralogical zonation from the base of the laterite profile upwards followed the sequence: serpentinized ultramafic rocks, clay zone, carbonate- and sulfide-bearing zone, Fe-oxyhydroxide zone and silica-rich zone. In addition, Fe-oxyhydroxides, smectite and opal-CT, and quartz increase towards the surface, whereas olivine, pyroxene and serpentine decrease upwards in response to chemical weathering. Micromorphological images revealed that smectite, kaolinite, and Fe-oxyhydroxides are the main alteration products of ultramafic units developed in dissolution voids via the circulation of meteoric water in the serpentinized ultramafic units. Texturally and micromorphologically, the presence of secondary calcite, gypsum, goethite, hematite, and pyrite in association with the laterite indicates the influence of chemical weathering processes. STEM determinations reveals that Ni occurs in the structures of smectite, berthierine, kaolinite, serpentine, goethite, pecoraite, asbolane, brindleyite and takovite. Ni-Co mineralization associated with Fe-oxyhydroxides and smectitic clays formed under wet and dry conditons, respectively as a result of an increased Fe_2O_3+Al_2O_3+Ni+-Co/MgO ratio. Thus, serpentine, smectite, and berthierine show average structural formulae of

$(Si_{3.61}Al_{0.07}Fe_{0.33})(Fe_{0.70}Mg_{4.91}Mn_{0.02}Cr_{0.05}Ni_{0.15})(Ca_{0.01}K_{0.01})$;

$(Si_{6.71}Al_{1.17}Fe_{0.12})(Al_{1.61}Fe_{1.10}Mg_{1.05}Ti_{0.37}Mn_{0.03}Ni_{0.62})(Ca_{0.11}Na_{0.02}K_{0.01})$; and

$(Si_{2.53}Al_{1.47})(Al_{0.60}Fe_{2.75}Mg_{0.27}Mn_{0.45}Ti_{0.001}Cr_{0.07}Ni_{0.81}Co_{0.07})(Ca_{0.06}Na_{0.08}K_{0.01})$;

respectively. Ni and Co substitute for octahedral Fe in the structure of serpentine, smectite, and berthierine. Thus, Ni and Co are concentrated significantly in altered units, and are correlated positively with Fe_2O_3 content, controlled mainly by the formation of Fe-rich clays, Fe-(oxyhydr)oxide phases in addition to Ni-minerals. Field observations, mineralogical and geochemical analyses reveal that the smectite formed under basic conditions controlled by multistage chemical weathering of ultramafic sand volcanics, and the concentration of Fe, Mg, Al, Si, Ca, and S. Precipitation of goethite, gypsum, pyrite, kaolinite, and berthierine developed under acid conditions in dissolution voids in association with smectite.

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Keywords: Ni-Co laterite deposit, Ni-minerals, Smectite, Clay minerals, Ultramafics, Çaldağ deposit, Turkey.

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MODELIZATION OF THE HYDROLYSIS REACTION OF SILOXANE BONDS IN THE TETRAHEDRAL SHEET OF PHYLLOSILICATES

A. Hernández-Laguna (1), N. Hernández-Haro (2), D. Muñoz-Santiburcio (3), C.I. Sainz-Díaz (1), A. Grand (4), J.Ortega-Castro (2), F.J. Huertas (1)*

(1) Instituto Andaluz de Ciencias de la Tierra (CSIC-University of Granada), Armilla (Granada), Spain, (2) Department of Chemistry, University of Balearic Islands, Palma de Mallorca, Spain, (3) Lehrstuhl für Theoretische Chemie, Ruhr-Universität Bochum, Bochum, Germany, (4) INAC, SCIB, Laboratoire "Lésions des Acides Nucleiques", UMR CEA-UJF E3, CEA-Grenoble, Grenoble, France

Phyllosilicates are important minerals usually found in the Earth's crust, as well as in the upper mantle. In rock and soils, weathering and alteration are induced by the interaction of water molecules with mineral surfaces. After adsorption on the surface, water reacts with the different superficial groups, hydrolyzing the structure. The dissolution mechanism of the SiO_4 groups proceeds by hydrolysis of siloxane bonds (Si-O-Si). As a general rule, acid pH conditions increase reaction rate.

In this work, basal tetrahedral sheet of phyllosilicate structure is modelled with quantum mechanical calculations by using the following molecular clusters: i) by linear models, resulting in a cluster of $HSi(OH)_2OSi(OH)_2OSiH(OH)_2$; and ii) by one model of hexagonal cavity made of SiO_4 units, being the dangling bonds saturated with H atoms, resulting in a cyclic molecular cluster of $Si_6O_{18}H_{12}$. The acid pH of the media is modeled by adding one proton to the siloxane oxygen. Critical points (CP) of the potential energy surface (PES) of the hydrolysis reaction on neutral and protonated models are calculated at the B3LYP/6-311++G(3df,2p)//6-311++G** level in gas phase and with a water SMD Polarizable Continuum Model.

Two main mechanisms are found: i) one water molecule attacks a O-Si-O group, forming a trigonal two-pyramidal reactant complex, and a hydrolysis transition state (TS) is found, where a H atom of the water molecule is transferred to the siloxane O atom, hydrolyzing the Si-O bond; and ii) in the acid model, a water molecule interacts with the closest Si-O bond to the protonated O atom, and the interaction of the water lets the H^+-O-Si bond reach a TS, decreasing the activation energy [Δ(Etotal+ZPE)] with respect to the previous TS of hydrolysis. The first mechanism is found in neutral and acid hydrolysis. However, the second mechanism is found only in the acid model, which could be considered as an acid dissolution mechanism, catalyzed by the water, which lets it reach the right molecular structure for breaking the Si-O bond.

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PRESSURE EFFECTS IN MUSCOVITE-PARAGONITE AND MUSCOVITE-PHLOGOPITE SERIES TO 9 GPa

Alfonso Hernández-Laguna (1)*, C. I Sainz-Díaz. (1), C. J Garrido. (1), N. Hernández-Haro (2), J. Ortega-Castro (2), C. Pérez del Valle (3), D. Muñoz-Santiburcio (4), I. Vidal-Daza (5), Antonio Sánchez-navas (6), M. Mookherjeee (7)

(1) Instituto Andaluz de Ciencias de la Tierra (CSIC-University of Granada), Armilla (Granada), Spain, (2) Departament de Química, Institut d'Investigació en Ciències de la Salut, Universitat de les Illes Balears, Palma de Mallorca, Spain, (3) Département de Chimie Moléculaire, Université Grenoble Alpes, France, (4) Lehrstuhl für Theoretische Chemie, Ruh-Universität Bochum, 44780 Bochum, Germany, (5) Apoyo a la Docencia-Centro de Servicio de Informática y Redes de Comunicaciones, University of Granada, Granada, Spain, (6) Department of Mineralogy, University of Granada, Granada, Spain, (7) Department of Earth, Ocean and Atmospheric Sciences, Florida State University, Tallahassee, Fl, USA

Phyllosilicates are abundant minerals in soils and rocks (igneous, metamorphic, and sedimentary rocks) of the Earth's crust, and even they are found in the Earth's upper mantle. They are typically formed as alteration products and helps in transporting significant amount of water into the Earth's interior via subduction. Muscovite (Ms) and Paragonite (Pg) belong to the 2:1 dioctahedral layer silicates, and Phlogopite (Phl) belongs to the trioctahedral layer silicates. They are considered useful petrogenetic and geological history indicators, and geobaro-thermo-meters.

Ms, Pg, and Phl are the ideal end members of the Ms-Pg and Ms-Phl series, which can be described by the following ideal formula $K_{1-x}Na_{x}Al_{2-y}Mg_{(y+y*0.5)}(Si_{4-z}Al_{z})O_{10}(OH)_{2}$, when $y = 0$, $0 \leq x \leq 1$ and $z \approx 1$ is the solid solution (SS) of Ms-Pg and when $x = 0$, $0 \leq y \leq 2$ and $z \approx 1$ is the SS of Ms-Phl. This computational research has been carried out in the $2M_1$ polytype. Pressure (P) affects significantly to the crystal structure and behavior of both SS. Most of the end members have been studied by different experimental techniques. In this work we present a systematic computational study of the effect of P on the crystal structure, polyhedrals, bulk moduli, atomic bulk moduli, elastic constants, excess properties and variation of the gap of solubility with P on both SS.

The SS have been calculated by DFT with Siesta and Quantum Espresso (QE) codes. Numerical atomic orbital with double-ζ plus polarization functions basis sets, GGA, PBE and Troullier Martins norm-conserving pseudopotentials have been used in Siesta calculations, and plane waves, B86BPBE corrected with the exchange-hole dipole moment (XDM) model and PAW potentials have been used in QE runs. P has been in the range of small tractions to 9 GPa.

The calculated crystalline structures and bulk moduli agree with the known experimentally values of some members of the SS. Behavior of the different members of the SS at different P is fitted to Birch-Murnagham EoS and finally studied as a function of the composition. Elastic constants of the Ms-Pg series are also calculated at different P. The interlayer modulus is the smallest of the crystal cell, and the atomic moduli of the K and O of the interlayer are also the smallest, giving us a compression mechanism. Volume excess properties are studied at different P, being fitted to a Redlich-Kister model, which let us to calculate the excess Gibbs free energy and study the behavior of the solvus of the SS as a function of P. The behavior of both SS is different.

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ORIGIN OF Mg-SMECTITE AND SEPIOLITE IN THE TRANSITION FROM MUD FLAT TO PALUSTRINE ENVIRONMENTS IN THE CERRO DE LOS BATALLONES DEPOSIT (MADRID BASIN, SPAIN)

Juan E. Herranz*, Manuel Pozo

Dpto. Geología y Geoquímica, UAM, 28035, Madrid, España
*juan.herranz@uam.es

The Neogene Madrid Basin has significant deposits of magnesian clays (e.g. sepiolite, Mg-bentonite) that were formed during the Miocene age. The environmental conditions correspond to lacustrine-palustrine environments developed in an endorheic basin under a semi-arid climate. The interest of these magnesian clay minerals is related mostly with their industrial applications but also with the establishment of their origin and the genetic relationship between them. Although different models have been proposed for their origin, the role of authigenic process (transformation vs. neoformation) still remains unclear in some sedimentary sequences. In this research, we study transitional lithofacies between mud flat and palustrine environments formed by Mg-smectite and sepiolite, respectively. The studied magnesian clays belong to the Miocene Intermediate Unit of the Madrid Basin and were sampled at the base of the Cerro de los Batallones sepiolite deposit (Torrejón de Velasco, Madrid).

The lithostratigraphic succession comprise the units I.1, I.2 and II previously defined by Pozo et al. (2014) [1]. Sub-unit I.1 (>20 m thick) consist of massive green-brown mudstone, clay-clast arenite and marly dolostone; it is interpreted as mud flat deposits formed in a lacustrine margin. Sub-unit I.2 (<2 m thick) is formed by sequences of laminated reddish to greenish lutites that evolve to massive yellowish white lutites showing evidence of nodulation and brecciation. Eventually, cm-thick white opals inserts were observed. This sub-unit has been interpreted as transitional lithofacies from mud flat to palustrine environments. The unit II (up to 9 m thick) is made-up by massive white to grey lutites which include the mined sepiolite deposit. The occurrence of opaline silicification forming nodules and layers that replace lutites is remarkable. The common root bioturbation and other evidence of subaerial exposure support palustrine environment interpretation. A total of 76 samples from 10 lithostratigraphic sections, mostly from unit I.1 and I.2, were collected. The analytical techniques used include X-ray diffraction (bulk sample and clay fraction), petrography (thin sections and SEM-EDX) and chemical analysis of major and trace elements (XRF).

The unit I.1 has a mineralogical association consisting of smectite (>70%, mostly trioctahedral) and illite, with variable percentages of quartz, feldspar, dolomite, kaolinite and sepiolite. The transitional unit I.2 is characterized by the predominance of low crystallinity sepiolite (LCS) (>60% and FWHM $\approx$ 1º 2Θ) with subordinate Mg-smectite and illite and minor quartz and feldspar contents. Lutites in the unit II are formed by high crystallinity sepiolite (>90% and FWHM $\approx$ 0.5º 2Θ) with traces of illite and opal CT.

Taking into account chemical analysis, Al_2O_3 content decrease from the mud-flat mudstones (10%) to palustrine lutites (<1.5%). Others major elements (Fe_2O_3, TiO_2, K_2O) have concentrations under 5%, with a good positive correlation with Al_2O_3 (R^2 values of 0.98, 0.93 and 0.93, respectively). Highlight that MgO content evolves conversely showing 6.5% in I.1 but near 22% in II. Regarding trace elements, in general they have a good direct correlation with Al_2O_3.

A genetic model of Mg-smectite and sepiolite formation is proposed. The origin of Mg-smectite should be related with the reaction of Mg-rich solutions with inherited Al-smectites, under suitable pH and salinity conditions in the mud flat environment (unit I.1). Lower “crystallinity” sepiolite formed by both dissolution-precipitation of Mg-smectites and neoformation in the mud flat-palustrine transition where groundwater played an important role (unit I.2). Under clear palustrine conditions high “crystallinity” sepiolite originated by neoformation with evidence of recrystallization (unit II). The excess of groundwater silica input explains the abundance of opal replacing sepiolite.

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CARBONATE CONTAMINATION DURING SYNTHESIS OF LAYERED DOUBLE HYDROXIDE-BASED ADSORBENTS

Toshiyuki Hibino

Environmental Management Research Institute, National Institute of Advanced Industrial Science and Technology, Tsukuba, Japan

Layered double hydroxides (LDHs) are a class of lamellar compounds that possess anion exchange property, which enable them to be used as anion adsorbents. In this context, numerous studies concerning water treatment by using LDHs have been reported. In the present study, LDH-agarose hydrogel composites were synthesized, and their dried forms were tested as adsorbents. LDH-agarose hydrogel composites were examined as prototype of LDH-polymer hydrogel composites. Those composites are easy to separate from aqueous reaction system. Moreover, even after drying, LDH-polymer hydrogel composites would swell in water, and pathways inside the composites generated by the swelling would make access of anions easy. Therefore, such composites can be one of solutions to improve efficiency of solid-liquid separation when used in water treatment. However, during drying the composite hydrogels, LDHs in the composites are vulnerable to carbonate contamination, which is caused by CO_2 in air. Because of high affinity of carbonate anion to LDHs, carbonate contamination substantially results in decrease of anion exchange capacity, which means decline of ability as anion adsorbents. In the present study [1], difference of carbonate contamination by drying methods were assessed by using LDH-agarose gel composites as well as LDH aqueous suspensions, and fundamental data concerning carbonate contamination during drying were provided.

First, aqueous suspensions of Cl-containing LDH were prepared. After preparation of Cl-containing LDHs by co-precipitation (low-crystallinity LDH) or by coprecipitation followed by hydrothermal treatment (high-crystallinity LDH), the LDHs were dispersed in water. LDH-agarose composite gels were prepared by the following simple method. Agarose was dissolved in water by heating, and then the hot agarose solution was mixed with the aqueous LDH suspensions at 70 ˚C. By cooling the mixture to room temperature, LDH-agarose composite gels formed. (Contents of agarose and LDH were 1 wt% each.) The gels were cut into cubes about 3 mm to a side, and dried in 3 ways: vacuum drying, oven-drying in air at 110 °C and air-drying. The aqueous LDH suspensions were also dried by the same ways to compare with the composite gels. In addition to drying method, effect of crystallinity of LDHs was tested. Adsorption abilities of those dried gels and LDHs themselves were evaluated by measuring SO_4^{2-} adsorption.

When drying methods were compared, adsorption abilities for SO_4^{2-} were decreased most by air-dried. On the contrary, reductions by oven- and vacuum-drying were small: the composite gels dried by these 2 drying methods retained almost the same adsorption abilities as those of their original composite gels. Next, effect of crystallinity of LDHs in the composites was evaluated. The difference between air-drying and the other 2 ways was greater when low-crystallinity LDH was used. When compared with the adsorption abilities with the original gels, on the basis of the amount of adsorbed SO_4^{2-} per unit weight of the original undried gel, air-dried gel containing low-crystallinity LDH reduced the ability by 56%. In contrast, reduction was 29% for the composite gel containing high-crystallinity LDH.

In the case of aqueous suspensions of LDHs were used instead of the composite gels, the same trend was observed in relationship between adsorption ability and drying method. These results revealed that drying method can significantly affect the adsorption abilities of LDH-based products or LDHs as anion adsorbents, especially for products containing low-crystallinity LDHs.

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DIOCTAHEDRAL CHLORITES AND RED BEDS: A DIAGENETIC HYPOTHESIS

Stephen Hillier (1,2)*, Rik Brydson (3)

(1) The James Hutton Institute, Aberdeen, AB15 8QH, United Kingdom, (2) Department of Soil and Environment, Swedish University of Agricultural Sciences, Box7014, Uppsala SE-750 07, Sweden, (3) Institute for Materials Research, SCaPE, University of Leeds, Leeds LS2 9JT, United Kingdom
*Stephen.hillier@hutton.ac.uk

Diagenetic chlorites are a common component of many sedimentary rocks. They form by various routes as diagenesis progresses towards the almost ubiquitous mica + chlorite assemblage of low grade metamorphic rocks. In most settings aluminous dioctahedral chlorites are rarer than ferro-magnesian trioctahedral types. In some ‘red beds’, however, this trend may be reversed. Indeed, the consistent and pervasive occurrence of dioctahedral chlorites (sudoite), as well as the allied mixed-layer dioctahedral chlorite-smectite mineral known as tosudite, indicates a clear association of dioctahedral chlorites with some red bedfacies which hitherto has not generally been recognized as a common clay mineral diagenetic pathway (Hillier 2003). Some examples include parts of the Triassic of the Colorado Plateau (Schultz, 1963), various Permo-Triassic sandstones in Germany (Kulke 1969), Poland (Biernacka 2014) and the North Sea (Purvis 1990), and many parts of the Old Red Sandstone of the United Kingdom (Garvie, 1992, Hillier et al., 2006). The widespread nature of the distribution of tosudite and/or sudoite in these settings argues against localized hydrothermal origins and a more pervasive diagenetic process appears to be operating. Features such as abundant kaolinite or dickite in association with many examples indicates that the type of reds beds in which they occur tend to have aluminous diagenetic clay mineral assemblages. This might be related to widespread leaching and flushing of red beds by meteoric water during early diagenesis, with consequent alteration of feldspars and micas. Pathways for the diagenetic formation of tosudite and sudoitehave not been yet been adequately established but might involve either a kaolin precursor, or perhaps a sequence beginning with aluminous (beidellitic) smectites that evolves to dioctahedral chlorite via tosudite as an intermediate step. Such a sequence would be entirely analogous to the well-documented saponite to corrensite to trioctahedral chlorite sequence in Mg-Fe^{2+} rich environments. Here it is also hypothesised that early formed hematite may play a crucial role as a buffer on the oxidation state of Fe in some red bed diagenetic systems. Under such conditions in the diagenetic progression towards the mica + chlorite assemblage, it is postulated that the formation of dioctahedral chlorites is favoured over that of their more common Fe^{2+} rich trioctahedral relatives because they can readily and preferentially accommodate Fe^{3+}. Support for this hypothesis is sought be an examination of the oxidation state of Fe in some examples using Electron Energy Loss Spectroscopy (EELS).

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ORIGIN OF PORE-LINING CHLORITES IN THE LAGGAN AND TORMORE FIELDS, WEST OF SHETLAND, UK

Stephen Hillier (1,2)*, Russell Gray (3)*, Evelyne Delbos (1)

(1) The James Hutton Institute, Aberdeen, AB15 8QH, UK, (2) Department of Soil and Environment, Swedish University of Agricultural Sciences, Box7014, Uppsala SE-750 07, Sweden, (3) Total E&P Limited UK, Crawpeel Road, Aberdeen, AB12 3FG, UK
*Stephen.hillier@hutton.ac.uk

Pore lining chlorites are often responsible for the preservation of anomalously high primary porosity in potential hydrocarbon reservoir sandstones. There may be several origins for such types of chlorites but understanding their specific origins can be important for many aspects of both exploration and production. Chlorite bearing Palaeocene sandstones and shales in the Laggan and Tormore fields to the west of Shetland deposited in a deep marine environment have been studied by a variety of mineralogical and geochemical methods to help determine the origin of the chlorite. The chlorites examined are all iron-rich varieties. Unlike many other examples of Fe-rich pore-lining chlorites, there is no obvious evidence for mixed-layering with 7 Å berthierine layers. Modelling of polytypes using Wildfire®, indicates random mixed-layer Ibb/Iaachlorite polytypes. Analysis of chlorites in the associated shales demonstrate similar mineralogical characteristics to those in sandstones, although chlorite is evidently much more abundant in the shales, often exceeding 15 wt% of the rock. Petrographic evidence, particularly in the shales reveals chlorite pseudomorphs after volcanic glass shards. Alteration of glass to chlorite also produced abundant anatase, which is concentrated at present and former grain boundaries, presumably because Ti cannot be readily accommodated in the chlorite structure. Selective dissolution of the chlorites by a nitric acid digest technique reveals that they contain elevated contents of transition metals (Sc, Cr, Mn, Co, Ni, Cu and Zn) with respect to some chlorites from other locations in the North Sea and elsewhere. They also are enriched in light rare earth elements (LREE) similar to patterns seen in Palaeocene tuffs from other locations in the North Sea region. Altogether, the data indicate that chlorites in Laggan and Tormore field have originated as alteration products of volcanic glass and tuffaceous material probably of Fe-Ti tholeiitic basalt composition.

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INTERCALATION OF A FLUORESCENT DIKETONE DERIVATIVE INTO A SYNTHETIC SAPONITE

Mutsumi Hirose (1), Fuyuki Ito (2), Tomohiko Okada (1)*

(1) Department of Chemistry and Materials Engineering, Shinshu University, Nagano 380-8553, Japan, (2) Department of Chemistry, Shinshu University, Nagano 380-8544, Japan
*tomohiko@shinshu-u.ac.jp

In recent years, aggregation induced emission (AIE) phenomenon, which means emission enhancement by forming aggregation, has been investigated [1]. Dinaphthoylmethane β-diketones are known as a class of the AIE fluorescent dyes [2], and the fluorescence intensity increases in a homogeneous system when the fraction of water to tetrahydrofuran (THF) increases. The restriction of intramolecular rotations by aggregation is a possible factor responsible for the AIE, however, the mechanism of the enhanced emission has not been essentially clarified. Smectite group of layered clay minerals is a candidate of the host materials to regulate conformation of the dyes, when the spatial distribution (density) can be controlled in the two-dimensional interlayer nanospace. It has been reported that emission of a cationic porphyrin was enhanced owing to more planar conformation by strong interactions of the four cationic sites with the nanosheets [3]. We report here the incorporation of pyridine groups into a dibenzoylmethane β-diketone to organize in the interlayer space of smectites through cation-exchange reactions, leading to exhibit AIE properties.

Based on the previous report [4], 1-(4-methoxyphenyl)-3-(4-pyridyl)-1,3-propandione was synthesized by Claisen condensation between methyl isonicotinate and 4’-methoxyacetophenone in dry THF in the presence of sodium amide. After the reactions were quenched with acetic acid and water, the resulting precipitate was repeatedly washed with diethyl ether. The purified product obtained by a column chromatography was characterized using 1H NMR and mass spectrometry. A synthetic saponite (Sumecton SA, abbreviated to SSA) was used as the dye support, and the cation exchange capacity (CEC) is 0.71 mEq/g. The adsorption of the dye was performed using a 3:2 mixed solvent of an aqueous HCl solution (pH3) and ethanol. Amount of the dye dissolved in the solution was 0.1, 0.5, 1 and 2 times the CEC, and the products were named as N^+-SSAX, where X indicates the added amount versus the CEC. The adsorbed amount was determined from the concentration change before and after the adsorption using a visible absorption spectroscopy (λ_{max}=356 nm). After the resulting solid was dispersed in water, the aqueous suspension was cast on a hydrophilic PTFE membrane filter. The fluorescence spectra of the cast film were measured with spectrofluorometer (the excitation wavelength of 380 nm).

The synthesized diketone derivative emitted at around 450 nm in THF/water mixtures. AIE properties exhibited because the fluorescence intensity increased with increasing the water fraction. The adsorbed amount of the dye was 0.042, 0.094, 0.073, and 0.33 mEq/g in N^+-SSA0.1, 0.5, 1, and 2, respectively. The basal spacing of the dye adducts was 1.21 nm for N^+-SSA0.1, 1.32 nm for N^+-SSA0.5, and 1.39 nm for N^+-SSA1 and N^+-SSA2. Irrespective of the adsorbed amount, the emission maximum was located on a longer wavelength region (around 540 nm), and each intensity was larger than the acidic solution. When the fluorescence intensity was normalized by the adsorption amount, the intensity of N^+-SSA1 resulted in the largest, and decreased in the order of N^+-SSA0.5, N^+-SSA0.1, and N^+-SSA2. When the diketone derivative in a solution was protonated by HCl addition, the peak in the fluorescence spectrum extremely decreased with appearing a peak at 540 nm. Thus, it is thought that the protonated diketone derivative was intercalated into SSA via cation-exchange reactions to aggregate for emerging the strong emission. An appropriate molecular aggregation state of the cationic diketone between the silicate layers will be discussed in the conference for representing AIE properties.

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DEVELOPMENT OF Fe-RICH CLAYS IN A WEATHERING PROFILE DERIVED FROM SERPENTINIZED ULTRAMAFIC ROCK IN NUI NUA MASSIF, VIET NAM

THAO HOANG-MINH (1), LAN NGUYEN-THANH (2), HORST-JÜRGEN HERBERT (3), JÖRN KASBOHM (4,5), LE THI LAI (6), MINH NGOC NGUYEN (1), RAFAEL FERREIRO MÄHLMANN (2)

(1) VNU University of Science, Vietnam National University, Hanoi, Viet Nam, (2) Institut für Angewandte Geowissenschaften, Technische Universität Darmstadt, Germany, (3) Gesellschaft für Anlagen- und Reaktorsicherheit mbH, Braunschweig, Germany, (4) Institut für Geographie und Geologie, Ernst-Moritz-Arndt-Universität, Greifswald, Germany, (5) Jörn-Kasbohm-Consulting, Germany, (6) Institute of Geological Sciences, Vietnamese Academy of Science and Technology, Hanoi, Viet Nam

We have investigated the chemical, mineralogical and weathering characteristics of a weathering profile of the Nui Nua serpentinized ultramafic-mafic massif (Thanh Hoa Province, Vietnam) using transmission electron microscopy coupled to an energy-dispersive X-ray (TEM-EDX), X-ray diffraction (XRD), and Fourier transform infrared spectrometry (FT-IR) methods. The weathering process in this area was controlled mainly by monsoon climate conditions. Clay minerals of this profile were characterized by temporary serpentine clay minerals though chlorite seemed to be stable and increased from the bottom to the top layer of the profile. This soil weathering profile developed on serpentinite in a tropical climate (Mg-rich weathering system) demonstrates that leached-Mg and oxidation of Fe are the main reasons for enrichment of Fe^{3+} and Al in early weathering stages. The Fe-pathway shown by TEM-EDX measurements indicates that the conversion of trioctahedral to dioctahedral minerals and changes of crystallochemistry of Fe-rich dioctahedral smectite seem to be driven by intense weathering by Fe^{2+}-oxidation. The oxidized Fe^{3+} is mainly incorporated into octahedral sheets of Fe-rich dioctahedral smectite and reduced significantly in higher grade of weathering. Consequently, Fe-rich smectite formed at the beginning of the weathering process (and initially the dominant dioctahedral phase) was transformed progressively to Al-rich smectite. Serpentine clay minerals were only temporary and were in turn replaced by Fe-rich smectite and chlorite which are more persistent in the long-term. The dioctahedral smectite phase is formed along with Fe^{3+} incorporation into octahedral sheets but it is gradually replaced by Al in octahedral sheets. The variation of charges, increase of CEC, and Si-diminution of tetrahedral Si towards the surface were all controlled by Fe-oxidation and drainage in the weathering system and those factors were also experimentally replicated.

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PHOTOPHYSICAL AND PHOTOCHEMICAL PROPERTIES OF AN IRON-RICH KAOLINITE

Erzsébet Horváth (1), János Kristóf (2), Dávid Fertig (1), Balázs Zsirka (1), Veronika Vágvölgyi (2), Katalin Győrfi (1)

(1) University of Pannonia, Institute of Environmental Engineering, P.O.Box 158, H-8201 Veszprém, HUNGARY, (2) University of Pannonia, Department of Analytical Chemistry, P.O.Box 158, H-8201 Veszprém, HUNGARY

TiO_2 (anatase+rutile) is a well-known photocatalyst. In the majority of cases anatase exhibits a higher photochemical activity due the higher amount of surface hydroxyls and to its favourable oxygen- and light-absorption properties. Based on this observation efforts were made to develop Al_2O_3- and clay-based nanomaterials. Composites made of semiconductive oxides and organic materials can also be listed among the potential photocatalysts. The use of e.g. dye-sensitized TiO_2, ZrO_2, WO_3, ZnO, ZnS, SnO_2, Fe_2O_3, as well as binary, ternary and quaternary mixed oxides was reported.

The band-gap value of the 1:1 (or TO)-type kaolinites is 3.7-3.9 eV (320-335 nm), which is comparable to that of anatase (3.2 eV; 387 nm) and rutile (3,02 eV; 410 nm). The structural order and morphology as well as the mineral and/or lattice contaminants present in minor amounts (0.1 to 3.0% w/w) can have little effect on the band gap values, only. However, the band gap values of kaolinites with high iron contents (10-20% w/w Fe_2O_3) can drastically shift towards the values of semiconductors (<3eV).

The photochemical activity of the iron-rich (19% w/w Fe_2O_3), kaolinite from Felsőpetény, Hungary, and its delaminated form (nanoclay) is the inherent property of the mineral structure. At the same time the results of the photophysical investigations (band-gap values, fluorescence properties, life-time data and photo-electrochemical properties) showed that the activity was increased with the increased iron content. Both the untreated and the exfoliated kaolinites can be excited in the 400-600 nm range. The lifetime of the excited states falls into the microsecond range, which is sufficient to initiate electron transfer processes. In the case of the exfoliated nanostructures longer lifetime values can be observed. The photochemical activity was investigated with the use of Na-benzenesulfonate model compound. The mechanism of decomposition (mineralization) was followed by FT-IR/ATR spectroscopy.

The results of the investigations carried out on the (photo)catalytic properties of iron-rich kaolins can be utilized in the pre-treatment/re-use of spent oils and in other environmental technologies (e.g. water treatment). On the other hand, exfoliated kaolinites can be considered as model systems in the study of the surface processes of Al-O and Si-O type catalysts/catalyst supports, as well.

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THIN-WALLED NANOSCROLLS BY MULTI-STEP INTERCALATION FROM TUBULAR HALLOYSITE-10 Å AND ITS SURFACE CHARACTERISATION

Erzsébet Horváth (1)*, János Kristóf (2), Balázs Zsirka (1), Tatjána Juzsakova (1), Róbert K. Szilágyi (3)

(1) University of Pannonia, Institute of Environmental Engineering, P.O.Box 158, Veszprém, 8201 HUNGARY, (2) University of Pannonia, Department of Analytical Chemistry, P.O.Box 158, Veszprém, 8201 HUNGARY, (3) Department of Chemistry and Biochemistry, Montana State University, Bozeman, MT 59717, USA

Surface modification of the halloysite-10 Å mineral with tubular morphology can be achieved by slightly modified procedures developed for the delamination of kaolinite minerals. The resulting delaminated halloysite nanoparticles have unexpected surface/morphological properties that display, new potentials in catalyst development.

In this work, a four-step intercalation/delamination procedure is described for the preparation of thin-walled nanoscrolls from the multi-layered hydrated halloysite mineral that consists of 1) intercalation of halloysite with potassium acetate, 2) replacement intercalation with ethylene glycol, 3) replacement intercalation with hexylamine, and 4) delamination with toluene. The intercalation steps were followed by X-ray diffraction, transmission electron microscopy, N_2 adsorption-desorption, thermogravimetry, and infrared spectroscopy. Delamination eliminated the crystalline order and the crystallite size along the '*c*'-axis, increased the specific surface area, greatly decreased the thickness of the mineral tubes to a monolayer, and shifted the pore diameter toward the micropore region.

Unexpectedly, the removal of residual organics from intercalation steps adsorbed at the nanoscroll surface with a peroxide treatment resulted in partial recovery of crystallinity and increase of crystallite size along the '*c*'-crystal direction. The d(001) value showed a diffuse pattern at 7.4-7.7 Å due to the rearrangement of the thin-walled nanoscrolls toward the initial tubular morphology of the dehydrated halloysite-7 Å mineral.

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SURFACE CHARACTERIZATION OF MECHANOCHEMICALLY MODIFIED EXFOLIATED HALLOYSITE NANOSCROLLS

Attila Táborosi (1), Robert K. Szilagyi (2), Erzsébet Horváth (1), János Kristóf (3), Balázs Zsirka (1), Péter Szabó (3), Dávid Fertig (1), Tatjána Juzsakova (1)

(1) University of Pannonia, Institute of Environmental Engineering, P.O.Box 158, Veszprém, 8201 Hungary, (2) Department of Chemistry and Biochemistry, Montana State University, Bozeman, MT 59717, USA, (3) University of Pannonia, Department of Analytical Chemistry, P.O.Box 158, Veszprém, 8201 Hungary

The surface modifications of kaolinite nanostructures fundamentally influence their morphology as a function of crystallinity and presence of contaminants. Beside morphology, the catalytic properties of 1:1-type exfoliated aluminosilicates are also influenced by the presence of defect sites that can be generated by mechanochemical activation in a controlled manner.

In this work, we investigated exfoliated halloysite nanoparticles with quasi-homogeneous, scroll-type secondary structure toward developing structure/function relationships for composition, atomic structure, and morphology. The surface properties of thin-walled nanoscrolls were studied as a function of mechanochemical activation expressed by (dry) grinding time. The surface characterizations were carried out by N_2, NH_3, and CO_2 adsorption measurements. The effects of grinding on the nano-halloysite structure were followed by thermoanalytical (TG/DTG) and infrared spectroscopic (FTIR/ATR) techniques. Grinding results in partial dehydroxylation with similar changes as observed for heat treatment above 300ºC. The employed mechanochemical activation shows decrease in dehydroxylation mass loss and the DTG peak temperature, decrease in specific surface area and number of mesopores, increase of surface acidity, and blue-shift of surface hydroxide bands and decrease in intensity in FTIR/ATR bands as a function of grinding time.

The experimental observations were used to guide atomic-scale structural and energetic simulations using realistic molecular cluster models for a nano-halloysite particle. A full potential energy surface description was developed for mechanochemical activation and/or heating toward nano-metahalloysite formation. The calculated differences upon dehydroxylation show remarkable agreement with the mass-loss values from DTG measurements.

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MICROANALYSIS AND INTERPRETATION OF CHLORITES IN HISTORICAL PAINTINGS

David Hradil (1,2)*, Janka Hradilová (1), Petr Bezdička (2)

(1) Institute of Inorganic Chemistry of the CAS, v.v.i., ALMA laboratory, 1001 Husinec-Řež, 250 68 Řež, Czech Republic,
(2) Academy of Fine Arts in Prague, ALMA Laboratory, U Akademie 4, 170 22 Prague 7, Czech Republic

Microanalysis of mineral pigments in paintings is not an easy task. Non-invasive investigation of artworks, which is rapidly developing in the field of cultural heritage research, could not provide complete mineralogical information, which is otherwise necessary for any provenance studies. Furthermore, micro-samples collected in the course of painting conservation are typically represented by flat chips with diameter not exceeding in any direction 1 mm, which contain both inorganic and organic components within complicated layered structure of paints. As a result, clay minerals in paint layers are routinely being described only by general terms (such as, e.g., "clays" or "alumino-silicates"), or they are completely omitted in the materials research of paints. Terms like "ochres" or "earths" are associated more likely with the identification of iron oxides affecting their colour despite the variable (and sometimes very significant) contents of clay minerals. These variable contents reflect the natural process of formation and, consequently, also the provenance of the material, and strongly affect its technological properties. The differentiating of clay minerals is particularly important in clay-based grounds (i.e. preparation layers on canvas), the composition of which was regionally specific in the Baroque period. By means of clay mineralogy therefore, anonymous paintings of Italian provenance can be clearly distinguished from those created in, e.g., Central Europe [1].

There is still a substantial lack of knowledge in methodological issues, because number of "standard" procedures widely applied to clays (preparation of oriented specimen, ethylene glycol solvation etc.) may not be applied when dealing with only minute amounts of rare heterogeneous material. We already reported the limits of Raman micro-spectroscopy to identify low scattering clay minerals in assemblage with simple iron and/or titanium oxides [2], and also the limits of X-ray powder micro-diffraction to provide quantitative analysis of clay minerals in micro-scale [3]. We described interactions of expandable clay structures with proteinaceous binders in paints modifying their d-spacing values and by using this knowledge we distinguished pure smectites from interstratified structures [3]. Proper identification and detailed characterization of chlorites is a next question that must be addressed. In this contribution, the mineralogy of selected Baroque clay-based grounds from Italy will be described in detailed with the aim to differentiate chlorites from kaolinite and/or smectite group minerals in microscale by using unconventional experimental approaches and to estimate their relative quantities, which are varying. Within comparative studies on artwork and reference samples specific mineralogical characteristics (polytypes, crystallochemistry, admixtures) will be applied to indicate possible source localities of the material in Northern Italy and possibly also differentiate paintings belonging to various artistic centers. Here presented finding of Fe-chlorites, which were further specified as *IIb* polytypes, is the first ever evidence of this group of minerals in historical paintings and is therefore highly valuable in the context of technical art history.

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HYDROXY-INTERLAYERED MINERALS: CRYSTAL STRUCTURE, FORMATION AND IMPLICATION FOR SOIL REACTIVITY

Fabien Hubert (1)*, Jean-Christophe Viennet (1,2), Liva Dzene (1,3), Emmanuel Tertre (1), Bruno Lanson (4), Eric Ferrage (1)

(1) IC2MP-Hydrasa, Université de Poitiers, UMR 7285 CNRS, 86073 Poitiers cedex 9, France, (2) CEED, University of Oslo -NO-0315 Oslo, Norway, (3) IS2M, Université de Haute-Alsace - UMR CNRS 7361, 68057 Mulhouse cedex, France (4) ISTerre, Université Grenoble 1 - UMR 5275 CNRS, F-38041 Grenoble, France
*fabien.hubert@univ-poitiers.fr

Acidic conditions in soils commonly lead to the formation of hydroxyl-interlayered minerals (HIMs) resulting from the adsorption of aluminium and its subsequent polymerization in the interlayer of 2:1 clay minerals. Formation of HIMs changes the soil reactivity by decreasing the cationic exchange capacity or by modifying the adsorption/desorption process of elements. The present work aims at providing new insights about the crystal structure of HIMs, the factors influencing their formation and finally on the role of their crystal structure in element mobility illustrated by the case of caesium sorption.

The detailed crystal structure analysis of HIMs from a surface horizon of a forest Aluminic Cambisol [1] shows that HIMs are complex illite-HI-expandable layer mixed-layer minerals (MLMs) and the different HIMs encountered in the soil sample mostly differ by the abundance of their constitutive layers. These results obtained using the X-ray diffraction profile modelling approach applied on various sub-fractions (<0.05, 0.05-0.1, 0.1-0.2 and 0.2-2 µm) also indicate that i) HIMs contain illite layers in all the sub-fractions and ii) with the decrease of particle size, HI and expandable layers are found to decrease and increase, respectively.

In order to provide additional insights on the formation mechanism of such complex HI-MLMs, experimental auto-aluminisation experiments of Ca and K-saturated Santa Olalla vermiculite under acidic conditions are performed on three size fractions (0.1-0.2, 1-2 and 10-20 µm). The mixed-layer nature of the HIMs evidenced in a previous study [2] is confirmed. In addition, the HIMs formed from Ca-saturated Santa Olalla vermiculite mainly depend on time irrespective of the particle size, contrastingly to HIMs formed from K-saturated vermiculite, whose formation is particle size dependant. The results show that HIMs formed from K-saturated vermiculite are MLMs constituted by original K-vermiculite layers, together with HI and expandable layers. Therefore, the persistence of K-vermiculite layers in all the sub-fractions and the extent of transformation with the decrease of particle size [3] lead to the same general trend as observed previously in soil samples [1].

The reactivity of HIMs formed from Ca-saturated Santa Olalla vermiculite is investigated through adsorption/desorption of caesium and determination of the crystal structure of the HIMs by using X-ray diffraction profile modelling approach. The results show that the crystal structure of HIMs controls the mobility of caesium. Indeed, the amounts of poorly and highly exchangeable caesium are governed by the relative abundances of expandable and HI layers, respectively.

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BENTONITES AND K-BENTONITES: ISSUES IN IDENTIFYING AND INTERPRETING ANCIENT TEPHRAS

Huff, W. D.

Department of Geology, University of Cincinnati, Cincinnati, Ohio USA 45221
huffwd@ucmail.uc.edu

Pyroclastic material in the form of altered volcanic ash or tephra has been reported and described from one or more stratigraphic units from the Proterozoic to the Tertiary. This altered tephra, variously called bentonite or K-bentonite or tonstein depending on the degree of alteration and chemical composition, is often linked to large explosive volcanic eruptions that have occurred repeatedly in the past. K-bentonite and bentonite layers are the key components of a larger group of altered tephras that are useful for stratigraphic correlation and for interpreting the geodynamic evolution of our planet. Bentonite is a clay deposit most commonly generated from the alteration of volcanic tephra, consisting predominantly of smectite minerals, usually montmorillonite. The formation of bentonite (beds containing smectite-group clay minerals including montmorillonite) and fuller's earth (a type of clay mineral deposit that has high capacity to absorb water) may occur primarily by diagenesis, although some deposits may also form by hydrothermal processes. Bentonite beds usually form from altered volcanic ash, but other types of rock may also serve as sources. Bentonites generally form by diagenetic or hydrothermal alteration under the influence of fluids with high Mg content and that leach alkali elements. Smectite composition is partly controlled by parent rock chemistry. Studies have shown that K-bentonites often display variations in layer charge and mixed-layer clay ratios and that these correlate with physical properties and diagenetic history. Tephra is well known to travel great distances - even across continents - and can thus serve to link not only volcanic zones but also to bind stratigraphic provinces together internally, and with each other. While residence time in the atmosphere of the very finest of these particles can be substantial, the deposition of the bulk of volcanic ejecta can be considered instantaneous on geological timescales. Often these volcanic products can be identified by various chemical and non-chemical means and if the eruption date is known, the occurrence of tephra from a given eruption in stratigraphic sequences provides a powerful means of dating such deposits, or of refining available dating schemes. Furthermore, the occurrence of tephra from the same eruption preserved simultaneously in various types of depositional environments including glacial, terrestrial and marine holds the potential of linking the regional causes of tectonic and stratigraphic change. In practice, tephrochronology requires tephra deposits to be characterized (or fingerprinted) using physical properties evident in the field together with those obtained from laboratory analyses. Such analyses include mineralogical and petrographic examination or geochemical analysis of glass shards or phenocrysts using an electron microprobe or other analytical tools including laser-ablation-based mass spectrometry or the ion microprobe. Tephrochronology provides the greatest utility when a numerical age obtained for a tephra is transferrable from one site to another using stratigraphy and by comparing and matching, with a high degree of likelihood, inherent compositional features of the deposits. Used this way, tephrochronology is an age-equivalent dating method that provides an exceptionally precise volcanic-event stratigraphy.

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ABSORPTION AND DESORPTION OF CO_2 IN VERMICULITE AND FLUOROHECTORITE CLAYS AS STUDIED BY PHOTOEMISSION AND TEMPERATURE PROGRAMMED DESORPTION

K. W. B. Hunvik*, X. Yu, S. Raaen, J. O. Fossum

Physics Department, NTNU, 7491 Trondheim, Norway
*kristoffer.hunvik@ntnu.no

CO_2 capture and retention by synthetic or natural clays could be a cheap and environmentally friendly alternative to zeolites and MOFs (metal-organic frameworks). In fact, clays may represent the adsorbents of the highest storage capacity, and may provide new innovative technological advancements in carbon capture and sequestration technologies.

Vermiculite and Na-, Ni- and Li-fluorohectorite clays were dried in vacuum at different temperatures from 150 to 220 °C, and subsequently exposed to CO_2 at various pressures and exposure times. The sample surfaces were characterized by X-ray photoelectron spectroscopy (XPS), and desorption of CO_2 and H_2O was investigated by temperature programmed desorption spectroscopy (TPD). TPD is an ultra-high-vacuum technique that is uniquely sensitive to the detection of e.g. intercalated CO_2 and H_2O that desorbs from the sample specimens. For example, it was found in a vermiculite and a Ni-fluorohectorite sample that was partially dried and still contained some water, CO_2 desorbed at lower temperatures as compared to the remaining water. This phenomenon was investigated for different drying procedures and CO_2 exposures for various clay samples.

Interaction of CO_2 with clay surfaces that were doped by Na, Li and Ni was investigated by XPS and TPD. Previous studies of fluorohectorite clays have shown a significant dependence with respect to the cation for CO_2 intercalation properties [1]. These findings motivate the study of interaction between CO_2 and the relevant cations by surface analytical tools. The clay surfaces were cleaned by removing surface layers by the Scotch-tape method *in situ*. Alkali metals were deposited using SAES alkali metal dispensers and Ni from a thermally heated tungsten basket. Electronic properties with respect to CO_2 interactions, as obtained by photoelectron spectroscopy, were studied in order to disentangle the counterion mechanism from the influence of the clay surface.

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MEASURING AND MODELLING SUB- AND SUPERCRITICAL ADSORPTION OF CO_2 AND CH_4 ON CLAY MINERALS

Junyoung Hwang*, Lisa Joss, Ronny Pini

Department of Chemical Engineering, Imperial College London, London SW7 2AZ, UK
*j.hwang16@imperial.ac.uk

The injection of CO_2 into deep geological formations has attracted much attention as a technical solution towards reducing anthropogenic emissions of this greenhouse gas. Promising geological storage sites for CO_2 injection that meet the required storage capacity include deep saline aquifers and gas reservoirs where enhanced gas recovery processes may be implemented, such as coal seams or shale formations [1]. Clay minerals are ubiquitous in these targets and are major constituents of the cap rock seals above them. These minerals are characterised by the presence of micro- and mesopores, which results in a large surface area available for physical and chemical interactions with the surrounding fluids. Of particular interest to this study is the sorption behaviour of CO_2 and CH_4 on clay minerals that leads to the trapping of these gases in the porous structure at liquid-like densities. For the geological storage of CO_2, gas adsorption on clays can have several implications including (i) an increase of storage capacity in reservoirs having larger clay contents [2] (ii) an advance in storage safety by limiting gas diffusion through cap rock seals[3], and (iii) an enhancement of gas production from tight shale formations through an adsorption/desorption (CO_2/CH_4) process, as observed for deep coal seams [4]. Remarkably, the study of gas adsorption in clay minerals at high-pressures and temperatures is still at the early stage of investigation, despite its importance. The main reason for this is the intrinsic difficulty in performing the experiments and in describing the complex interactions between the gases and clays [2].

In this study, adsorption data of CO_2 and CH_4 on pure clay minerals - montmorillonite (STx-1) and illite-smectite mixture (ISMt-2) - have been measured using a Rubotherm magnetic suspension balance (Bochum, Germany) in the pressure range 0-25 MPa at varying temperatures 40-80 °C. Cryogenic low-pressure N_2 adsorption experiments have been conducted on the samples to determine the microscopic properties, such as their pore size distributions, surface areas, and pore structure. The adsorption data on clay minerals are compared to that of reference materials (e.g., mesoporous silica and zeolites) and of selected shale samples to quantitatively determine the contribution of clay components in CO_2/CH_4 adsorption. As such, this study contributes to estimating the CO_2 storage/retention capability of various rock formations under subsurface conditions. To support the experimental observations, the measured adsorption isotherms have been described using the lattice density functional theory (LDFT), which is a statistical thermodynamic model that describes the adsorption phenomena within a specified pore geometry based on a generalisation of the Ono-Kondo equations [5]. This modelling approach requires information on the structure of clays as input parameters; therefore, it represents a significant departure from conventional empirical approaches that use Langmuir- or BET-type of models. We present a comprehensive LDFT model that can describe both sub- and supercritical adsorption with a set of generalised equations and pre-determined parameters. The model is compared to experimental data for both low-pressure N_2 adsorption and high-pressure CO_2/CH_4 adsorption, and results are compared to predictions from other theoretical models (e.g., Kelvin equation) used to describe fluid densification in nanopores.

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EXFOLIATION OF RHODIUM-DOPED LAYERED COMPOUNDS AND THEIR PHOTOCATALYTIC ACTIVITY

Shintaro Ida (1,2)*, Hidehisa Hagiwara (1,2), Tatsumi Ishihara (1,2)

(1) Department of Applied Chemistry, Faculty of Engineering, Kyushu University, Fukuoka 819-0395, Japan, (2) International Institute for Carbon Neutral Energy Research (I2CNER), Kyushu University, Fukuoka 819-0395, Japan

Hydrogen production from water using solar energy is the ultimate goal in renewable energy research. Various oxides and oxynitrides have been reported as potential photocatalysts capable of decomposing water. However, there are several issues preventing their practical application, such as low quantum efficiency in the visible light region. One factor that causes a decrease in the photocatalytic activity is a recombination reaction between the electron and hole. When a photocatalyst is illuminated by light with an energy greater than the bandgap energy, a photo-excited electron and hole are generated within the powder. In order for these carriers generated within the powder to react with water, they must travel a long distance to the surface. During this trip, they may recombine or get trapped at defect sites. A two-dimensional structure may satisfy the requirement described above. Specifically, a two-dimensional crystal (nanosheet) prepared by exfoliation of a layered compound is a single crystal with a homogeneous ultrathin thickness, and has a lateral dimension of several hundred nanometers to several micrometers. Therefore, the travel distance of the photo-excited carriers is short, and many photons can be absorbed by the nanosheet in a remarkably short time under low photon flux density due to its large section area. Recently, there have been many reports on p-type and n-type semiconducting nanosheets and nanosheet photocatalysts with visible light response, and studies on nanosheet photocatalysts have been becoming more frequent. The characteristic performance of nanosheet photocatalysts has been reported. For instance, it is well known that a photocatalyst without co-catalyst loading has poor photocatalytic activity for water splitting. However, a particular type of oxide nanosheet shows a high photocatalytic activity for hydrogen evolution from water without co-catalyst loading. Graphene-based materials, layered double hydroxide nanosheet-based materials, {Gunjakar, 2011 #109} and MoS_2 nanosheet-based materials are also candidate photocatalysts, and new insights on photocatalytic reactions have been reported. Thus, the two-dimensional structure is expected to contribute to the development of photocatalysts for water splitting in the future. In this presentation, a short overview of our recent research activities related to oxide nanosheets [1], nanosheet p-n junction photocatalysts, and attractive approaches for understanding the reaction mechanism [2]. For instance, Rh-doped oxide nanosheets exhibit high catalytic activity for H_2 evolution. In this system, the Rh dopant in the crystal lattice can act as a photocatalytic reaction site. The photocatalytic H_2 production rate of the Rh-doped titania nanosheets was approximately 10 times larger than that of undoped nanosheet. Rh-dopants in the lattice of nanosheet was directly observed by HAADF-STEM. These results indicate that Rh is doped with a single dispersion state and is substituted onto a Ti^{4+} site in the lattice of the nanosheet.

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XRD, SEM, DTA/TGA AND FTIR: POTENT TOOLS IN THE CHARACTERIZATION AND IDENTIFICATION OF CLAY MINERALS SOURCED FROM THE LOWER BENUE TROUGH, NIGERIA

S.O. Idakwo (1)*, A.T. Bolarinwa (2), D.L. Bish (3)

(1) Department of Earth Sciences, Kogi State University, P.M.B. 1008, Anyigba, Kogi State, Nigeria, (2) Department of Geology, University of Ibadan, Ibadan, Nigeria, (3) Department of Geological Sciences, Indiana University, Bloomington, Indiana, U.S.A.

A combination of methods (X-ray powder diffraction (XRD), differential thermal analysis/thermogravimetric analysis (DTA/TGA), scanning electron microscope (SEM), and Fourier transform infrared spectroscopy (FTIR)) was used to characterize the clay mineralogy of the Lower Benue Trough of Nigeria to interpret paleoenvironmental conditions, the paleoclimatic significance of the trough, and effects of weathering on the minerals as factors that favour its deposition/accumulation within the trough which host other important industrial minerals like coal, barite, limestone etc. Bulk-sample random-powder XRD data and data for clay fractions deposited onto zero-background quartz plates were measured. The samples contained kaolinite, vermiculite, and traces of smectite, and the non-clay phases included quartz, microcline, and muscovite. All samples were unaffected after glycolation, confirming the absence of significant smectite. Muscovite was characterized by the nature of its 10 Å basal peak, which was very sharp with a width of <0.10° 2θ. DTA/TGA results support the presence of kaolinite, and the characteristic kaolinite O-H, Al-OH, Si-OH and Si-O-Al FTIR bands also confirmed its presence. Vermicular and book-like morphologies were observed under the SEM, typical of kaolinitic clay from in situ alteration. High kaolinite abundance in these sediments is consistent with intense weathering of Al-rich source rocks under wet/tropical climatic conditions with fresh and/or brackish water conditions in a continental setting. The variety of observed morphologies suggests that the deposits suffered more of chemical weathering.

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STRUCTURE AND APPLICATION OF A NATURAL LAYERED SILICATE MAGADIITE

Yusuke Ide (1)*, Hiroyuki Kono (2), Satoshi Tominaka (1)

(1) International Center for Materials Nanoarchitectonics, National Institute for Materials Science (NIMS), Tsukuba, Ibaraki 305-0044, Japan, (2) Department of Earth Sciences, Waseda University, Shinjuku-ku, Tokyo 165-8050, Japan
*IDE.Yusuke@nims.go.jp

Layered silicates nowadays find a range of applications in ion-exchange, adsorption, catalysis, fabrication of polymer nanocomposites and precursors of zeolites. Magadiite, found in Lake Magadi, Kenya[1], is one of the most widely studied layered silicates owing to the rich intercalation chemistry and large-scale synthesis by a simple hydrothermal reaction. A full understanding of potential of any layered silicates for the applications requires that its structure be known. However, the structure of magadiite has never been solved. Herein, we uncover the structure of magadiite by X-ray pair distribution function (PDF) analysis. We moreover show a critical application of magadiite.

Partial oxidation of organic compounds by photocatalysis is green fine chemical synthesis alternative to conventional processes that often require the use of hazardous and expensive reagents and materials under rather strict conditions. Due to its abundance, non-toxicity and high stabilities, TiO_2 is a promising photocatalyst for the purpose. However, organic substrates tend to be overoxidized to undesired by-products such as CO_2 on TiO_2 due to the presence of highly oxidizing species. We have recently reported that when the oxidation of benzene to phenol, which is one of the most desired partial oxidations in chemical industry, is conducted using TiO_2 in the presence of a layered silicate that precisely recognize phenol, only phenol can be recovered effectively[2]. This resulted from that formed phenol was rapidly, selectively and efficiently captured by the adsorbent to prevent the overoxidation, after which the captured phenol could be easily eluted by simple washing[2,3]. In this presentation, we successfully expand this approach to another crucial and as-yet challenging partial oxidation, the oxidation of toluene to benzoic acid. We discuss how the structure of magadiite affects benzoic acid separation by using another widely used layered silicate, octosilicate, as reference.

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INTERCALATION OF DOUBLE CHAIN SURFACTANTS INTO A BENTONITE WITH CONTROLLED AMOUNT

Kamonnart (JAA) Imwiset (1)*, Makoto Ogawa (2)

(1) School of Molecular Science and Engineering, (2) School of Energy Science and Engineering, Vidyasirimedhi Institute of Science and Technology, Rayong 21210, Thailand

The interlayer cations of smectites are replaced with such cationic surfactant as quaternary ammonium to obtain “organophilic clays” [1-2]. Application of organophilic clays includes adsorbents for organic contaminants in environments, rheology controlling agents in cosmetics and paints as well as plastic additives. The properties of the organophilic clays are largely dependent on the surfactants and clays, so that the various cationic surfactants and clays have been complexed to obtain organophilic clays with desired properties [1-4]. In this study, the intercalation of double chain surfactants, dioctadecyldimethylammonium ion (abbreviated as 2C18, which has been used extensively in the organic modification of smectites) and dioleyldimethylammonium ion (abbreviated as DODA, which has never been reported for the intercalation), into a bentonite (cation exchange capacity is 69 meq/100g) was examined. In addition to the application of new surfactant (DODA), the effects of the amount of surfactant on the properties of the resulting organophilic-clays is examined.

The ion exchange of the bentonite with DODA or 2C18 was conducted by the conventional ion exchange method using aqueous media and the products were characterized by XRD, IR and TGA. The initial amount of surfantants varied from 40, 80, 100, 200 and 400 meq/100g of bentonite in order to control the adsorbed amount of the surfactant.

The results of the XRD and TGA indicated that there is a linear relationship between the d-spacing and the amount of the intercalated surfactant for both surfactant systems. In addition, DODA and 2C18 gave different d-spacing even when the adsorbed amounts were same. These observations suggested that both the surfactant structure and the adsorbed amount affected the structure of the resulting “organophilic clays”.

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CHEMICAL COMPOSITION OF CHLORITE COEXISTING WITH PINKISH COLORED EPIDOTE IN A GEOTHERMAL FIELD, JAPAN

Atsuyuki Inoue (1)*, Minoru Utada (2)†

(1) Chiba University, Chiba, Japan, (2) Futo, Ito, Japan †deceased
*atinoue@earth.s.chiba-u.ac.jp

The Fe content and $Fe^{3+}/\Sigma Fe$ ratio in chlorite are a function of T, P, fO_2, fS_2, fCO_2, and bulk rock composition. Thus we can infer such physico-chemical conditions of chlorite formation from the compositional data. We have developed an empirical geothermometer to estimate the formation temperatures taking into account the $Fe^{3+}/\Sigma Fe$ ratios [1]. More recently, Vidal et al. [2] refined thermodynamic properties of ferri-sudoite and utilized them to estimate fO_2 conditions for the formation of chlorites coexisted with magnetite. However, chemical variations of chlorites associated with hematite, which formed under more oxidative conditions, are still poorly understood. Here we will describe occurrence and chemical composition of chlorites formed under oxidative conditions, interestingly associated with pinkish colored epidotes. The samples studied were found in cores from a geothermal exploration well NB-1, Noboribetsu, Hokkaido, Japan. Pinkish epidotes occurred mainly as vein- and druse-fillings in volcaniclastic rocks of the Miocene Osarugawa Formation in association with brownish chlorites, K-feldspar, illite, and quartz, in addition to minor hematite, titanite, and/or apatite in the rock matrix. The mineral assemblages were produced by local K-alteration that overprinted early-formed regional propyritization associated with ordinary greenish epidotes and chlorites. From SEM-EDX analyses, the piemontite (Mn^{3+}) components of pinkish epidote solid solutions were generally low (<0.024), while the pistacite (Fe^{3+}) components were <0.28. The Fe^{3+} contents in greenish epidotes from propylites ranged 0.20-0.36. Associated brownish colored chlorites were characterized by low total Fe ($0.09<Fe/(Fe+Mg+Mn)<0.30$) and relatively high Fe^{3+} contents ($Fe^{3+}/\Sigma Fe = 0.25$), which were quite distinct from those of greenish chlorites in surrounding propylitic rocks:$0.36<Fe/(Fe+Mg+Mn)<0.56$ and $Fe^{3+}/\Sigma Fe = 0.05\text{-}0.13$. Using semi-empirical chlorite geothermometers, the formation temperatures were estimated to be 230-300 °C, lower than those of greenish chlorites (250-380 °C). The above $Fe^{3+}/\Sigma Fe$ ratios were estimated assuming that the formation temperatures calculated by two geothermometers of ours [1] and Bourdelle's [3] are equal to each other. Finally, taking into account the above mineral assemblage: K-feldspar+illite+chlorite+epidote+hematite, we estimated the physico-chemical conditions of brownish chlorites coexisted with pinkish epidotes: $-6.5<\log a\ H_2(aq)<-5.5$ (or$-32.5<\log a\ O_2(aq)<-30.5$) and $6.5<pH<7.5$at given 250 °C, P_{sat}. The estimated pH values are dependent on the assumed ionic strength in fluids; the more the ion strength increases, the more pH decreases. The above conditions are similar to those estimated for many adularia-sericite type epithermal ore deposits [4], though the Fe, S, and Cl contents in fluids may be lower than those in epithermal ore-forming fluids.

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HIGH RESOLUTION TRANSMISSION ELECTRON MICROSCOPY (HRTEM) STUDY OF STABILITY OF FE-RICH SERPENTINE GROUP MINERAL AND CHLORITE

Sayako Inoue (1)†*, Stephen Hillier (2,3), Toshihiro Kogure (1)

(1) Department of Earth and Planetary Sciences, Graduate School of Sciences, The University of Tokyo, Tokyo, Japan,
(2) The James Hutton Institute, Aberdeen, Scotland, UK (3) Department of Soil and Environment, Swedish University of Agricultural Sciences, Box 7014, Uppsala SE-750 07, Sweden, † Present address: Department of Geosciences, Virginia Tech, Blacksburg, USA
*inouesayako@gmail.com

Fe- and Al- rich serpentine group minerals, berthierine and odinite, are strongly related to the formation mechanism of chlorite and often considered as a low temperature precursor of Fe-rich chlorite. The formation pathway of chlorite is known to be strongly linked to the temperature and chemical composition namely Fe/(Fe+Mg) value. It is generally accepted that 7 Å minerals converts to chlorite via a 7 Å - 14 Å interstratified mineral with increasing temperatures in iron rich environment. The conversion to 14 Å chlorite is believed to be completed at temperature in a range of 100 to 200 ºC [1]. However, a range of temperature where each stage of chlorite formation occurs and how Fe/(Fe+Mg) values influence to the formation processes are still open to discussion. In Inoué and Kogure (2016) [2], the crystallochemical characteristics of Fe-rich chlorite from hydrothermal systems were investigated by high resolution transmission electron microscopy (HRTEM). These chlorites have Fe/(Fe+Mg) values in a range of 0.5 to 0.99 and were formed at temperatures higher than 200 ºC. Our results suggested that the 7 Å minerals can occur at temperature higher than 200 ºC when Fe/(Fe+Mg)>0.8.

In the present study, we observed the crystal structure of pore-lining Fe-chlorite from diagenetic systems by HRTEM. The present samples were formed at temperature in a range of 100 to 220 ºC, and have a range of Fe/(Fe+Mg) values between 0.7 and 0.8 [3]. The samples contain small amount of interstratified 7 Å layers but they are mostly consisting of 14 Å layers. The results imply that the conversion from 7 Å mineral to 14 Å mineral started at temperatures below 100 when Fe/(Fe+Mg)<0.8. Our study strongly suggested that the stability of Fe- and Al-rich serpentine group mineral is not only linked to the temperature condition but also Fe/(Fe+Mg) value.

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PHOTOCATALYTIC BEHAVIOR OF ZINC OXIDE INCORPORATED IN NIAL-LAYERED DOUBLE HYDROXIDE

Sonchai Intachai (1), Nithima Khaorapapong (1)*, Makoto Ogawa (2)

(1) Materials Chemistry Research Center, Department of Chemistry and Center of Excellence for Innovation in Chemistry, Faculty of Science, Khon Kaen University, Khon Kaen 40002, Thailand, (2) School of Energy Science and Engineering, Vidyasirimedhi Institute of Science and Technology, Rayong 21210, Thailand

Metal oxides including titanium dioxide (TiO_2), zinc oxide (ZnO) and copper oxide (CuO) are receiving much consideration due to their size- and shape-dependent properties. Among all of them, ZnO is an interesting material with wide band gap (3.37 eV) and large exciton biding energy (6 meV) for such applications as sensor, solar cell, photocatalyst, optical nanodevice and so on. Hybridization of ZnO with layered inorganic solids offers possibility to control particle size and promote unique optical properties. *Herein*, we report the preparation of ZnO in Ni-Al-layered double hydroxide (NiAl-LDH) without using any anion base species and their photocatalytic activity. The products were carried out by the reaction between an aqueous solutions of $ZnCl_2$ and CO_3^{2-}-NiAl-LDH at the ratio of Zn^{2+} to CO_3^{2-} = 1, 2 and 4 times of the anion exchange capacity (300 meq/100 g of the LDH) under hydrothermal treatment at 150 °C for 24 h and then the resulting powders were further calcined at 250 °C for 6 h. The final products were donated as $(ZnO)_x$@NiAl-LDHs, where x = 1, 2 and 4. The XRD patterns of the products revealed the expansion of the interlayer space of *ca*. 0.29-0.31 nm. The *(100)*, *(002)*, *(101)* and *(110)* reflections due to hexagonal phase of ZnO at 2θ = 32, 35, 36 and 57 degrees were also observed in the XRD patterns of the products. This result indicated the formation of ZnO in the interlayer space and the external surface of NiAl-LDHs. The band gap energy of the products (3.67 eV for $(ZnO)_1$@NiAl-LDH, 3.62 eV $(ZnO)_2$@NiAl-LDH and 3.57 eV for $(ZnO)_4$@NiAl-LDH) was wider than that of bulk ZnO (2.96 eV), interpreting to the formation of ZnO nanoparticles in the hybrids. The photoluminescence bands were observed at 548 nm for bulk ZnO, at 440 nm for $(ZnO)_4$@NiAl-LDH, at 437 nm for $(ZnO)_2$@NiAl-LDH and at 435 nm for $(ZnO)_1$@NiAl-LDH. The emission intensities of the products decreased with increasing the amount of Zn^{2+} cations in the series of bulk ZnO (130) < $(ZnO)_4$@NiAl-LDH (297) < $(ZnO)_2$@NiAl-LDH (347) < $(ZnO)_1$@NiAl-LDH (400). The blue-shift of the emission band and the increase of the luminescence intensity of the products compared with those of bulk ZnO might be due to the restricted environment of the LDH that prevented the aggregation of the intercalated particles. The photodegradation of methyl orange solution (100 ppm, 300 mL) was determined by following procedure; 100 mg of photocatalysts was dispersed in the methyl orange solution in a quartz bottle and the suspension was stirred in dark or under UV irradiation for 9 h. The amounts of methyl orange photodegraded by $(ZnO)_4$@NiAl-LDH,$(ZnO)_2$@NiAl-LDH,$(ZnO)_1$@NiAl-LDHand bulk ZnO were 100, 87, 72 and 47%, respectively. The superior photocatalytic perfromance of $(ZnO)_4$@NiAl-LDH was arisen from the narrowest band gap energy compared with those of $(ZnO)_2$@NiAl-LDH and $(ZnO)_1$@NiAl-LDH, and the migration of the electron and hole between the energy levels of ZnO and the LDH.

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PREPARATION OF CADMIUM SELENIDE IN THE INTERLAYER SPACE OF MAGADIITE

Sonchai Intachai (1), Poonsuk Poosimma (1), Areeporn Ontam (1,2), Wen-An Chiou (3), Nithima Khaorapapong (1)*, Makoto Ogawa (4)

(1) Materials Chemistry Research Center, Department of Chemistry and Center of Excellence for Innovation in Chemistry, Faculty of Science, Khon Kaen University, Khon Kaen 40002, Thailand, (2) Department of Applied Chemistry, Faculty of Sciences and Liberal Arts, Rajamangala University of Technology Isan, Nakhon Ratchasima 30000, Thailand, (3) AIM Laboratory, Maryland NanoCenter, University of Maryland, College Park, MD 20742-2831, USA, (4) School of Energy Science and Engineering, Vidyasirimedhi Institute of Science and Technology, Rayong 21210, Thailand

Intercalation is one of the methods to prepare hybrid materials of two dimensional nanostructure and a variety of guest species [1-2]. Magadiite with ideal formula $Na_2Si_{14}O_{29}\cdot nH_2O$ is an examples of such layered silicates, which is capable to form intercalation compounds [3-4]. Here, we synthesized the hybrids of cadmium selenide (CdSe) and organically modified magaditte in order to control particle size and optimize optical properties of the intercalated semiconductor. The intercalation of CdSe into the interlayer space of cetyltrimethylammonium modified magaditte was conducted by ion-exchange reaction between cetyltrimethylammonium cation and magaditte, and then subsequently reacted with the aqueous solutions of cadmium sulfate and sodium selenosulfite (Na_2SeSO_3) for one day. The products were characterized by XRD, TG-DTA, HRTEM, FT-IR, as well as UV-visible and photoluminescence spectroscopies. The appearance of CdSe nanoparticles with diameter range of 2-5 nm in between the silicate layers was confirmed by TEM images. The products exhibited photoluminescence (at 534-547 nm) arising from the intercalated CdSe [5-7]. The emission intensity varied in accordance with the amount of CdSe incorporated in the products and the size of CdSe. The luminescence intensities were increased by storage for longer time, indicating to the change in the size and size distribution of the intercalated CdSe.

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PREPARATION OF LAYERED DOUBLE HYDROXIDE INTERCALATION COMPOUNDS BY THE HOMOGENEOUS PRECIPITATIONOF HEXAMETHYLENETETRAMINE

Soontaree (Grace) Intasa-Ard (1)*, Makoto Ogawa (2)

(1) School of Molecular Science and Engineering, (2) School of Energy Science and Engineering, Vidyasirimedhi Institute of Science and Technology, 555, Payupnai, Wangchan, Rayong 21210, Thailand

Layered double hydroxides (LDHs) have received great attention in various applications due to its versatile physiochemical properties and facile preparation. Homogeneous precipitation using urea hydrolysis has been used to prepare well-defined LDHs [1-6]. Urea hydrolysis isideal for the carbonate type LDH because the decomposition of urea produces ammonia (pHraise) and carbonate. On the other hand, this is a drawback for the preparation of LDHs with various interlayer anions.

In the present study, the preparation of LDH-intercalation compounds (interlayer anion is not carbonate anion) by homogeneous precipitation was examined. In order to incorporated various anions in the interlayer space, hexamethylenetetramine (HMT) was used in the present study. HMT has been used as a precipitating agent of LDHs [7]. The hydrolysis of HMT produce ammonia and formaldehyde, which are not expected to be incorporated into the resulting LDHs.

In the preliminary experiment using nickel nitrate and aluminum nitrate as the starting materials and the hydrothermal treatment at 150 °C for 24 h, the formaldehyde was oxidized to form carbonate anions, resulting the precipitation of the carbonate form LDHs. In order to suppress the oxidation of formaldehyde during LDH preparation, the reaction was conducted in the presence of methanol.

The XRD pattern of the samples prepared from nickel nitrate and aluminum nitrate showed characteristic diffraction peaks of NiAl-LDH. The basal spacings were 0.85 and 0.81 nm for the samples prepared by the solution with methanol and without methanol, respectively. The observed basal spacings were ascribed to the presence of carbonate along with nitrate anion in the interlayer space (basal spacing of carbonate-LDHs is 0.76 nm). CHNS elemental analysis showed higher amount of nitrogen for the product prepared in the presence of methanol (corresponding to the NO_3 amounts of 21 and 18 wt.% for the sample from methanol solution and that from aqueous solution, respectively) indicating the important role of methanol as stabilizing agent of formaldehyde, by suppressing its oxidation to formic acid and to carbonate, to obtain the nitrate anion intercalated LDHs.

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HYDROTHERMAL CLAY MINERALS RECOGNIZED BENEATH AND AROUND SEAFLOOR SULFIDE MOUNDS IN THE OKINAWA TROUGH

Jun-Ichiro Ishibashi*, Saki Tsutsumi (1), Youko Miyoshi (1,2)

(1) Graduate School of Science, Kyushu University, Fukuoka 819-0395, Japan, (2) Research Institute for Geo-Resources and Environment, National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba 305-8576, Japan

Seafloor massive sulfides recognized in hydrothermal fields in arc-backarc settings in the western Pacific have been considered a modern analogue for ancient volcanogenic massive sulfide (VMS) deposits. A series of scientific drilling campaigns were conducted at Iheya North Knoll in mid-Okinawa Trough, where active venting of high temperature fluid (T>300 ºC) from sulphide mounds had been located at some sites. In September 2010, five sites were drilled at Original Site (27°47.5' N, 126°53.8' E; water depth = 1000 m) during IODP (Integrated Ocean Drilling Program) Expedition 331 [1]. Two drilling campaigns CK14-04 in July 2014 and CK16-01 in March 2016 followed, which targeted at another active field named Aki Site (27°46.1' N, 126°54.1' E; water depth = 1070 m). Although massive body of sulphide deposit was not recognized, most of sediment cores obtained from beneath and around actively forming hydrothermal mounds were characterized by intense and diverse hydrothermal alteration [1-4]. We conducted mineralogical and geochemical studies of the hydrothermal clay minerals to clarify their occurrence and characteristics.

Occurrence of hydrothermal clay minerals at the Original Site was characterized by zonal distribution of distinctive clay mineral assemblage; Zone 1 consists mainly of montmorillonite and sometimes of kaolinite, Zone 2 of chlorite and chlorite-smectite mixed-layer mineral, and Zone 3 represented by co-occurrence of illite (sericite) and chlorite, from shallow to deep [2]. Similar sequence of clay mineral assemblages was recognized also at the Aki Site. Occurrence of kaolin minerals was minor but notable in both sites, as previously reported for other active hydrothermal fields in the Okinawa Trough [5]. Especially, at the peripheral locality of the Aki Site, focused formation of kaolin minerals was recognized in rather shallow depth (from 8.5 to 11.0 meters below the seafloor), where dominant kaolin minerals changed along the depth from halloysite, kaolinite to dickite. The zonal distribution of clay minerals may reflect hydrothermal structure developed in piles of volcanoclastic sediment, and the drastic change of clay mineral assemblage along the depth could be attributed to distinctive fluid-sediment interactions.

We recognize occurrence and characteristics of hydrothermal clay minerals in Iheya North Knoll show strong similarity to those had been reported for Kuroko-type VMS deposits in the northeast Japan. For example, significantly Mg-rich composition of the chlorite is commonly notable in spite of Mg-poor composition of the surrounding felsic volcanic materials. Comparative studies of hydrothermal clay minerals would provide keys to understand common hydrothermal interactions among modern and ancient systems which could play an important role in formation of VMS deposits.

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INTERFERENCE OF PEDOGENETIC PROCESSES IN THE VALIDITY OF KAOLINITE CRYSTALLINITY INDEXES

Déboraayumi Ishida (1), Antonio Carlos Vieira Coelho (2), Adolphojosé Melfi (1), Yves Lucas (4), Céliaregina Montes (3)*

(1) Instituto de Energia e Ambiente, Universidade de São Paulo, São Paulo, Brazil, USP(2) Escola Politécnica, São Paulo, USP(3) Centro de Energia Nuclear na Agricultura, Piracicaba, São Paulo, USP(4)Laboratoire PROTEE, UniversitéduSud Toulon, France
Núcleo de Pesquisa em Geoquímica e Geofísica da Litosfera (NUPEGEL)
*crmlauar@usp.br

The studied soil catena, that represents a Ferralsol-Podzol soil system, is located at 26 km from São Gabriel da Cachoeira city, Amazonas state, Brazil, at 0°6′21″S and 66°54′22″W. It is developed from crystalline rocks from the São Gabriel da Cachoeira granitic body [1]. The samples were collected in four profiles classified as Podzol at the upper part (P1 profile), Ferralsols at the middle part (P2 and P3 profiles) and Gleysol at lower part (P4 profile) of the catena [2,3]. The results presented in this work were tooken from P1 and P3 profiles. The kaolinites may present different degrees of structural disorder, depending of their genetic conditions. The aim of the present study was to obtain crystallographic characteristics of kaolinites related with different pedogenetic forming process using structural order-disorder degrees estimated by X-ray diffraction. The structural order-disorder degrees were evaluated by Hinckley (IH) [4], Aparicio-Galán-Ferrell (IAGF) [5], Liètard (R2) [6] and Plançon-Zacharie (IPZ) [7] kaolinite crystallinity indexes. Ideally, the indexes should be able to separate populations of kaolinite, which have different structural order. The IH, IAGF and R2 indexes not produced consistent results in the P1 profile, probably due to the more aggressive Podzol genetic conditions (acidity and temporary hydromorphy [3]). The soil from P3 profile (Ferralsol), less influenced by the acidity of the solutions, presented consistent results for all indexes. The Plançon-Zacharie index, probably due to the greater number of crystallographic parameters used to determine structural order-disorder of kaolinite, presented results that were considered consistent in both profiles. The results obtained suggest that the pedogenetic processes involved in the formation of Podzols at the expense of Ferralsols may limit the application of the structural order-disorder evaluation methods used in this study.

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BIOELECTROCATALYSTS WITH IMPROVING THE DIRECT ELECTRON TRANSFER AND STABILITY BY IMMOBILIZATION OF ENZYME ONTO CARBON-COATED MESOPOROUS SILICA MEMBRANE

Tetsuji Itoh (1,2)*, Akira Yamaguchi (3), Yasuto Hoshikawa (4), Tatsuo Tsunoda (1), Taka-Aki Hanaoka (1), Takashi Kyotani (4), Galen D. Stucky (2)

(1) National Institute of Advanced Industrial Science & Technology (AIST), Nigatake 4-2-1, Miyagino, Sendai, Japan, (2) Department of Chemistry & Biochemistry, University of California, Santa Barbara, CA, USA, (3) Department of Chemistry, College of Science, Ibaraki University 2-1-1 Bunkyo, Mito, Ibaraki, Japan, (4) Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, 2-1-1 Katahira, Aoba, Sendai, Japan
*T-itoh@ni.aist.go.jp

Proteins/enzymes have been industrially applied as biocatalysts in production of functional chemicals, biosensors and biofuel cells in environmental diagnosis, etc. Especially, bioelectrocatalysts using redox enzymes are expected in a high-performance biosensor and a biofuel cell. Electrochemical biosensors using bioelectrocatalysts enable direct, reliable and reproducible measurements. In particular, amperometric biosensors with an immobilized enzyme electrode can offer high sensitivity, high selectivity, and a short response time without requiring any substantial or complicated instrumentation. Also, biofuel cells are energy conversion systems, which utilize enzymes as bioelectrocatalysts and can operate under mild conditions. All compounds to be utilized by living things such as sugars, alcohols, amines, organic acids and hydrogen and also, in principle, other variety of large molecular-weight biomasses are possible substances for biofuel cells. There are varieties of redox enzymes that catalyze the oxidation of these substances in nature. Those reactions are classified into two types: one is direct electron transfer type, and the other is mediated electron transfer type. The mediated electron transfer type system has also several disadvantages. One of the disadvantages is that the system has high risk of mediator-leaking (or desorption) from electrodes, because the mediator-leaking causes serious crossover reactions: mediators desorbed from anodes will react at cathodes or vice versa, leading to a decrease in the cell power by merely converting the redox reaction energy into heat. In order to avoid the risky crossover, separators may be incorporated into sensor or biofuel cells, which would lose simplicity in structure of sensors or biofuel cells. Additionally, biosensors or biofuel cell using bioelectrocatalysis have a problem that seriously affects the its performance; the immobilization procedure causes a substantial decrease in the enzyme activity, the enzyme itself has poor stability under the reaction and against environmental factors such as temperature, medium and pH, etc. Thus, we require developing new techniques of bioelectrocatalysis with both direct electron transfer ability and high stability. Among recent advances in nanostructured materials, mesoporous materials have attracted significant interest because they have a potential application for enzyme immobilization, in which the mesoporous materials can increase the stability of enzymes. We had reported that about several kinds of enzymes their encapsulation in mesoporous silica enhances their stability [1,2]. Also, we tried the synthesis of nanoporoussilicas in anodic alumina pores, and reported the resultant composite membranes have high potential as artificial membrane supports, owing to a large number of interconnected pores [3] and successfully achieved high sensitive prototype sensor with good stability by encapsulation of enzyme into pores of those membrane [2,4]. If mesoporous silicas can be coated with an extremely thin carbon layer such as a single graphene sheet, the resulting mesoporous silicas would acquire not only adsorption ability for stability but also electrical conductivity to the electron transfer occurs directly between enzymes and electrodes, with their ordered mesopore structures almost intact. We apply the carbon-coating technique to uniformly deposit a thin carbon layer (only 1-2 graphene sheets) on the pore walls in a large (40 mm φ) mesoporous silica membrane (F127-MST) by the chemical vapor deposition (CVD) using acetylene. We then use the resulting carbon-coated mesoporous silica membrane (C/F127-MST) directly as an electrode and evaluate its performance in terms of electrical conductivity inside the continuous mesopore network. Then, we load an enzyme as bilirubin oxidase (BOD) into the uniform mesopores in C/ F127-MST to confirm its electron transfer ability to BOD. At the same time, we enhance the storage stability of BOD (stable 20 days) and also can control enzymatic reaction by electric potential.

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THE ROLE OF NANOSIZED MINERAL PARTICLES AND THEIR SURFACE PROPERTIES ON FORMATION OF MICROAGGREGATES IN SOILS FORMED IN DIFFERENT PEDOENVIRONMENTS

Maja Ivanić (1)*, Goran Durn (2), Ivan Sondi (2), Srečo D. Škapin (3)

(1) Ruđer Bošković Institute, Zagreb, Croatia, (2) Faculty of Mining, Geology and Petroleum Engineering, Zagreb, Croatia, (3) Jožef Stefan Institute, Ljubljana, Slovenia

The submicron-sized inorganic particles, omnipresent solids in natural environments, comprise the majority of reactive surfaces, responsible for transport, sequestration and removal of contaminants [1,2]. The surface properties of these mineral particles in natural environments are under significant influence of organic and inorganic coatings. These associations mostly result in formation of organo-mineral aggregates, thus modifying the surface reactivity, stability, behaviour and availability of mineral surfaces [3].

The presented research investigates the role of nano-sized mineral particles and their surface properties on the formation of microaggregates in soils formed in different pedoenvironments. For this investigation, Cambisols from the Mljet Island and the Kuti Lake, and a Cretaceous paleosol from Istria, all developed on hard limestones, were sampled and analysed in detail. Cambisols were formed in an oxidative pedogenic environment and contain both goethite and haematite while the paleosol was formed in a reductive pedogenic environment and contains pyrite. The main mineral phases comprising the clay fraction of Cambisols are kaolinite and illitic material, while in the paleosol clay fraction illitic material and illite/smectite mixed-layer minerals prevail.

This study is based on a detailed mineral characterization of the submicron- and the nano-sized mineral fractions of these soil samples, investigation of their surface properties and complex interactions with organic matter and iron mineral phases. Soil samples were treated with sodium hypochlorite to remove the organic matter and the submicron-sized fractions were collected by gravitational settling and the size range was confirmed by dynamic light scattering. Samples were mineralogically (XRD) and morphologically (FE-SEM) characterized, their physico-chemical properties (specific surface area, SSA and cation exchange capacity, CEC) determined. As such, this study contributes to a better understanding of the process governing the formation of nanostructured soil microaggregates worldwide.

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STRUCTURAL ANALYSES OF AQUEOUS SUSPENTIONS OF CLAY MINERALS BY SMALL ANGLE NEUTRON SCATTERING COUPLING WITH RHEOLOGICAL MEASUREMENT (RHEO-SANS)

Hiroki Iwase (1), Yoshiaki Fukushima (1)*, Hiroshi Sakuma (2), Kenji Tamura (2)

(1) Neutron Sci. & Tech. Center, Comprehensive Res. Org. for Sci.& Soc.(CROSS), Tokai, Japan, (2) Functional Clay Materials Group, Res. Center for Functional Materials, National Institute for Materials Science, Tsukuba, Japan

A “clay” was widely used porcelain production since ancient time. The condition of a dispersion of clay minerals are one of the key technology in their processing. Dispersions of silicate layers of clay minerals in liquid matrix have been interested in colloid science due to their nanometre size with anisotropic shape and surface charges. Light, X-ray and/or neutron small-angle scattering technique are accessible in length scale of several nm to 1Mm that is correlated with clay colloid systems. Although the neutrons have a fateful flaw in their high-cost equipment and low beam flux, they are highly penetrating in materials which is attractive to install complex sample environments such as rheological equipment. In addition, neutron scattering offer an advantage in studying multicomponent system using labelling and contrast matching by isotope substitution technique. As the small angle neutron scattering (SANS) coupling with rheological measurements (Rheo-SANS) is one of the distinguishing methods for utilizing the neutron scattering, the Rheo-SANS has been applied for hydrogels, polymer melts, emulsions, micelles and polymer/nanoclays [1,2].

Although clay mineral aqueous suspensions was studied [3,4], they focused on relatively low concentration and viscosity thinning process during the increasing process of sheer stress. The viscosity thinning and an apparent viscosity were discussed in terms of the shape and the size of silicate layers and bounded water. Another important point of surface charge could be studied by structure recovery process during decreasing sheer rate and following aging periods.

We introduced a rheometer (Anton Paar MCR302) at the Small and Wide Angle Neutron Scattering Instrument (TAIKAN); BL15 [5], installed at Materials and Life Science Experimental Facility (MLF) in Japan Proton Accelerator Research Complex (J-PARC). A double cylinder type rheometer of titanium or quartz glass inner rotor with 48 mm Φ and quartz glass outer status cylinder with 50 mm Φ of inner diameter was set up at the pulsed neutron path. Information of small angle scattering both radial using 10 mm Φ neutron beam and tangential using 0.5 mm × 10 mm beam were collected under shear rate of 10^0-10^3 sec^{-1} at 30 °C. Using the write neutrons in the wide range of wavelength (λ = 1 Å - 7.8 Å) based on time-of-flight (TOF) method and the four area detector banks, wide 5×10^{-3} $Å^{-1} < Q < 15$ $Å^{-1}$, that is corresponding 0.1 nm $< r < 125$ nm in real space, information are collecting during the rheological measurements.

Synthetic hectorite; Laponite-RD®, and Na-montomorillonite purified by natural bentonite from Yamagata, Japan; Kunipia-F®, were dispersed in deuterated water. The rheological properties and the small angle neutron scattering in quartz container for the aqueous suspensions of 1 wt% - 8 wt% were obtained, followed by the Rheo-SANS. Thixotropic character was confirmed and the size and thickness of silicate layers and correlation length in the suspensions were estimated. The SANS spectra at radial and tangential positions were collected during increasing the shear rate from 0 to 500 sec^{-1} and decreasing to 0 sec^{-1} followed by aging. The obtained results are analysed by using plate and/or ribbon shaped nano-particle models.

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FORMATION OF ACTIVATED MOLECULES BY CONDENSATION ON MINERAL SURFACES - A CONTRIBUTION TO PREBIOENERGETICS

Houssein Bazzi (1), Mariame Akouche (1,2), Jean-François Lambert (2), Thomas Georgelin (2), Maguy Jaber (1)*

(1) Sorbonne Universités, UMR 8220, Laboratoire d'Archéologie Moléculaire et Structurale, Paris, France, (2) Sorbonne Universités, UMR 7149, Laboratoire de Réactivité de Surface, Paris, France

The condensation of oligomers (amino acids, nucleotides) into the corresponding biopolymers on mineral surfaces, with or without activators, is a part of many prebiotic scenarii [1,3]. While it has long been evidenced experimentally, a satisfactory physico-chemical description is still lacking, and would constitute a prerequisite to determine the likelihood of "surface scenarii". The corresponding polymerization reactions in aqueous solutions are endergonic and therefore do not occur spontaneously.

What makes them thermodynamically allowed on surfaces is simply the possibility of working in conditions of very low water activity, as all reported successful instances of polymerization involve drying steps. Since these condensation reactions result in the production of one water molecule ($R\text{-}COO^- + R'\text{-}NH_3^+ = R\text{-}CO\text{-}NH\text{-}R' + H_2O$), simple thermodynamic arguments (Lechâtelier's principle) ensure that decreasing water activity will favor condensation. This is of course not a catalytic effect since catalysis cannot change the thermodynamics.

The same argument holds for several reactions of fundamental importance in current bioenergetics, such as the formation of ATP (P-O-P from P-OH condensation) or various phosphorylations (C-O-P from C-OH and P-OH).

This work is focused on the characterization of solids based on smectites and silica with amino acids and nucleotides prepared by incipient wetness impregnation (IHN). We have compared on the same supports the dimerization of different amino acids with the formation of ATP from ADP and inorganic phosphate. The solids were analyzed by thermogravimetry (TG), vibrational spectroscopy (middle IR), MALDI-TOF mass spectroscopy, and solid state NMR (13C) to characterize the state of amino acids and nucleotides, both after adsorption and after thermal activation under argon. DTG curves allowed to identify a low-temperature event attributable to peptide bond formation or phosphorylation and glycosylation of sugar, and in addition to quantify the amount of adsorbed bioorganic molecules. MALDI TOF shows the nature of obtained biomolecules after thermal activation.

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EFFECT OF TIDES ON CLAY MINERAL DIVERSITY OF KHUZESTAN FLOOD PLAIN, IRAN

Siroos jafari

Soil science department, Ramin agriculture and Natural Resources University of Khuzestan, Ahwaz, Iran
siroosjafari@yahoo.com

The study area includes part of the Mesopotamia plain, Khuzestan province, southwest Iran. This area is located on the Iranian side of the Arvand River. Date palm and vegetable have been cultivated in this area, which was irrigated and drained by tides for more than 100 years. The soils show redoxomorphic features due to tidal influence, especially in surface soil. These soils and their clay minerals were affected by this phenomenon. In order to study the effects of tides on soils, 12 profiles were dug and described according to standard methods. Clay minerals were identified by X-ray diffraction (XRD) in some profiles after treatment to remove organic matter, carbonates, and oxides and hydroxides of Fe and Mn according to Kittrick and Hope (1960). The citrate-dithionate-bicarbonate (CDB) method was applied for extraction of total Fe from these soil samples. Then, pure clays were saturated or treated by Mg, Mg+ethylene glycol, K, K+550 ºC. Specimens for XRD were analysed at 40 kV and 30 mA. XRD diffractograms were interpreted according to Grim (1964). Also, magnetic susceptibility (MS) was determined in all samples at high (4.6 kHz) and low (0.46 kHz) frequency. The results show that total Fe (extractable by CDB) decreases from surface to subsurface. This trend may be due to more organic matter in surface and more exposure to drying and wetting periods. Drying and wetting was happen due to tidal influence, and changing oxidation and reduction situation. Fe may be released from clay mineral under this situation, making it potentially mobile, e.g. around root channels or macro pores between peds that have oxidizing potential. MS was at a maximum in surface soil samples and decreased from surface to subsurface. This trend was related to Fe movement from the reduced zone (subsurface) to oxidized zone (surface) in a profile. On the other hand, calcium carbonate did not significantly change in the profiles. The XRD patterns show that chlorite was transformed to expandable clay minerals in some part due to Fe release from this clay mineral. Also, the brucite layer has been removed under leaching or low Mg concentration, leading to transformation of chlorite to smectite. The 1.4 nm peak shifts to 1.68 nm under Mg+ETG treatment. The 1.4 nm peak intensity was increased under Mg treatment for clay minerals of surface horizons. This trend was not observed in subsurface soils. This may be related due to higher Mg concentration at this soil depth. High Mg concentration and EC make good situation for chlorite stability in subsurface soil. Smectite peak intensity decreased from surface to subsurface, inversely proportional to chlorite abundance. Also, the 060 d-spacing of the chlorite was 0.154 nm, showing that this clay is trioctahedral, and the presence of Fe or Mg is consistent with our theory for clay transformation under leaching or redoxomorphic changes. The XRD patterns show that the 1.0 nm peak intensities were increased after K+550 ºC treatment in conjunction with decrease of 1.4 nm peaks. This trend was observed in subsurface more than surface. This can be related to K fixed by depleted illite layers after this treatment. The K has been removed by palm date uptake or leaching from soil solution. The palm dates uptake more K in comparison to other crops. Following this result, all palygorskite was removed from subsurface but a small peak (low intensity) was observed at 1.05 nm in surface soil. It may be related to one of these sources: (1) palygorskite may be came from dust storms in this arid zone, or (2) from irrigation water. Palygorskite fibers are dispersed in water very well and can transfer to far away in water. Palygorskite was identified in upward land of Arvand River that could be a source. Palygorskite was transformed to smectite under high precipitation (more than 400 mm) or heavy irrigation. Therefore, palygorskite can be transformed or collapsed in moist soil conditions.

Keywords: clay, transformation, palygorskite, smectite.

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EFFECT OF PARENT MATERIAL AND IRRIGIATION ON SEPIOLITE AND PALYGORSKITE DISTRIBUTION IN SOME GYPSIFEROUS SOILS OF KHUZESTAN PROVINCE, IRAN

Siroos Jafari*, Yones Abdoli

Soil science department, Ramin agriculture and Natural Resources University of Khuzestan, Ahwaz, Iran
*siroosjafari@yahoo.com

Some parts of Iran contain evaporite deposits of Quaternary age. This parent material is composed of calcareous minerals, gypsum, anhydrate, and some clay minerals. Sepiolite and palygorskite were formed under this situation, especially along with crystallization of anhydrate or gypsum. Sepiolite and palygorskite impart special characteristics to soils with or without gypsum. The aim of this study was to examine the effect of parent material and irrigation on sepiolite and palygorskite distribution in the some gypsiferous soils. The soil moisture and temperature regimes are Ustic and Hyperthermic. In this manner, 10 profiles were dug and described (soil survey staff, 2012). These profiles had different drainage class and some of them were irrigated for more than 100 years. All horizons were sampled and clay minerals were purified and treated by Mg, Mg+ethylene glycol, K, and K+550 ºC from these soil samples. The Aridisols, Entisols, and Inceptisols were identified in this area (Key to soil taxonomy, 2014). Then, XRD patterns were collected from oriented samples and interpreted by Grim's XRD patterns (1968). Smectite, kaolinite, illite, chlorite, palygorskite, vermiculite, sepiolite, and quartz were identified in these soils. Kaolinite and illite were inherited from parent material. Chlorite was inherited and also was formed from smectite transformation. This transformation can be related to sepiolite transformation under heavy irrigation in this arid region. With increasing soil moisture under irrigation, sepiolite is unstable and collapses or is transformed to smectite. If collapsed, Mg will be released from this clay and can make suitable conditions for a brucite sheet in the chlorite. The sepiolite stability was observed in low electrical conductivity, high pH, and high Mg content. The sepiolite proportion is inversely correlated with the gypsum content in unirrigated soils. In despite of sepiolite, palygorskite proportion increased with gypsum content in unirrigated soils. Also, an inverse correlation was observed between palygorskite and smectite proportion. Maximum palygorskite was in surface soil and smectite was abundant in subsurface soil horizons. The smectite may be formed by palygorskite transformation in subsurface soil due to more soil moisture especially in weak drainage. Palygorskite may be originated from irrigation water or dust storms that happen frequently in this region. Therefore, smectite was abundant in subsurface soil with good drainage class. Vermiculite has been formed in irrigated surface soils. This clay mineral was identified from increasing intensity of the1.0 nm peak with K+550 ºC in irrigated surface soil. Vermiculite can be formed from transformation of illite to smectite stage. This may happen under high leaching of K or plant uptake in irrigation soils.

Keywords: palygorskite, gypsic sepiolite, Quaternary.

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POTENTIAL OF DIFFERENT SOILS AND MINERALS FOR LEAD, CADMIUM AND NICKEL ADSORPTION FROM CONTAMINATED WATER

Siroos Jafari (1), Jamil Mohammadian Dehgolan (2), Nafiseh Rangzan (3), Mansor Ghanian (4)

(1) Associate Professor, (2) MSC, (3) Ph.D, Soil science department, (4) Human Geography & Rural Planning, Ph.D, Ramin agriculture and Natural Resources University of Khuzestan, Ahwaz, Iran
*siroosjafari@yahoo.com

Industrial effluents contain significant amounts of heavy metals which are leached from soil to the groundwater when these are added to soils. This study was conducted to evaluate the efficiency of clay minerals and different Khuzestan's soils for removing of lead, cadmium and nickel from contaminated water at different pH levels and metal concentrations. Absorbent soil series were 1) Karoon series with low contents of smectite and organic matter and under cultivation for few years, 2) and Demcheh series which has been under cultivation for a long time and has high contents of organic matter and smectite. Two minerals were garnet and bentonite (from Iranian central mines) and sand was used as a blank adsorbent. All absorbents were contaminated with Pb, Cd and Ni in two concentration (i.e., 100 and 200 mg/l) and two pHs (i.e., 7 and 8). Factorial experiment laid out in a completely randomize design with two replications. We added 400 ml of contaminated water to each adsorbent column with constant speed under 2 cm constant head during required time. Results show that the metal amounts adsorbed by applied adsorbents were significantly different for different concentrations and the pH levels. The adsorption capacity was in the order: bentonite > garnet > soil with high smectite (Demcheh) > soil with low smectite (Karoon) > sand. The Demcheh soil adsorption was equal 50% in comparison of the bentonite or garnet minerals. The adsorption capacity of heavy metals was related to the amount of organic matter content and CEC of the two soils. Also, with increasing in pH level from 7 to 8, the amount of heavy metal adsorbed increased by bentonite (10.66%), Garnet (9.17%), Demcheh soil (9.37%) and Karoon soil (9.14%). There was no changed in the adsorption behavior of sand with change in solution pH. Similarly, with increasing the concentration of each metal from 100 to 200 mg/L, significant positive effect was observed on adsorption amount of Pb, Ni, Cd by bentonite (6.64), garnet (10.71), Demcheh soil series (9.43%), Karoon soil series (8.61%). We conclude that Demcheh soil series has a good potential for the adsorption of heavy metals due to its high organic matter and smectite content, and may be used for the disposal of industrial effluents.

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THE NATURE AND GENESIS OF CLAY MINERALS IN SOILS UNDER THE INFLUENCE OF URMIA LAKE IN NORTHWEST OF IRAN

Hawzhin Muhealddin Jalil*, Salar Rezapour, Nader Ghaemyan

Soil Science Department, Urmia University, P.O. Box 165, Urmia, 57134, I.R. Iran
*hawzhinjalil@gmail.com, S.rezapour@urmia.ac.ir, S_Rezapour2000@yahoo.com, ghaemyan-sl@yahoo.com

The nature, trend, and formation of clay minerals are important for applied clay scientists to consider. However, in the salt-affected soils of the world (such as Iran) few studies have examined the genesis and distribution of clay minerals mainly in marginal to saline lakes. In this study, the clay mineralogy of soils under the influence of Urmia Lake (a hypersalic lake) in northwest of Iran were assessed to determine their origin and factors controlling their distribution pattern in soils. In the light of this, 7 soil profiles belonging to different soil types were dug, described, and sampled. Soil samples were analyzed and the minerals of clay fraction were determined using XRD. Soils showing pH <8.5, exchangeable sodium percentage (ESP) >15, sodium adsorption ratio (SAR) >13, and electrical conductivity (EC >) 4 dS m^{-1} are referred to as saline-sodic soils. The XRD patterns of the clay fraction from all of the soil profiles exhibited a similar composition of phyllosilicate minerals, including illite, smectite, chlorite, vermiculite, and kaolinite. Indeed, the minerals were similar in type but some differences were observed in the intensity, position, and peak shape of them (except kaolinite) as well as in their relative amounts mainly due to the change in drainage condition and ground water table depth. The general increase in smectite content with depth may be associated to its neoformation from soil solution under unsuitable drainage conditions of the deeper horizons. The occurrence of illite, chlorite and kaolinite, which together accounted for >60% of the clay fraction of these soils, is largely related to their presence in the parent rock. The presence of conditions such as high pH, low Al activity, and large amounts of Si and Mg in the study soils lead to the rare occurrence of vermiculite. This condition, in contrast, was favorable for smectite formation.

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LIGHTWEIGHT AGGREGATES IN TUNISIA

Fakher Jamoussi (1)*, Emna Fakhfakh (1), Béchir Moussi (1), Mondher Hachani (1,2), Fernando Rocha (3), Alberto Lopez Galindo (4), Nouri Hatira (5), Hédi Ridha Chaftar (5), Johan Yans (6)

(1) Georessources Laboratory, CERTE, 273, 8020 Soliman, Tunisia, (2) ISE Borj Cédria, Tunisia, (3) Geobiotec, Geosciences Dept, University of Aveiro.3810-193 Aveiro. Portugal, (4) (IACT), CSIC-University of Granada, Aveda. Palmeras 4, Armilla, Granada, Spain, (5) Office National des Mines, Tunisia, (6) University of Namur, 61, rue de Bruxelles, 5000 Namur, Belgium
*fjamoussi@yahoo.com

Tunisia contains large quantities of clays located in sedimentary formations, Permian to Quaternary in age, which include levels rich in smectite, illite, kaolinite and/or palygorskite. Sometimes halloysite is also found in lenses (Jamoussi, 2001).

The first tests of manufacture of lightweight aggregates (LWA) in Tunisia were carried out by our team since 2006 (Fakhfakh, 2006; Fakfakh et al., 2007) using Cretaceous materials. These encouraging tests have led us to cover almost all the territory and the whole stratigraphic series by testing the potentiality of different kinds of clays. The studied levels are as follows: [1] Lower Cretaceous clay of Tataouine, [2] Triassic clay of the Saharan Platform, [3] Lower Cretaceous clay of the Kebeli Region, [4] Santonian - Coniacian clay of El Hamma, [6] Campanian - Maastrichtian clay of Oued Tfal Gafsa basin, [7] Maastrichtian - Paleocene clay of Jebel Stah Gafsa basin, [8] Barremian clay of Jebel Oust, [9] Pliocene clay in North East of Tunisia, [10] Eocene clay of Nefza area.

Despite the abundance of clays likely to be used in the manufacture of LWAs, no unit exists either in Tunisia or in Africa. A unit of this kind could satisfy both the needs of Africa and the Middle East in these LWAs.

Because of their lightness and porosity characteristics, LWAs can be used as thermal and acoustic insulation, showing fire resistance, freeze-thaw resistance and chemical inertness. These materials are heavily used in building and engineering work civil society.

After the mineralogical and geochemical characterization of the studied clays, we carried out tests for the production of LWAs with the raw materials or after the addition of materials improving the expansion. The firing temperature varied between 1130 and 1180 °C. A characterization of the aggregates gave the following results: bulk density (0.26-0.58 g/cm^3), compressive strength of granule (0.1-1.73 KN /mm^2) and water absorption (1-58%). The obtained results are encouraging, and they could make highly feasible the industrial production of these materials in Tunisia from local clays, and, therefore, would be a great contribution to local, national and even North African economic development.

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ADSORPTION OF PESTICIDES ON PHOSPHONIUM ORGANOCLAYS

Lubo S. Jankovic

Institute of Inorganic Chemistry SAS, Bratislava, Slovakia

The large use of chemicals in agriculture, especially herbicides, has been serious environmental concern because of the potential run-off and leaching of these compounds through the soil, contaminating surface and ground waters. Herbicide run-off and leaching down the soil profile have become a serious environmental problem and a primary source for polluting surface- and groundwater. Widely used herbicides such as atrazine, isoproturon, diuron and alachlor are the main compounds found in groundwater. The most common technique for removal of pesticides like atrazin from water involves use of an activated carbon adsorption system. Unfortunately, activated carbon lacks selectivity for atrazine and adsorbs innocuous organic compounds. As a consequence, it is desirable to investigate complimentary supplements to activated carbon such as organically intercalated clays.

The clay exchanged with suitable organic cations forms a basis for ecologically acceptable formulations of herbicides with reduced leaching, ground water contamination and enhanced weed control efficacy. Incomplete neutralization of the clay surface charge by an organic cation may be advantageous in achieving maximal adsorption of hydrophobic herbicides. One conclusion from these studies is that optimization of clay-based herbicide formulations requires a selection of structurally compatible organic cations preadsorbed on the clay at optimal coverage.

The objective of the research reported herein was to create alkylphosphonium based organoclays with four structurally different phosphonium organocations: tetrabutylphosphonium (4P4), tetraoctylphosphonium (4P8), tributylhexadecylphosphonium (3P4-C16) and trioctylhexadecylphosphonium (3P8-C16) and to investigate the ability of these organoclays to sequester atrazine from water. The studies characterized the apparent adsorption of atrazine on and desorption from organoclays created with the surfactant and a purified montmorillonite, and quantified the impact of the ratio of surfactant to clay in the organoclay.

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9,10-DIHYDROXY-OCTADECYLAMMONIUM: A STRUCTURALLY UNIQUE CLASS OF CLAY INTERCALABLE SURFACTANT

Luboš Jankovič (1)*, Juraj Kronek (2), Jana Madejová (1), Viktor Hronský (3)

(1) Institute of Inorganic Chemistry, Slovak Academy of Sciences, Bratislava, Slovakia, (2) Polymer Institute, Slovak Academy of Sciences, Bratislava, Slovakia, (3) Department of Physics, FEEI, Technical University of Košice, Košice, Slovakia

The intercalation of montmorillonite with a broad range of organic cationic surfactants, with the aim of preparing inorganic additives for polymers, has attracted wide attention from academic and industrial researchers because polymer-clay nanocomposites frequently exhibit unexpected properties arising from the synergy of their components.

The structurally unique surfactant 9,10-dihydroxy-octadecyltrimethylammonium iodide (OH-ODTMA), prepared by a two-step synthesis from commercially available oleylamine, was successfully intercalated into montmorillonite. In addition, oleyl trimethyl ammonium cation (OLEYL-TMA), the precursor of the aforementioned novel surfactant, as well as the commercially available and widely used octadecyltrimethylammonium (ODTMA) cation were also intercalated into montmorillonite. The resulting organoclays were characterized in detail by various physicochemical techniques to understand the effect of alkyl chain functionalization on surfactant properties and arrangement in montmorillonite interlayers. The XRD showed a definite intercalated structure for all three surfactants, manifesting a pseudo-trilayer arrangement. The combination of IR and MAS NMR spectroscopy allowed investigation of the effect of unique surfactant functionalization on the structural features at the nanometer level of composites consisting of the organic surfactant and inorganic montmorillonite.

Infrared spectroscopy, based on the shift of the stretching and overtone CH_2 bands, showed that the gauche conformation was extensively adopted by the novel structurally unique surfactant OH-ODTMA, while the well-known ODTMA cation mostly adopted the more ordered trans configuration.

The ^{13}C MAS NMR spectra revealed that the surfactant ODTMA was arranged in a more orderly fashion within clay interlayers than OLEYL-TMA and novel OH-ODTMA, as confirmed by the calculation of the ratio of *gauche*: *trans* conformers after deconvolution of NMR signals 30 and 33 ppm.

The novel alkylammonium surfactant functionalized with two OH groups in the middle of the backbone represents a prospective ingredient for organoclay-polyurethane nanocomposites.

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TEMPERATURE RESPONSE OF CHARGED COLLOIDAL PARTICLES BY MIXING COUNTERIONS UTILIZING Ca^{2+}/Na^{+} MONTMORILLONITE AS MODEL SYSTEM

Maria Jansson (1)*, Axel Thuresson (1), Tomás S. Plivelic (2), Marie Sekpö (1)

(1) Division of Theoretical Chemistry, Department of Chemistry, Lund University, Lund, SE-221 00, Sweden, (2) MAX IV Laboratory, Lund University, Lund, SE-221 00, Sweden
*maria.jansson@teokem.lu.se

The properties of charged colloidal particles are strongly affected by the valency of the counterions. With monovalent counterions, the electrostatic interaction between the particles is repulsive, whereas for multivalent counterions, the interaction can be attractive due to electrostatic ion-ion correlation effects.

The osmotic pressure and the aggregation of charged colloids as a function of temperature have been investigated using Monte Carlo and Molecular Dynamics simulations for different ratios of monovalent and divalent counterions.[1] In the simulations the water is treated as a temperature-dependent dielectric continuum, and only the electrostatic interactions are considered. It was found that the electrostatic interactions alone can give a positive, negative, or constant osmotic pressure response with temperature, depending on the monovalent/divalent counterion ratio. The increase in osmotic pressure with temperature, which occurs at low enough surface charge density, and/or low fraction of divalent counterions, can be understood from the DLVO-theory. The origin of the opposite behavior can be explained by the enhanced attractive electrostatic ion-ion correlation interactions with temperature. The fraction of divalent counterion charges neutralizing the colloid, where a crossover from positive to negative pressure response with temperature is found, depends on the surface charge density, the pressure (or volume fraction), and other components such as the rotational entropy and the size of the colloid. The current conclusions are supported by the microstructural characterization of the swelling clay mineral montmorillonite, where it has been recently shown that the swelling pressure of montmorillonite as a function of temperature can be understood from ion-ion correlations.[2] For this purpose, mixtures of Ca^{2+}- and Na^{+}-montmorillonite in water have been measured with small angle X-ray scattering (SAXS) at four different temperatures, and it was found that Bragg peaks appear for a sodium content of ~ 20% or less, which indicates that tactoid exist in those compositions. As the sodium content was reduced, the number of platelets per tactoid increased. By increasing the temperature, the separation between the platelets in the tactoids decreased and the number of platelets per tactoid seems to increase slightly. For a sodium content of ~ 40%, or more, no tactoids were found, which indicates that the interaction between the platelets are dominated by repulsive interactions.

Our theoretical predictions are in qualitative agreement with the SAXS experiments, giving a further indication that our model can explain the underlying physics. The theory presented here is general and predicts that the temperature response for all types of charged colloids can be controlled by mixing counterions of different valence, if the interactions in the system are dominated by electrostatics.

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INSIGTH INTO THE INSERTION OF Zn(II) INTO BAYERITE

Nicholai D. Jensen (1)*, Suraj S. C. Pushparaj (1), Camila A. Rasmussen (1), Andreas Ø. Drejer (1), Claude Forano (2,3), Gregory J. Rees (4), Vanessa Prevot (2,3), John V. Hanna (4), Dorthe B. Ravnsbæk (1), Morten Bjerring (5), Ulla Gro Nielsen (1)

(1) Department of Physics, Chemistry, and Pharmacy, University of Southern Denmark, Odense, Denmark, (2) Institut de Chimie de Clermont-Ferrand, Université Clermont Auvergne, Université Blaise Pascal, Clermont-Ferrand, France, (3) CNRS, Aubiere, France, (4) Department of Physics, University of Warwick, Coventry, United Kingdom, (5) Department of Chemistry and Interdisciplinary Nanoscience Center, Aarhus University, Aarhus, Denmark
*Dauaard@sdu.dk

Layered double hydroxides (LDHs) can be dived into two groups: brucite and aluminium hydroxide derived, which have a chemical composition of $[M(II)_{1-x}M(III)_{x}(OH)_{2}A^{n}_{x/n}]$ and $[M(II)Al_{4}(OH)_{12}A^{n}_{1/n}]$, respectively, where M(II) (M(III)) are divalent (trivalent) cations and A an anion needed for charge balance. The most common LDHs are brucite-derived and have been extensively studied [1], whereas only a few studies of M(II) insertion in the aluminium hydroxide derived LDHs have been published. This work investigates the insertion of zinc sulphate and nitrate into bayerite, one of the two common $(Al(OH)_{3})$ polymorphs, leading to a so-called $ZnAl_{4}$-LDH with an ideal chemical composition of $ZnAl_{4}(OH)_{12}SO_{4}$ and $ZnAl_{4}(OH)_{12}(NO_{3})_{2}$, respectively. These materials have very interesting potential applications inside many areas, however only a few in-depth studies of the structure have been published and some of these contains uncharacteristic binding environments like Zn with bond length varying from 1.5 Å to 2.3 Å furthermore is it problematic to obtain pure sample [2]. Thus, in order to study the structure a sample of sufficient purity is need. With that goal have the effect on the purity of the synthesized $ZnAl_{4}$-LDHs on systematic variation of temperature and time of hydrothermal treatment been studied. The sample quality was assessed by powder X-ray diffraction, solid state NMR (SSNMR), TEM, and elemental analysis. An extensive structural investigations of the best products utilising PXRD combined with Rietveld refinement, ICP, TEM, IR, Raman, SSNMR, and first principle DFT calculations were performed in order to gain insight into the structure [3,4]. Four different structural models were assessed:, an ideal model, a model with vacancies on the Zn positions, a model with vacancies on Zn andSO_{4} positions, and a model with vacancies on the Zn, Al, and SO_{4} positions. However, Rietveld refinement could not distinguish between these models. By combing the information obtained from all techniques was it found that the structure follows the ideal model, with only few defects.

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Fe-BEARING KAOLINITE IN GREEN SAPROLITE BENEATH SEDIMENTARY KAOLIN DEPOSITS, SETO DISTRICT, CENTRAL JAPAN

Mayumi Jige (1)*, Tetsuichi Takagi (2), Yoshio Takahashi (3), Yuki Tsunazawa (2), Kazuya Morimoto (2), Mihoko Hoshino (2), Katsuhiro Tsukimura (2)

(1) Osaka-Ohtani University, Faculty of Education, Tondabayashi, 584-8540 Japan, (2) Geological Survey of Japan, AIST, Tsukuba, 305-8567 Japan, (3) University of Tokyo, Faculty of Science, Bunkyo-ku, 113-0033 Japan
*jigemayu@osaka-ohtani.ac.jp

The Seto district is one of the largest sedimentary kaolin fields in the Japan Arc. The kaolin deposits occur as fluvial and lacustrine arkose sediments of late Miocene to Pliocene, and were subjected to intense kaolinization after sedimentation [1]. The kaolin deposits unconformably overlay Cretaceous granitic rocks. The upper parts of the granitic rocks were weathered to clayey saprolite showing greenish gray to dark green in color. We tentatively call the saprolite “green saprolite” in this study. The green saprolite is several to 20 meters in thick, and comprises coarse-grained quartz, feldspars with minor amount of biotite and clay minerals, but no chlorite is detected. The fraction of clay minerals accounts for about 10 wt. percent of green saprolite, and is composed mainly of kaolinite. The kaolinite commonly contains small amount of Fe based on SEM-EDS analyses. The color of green saprolite would be acquired by the Fe-bearing kaolinite.

We have investigated two green saprolite samples, M01 and 07. M01 was collected near the top of saprolite, and M07 in 3 meters deep. Kaolin clay was extracted by elutriation and centrifuge. The semi-quantitative analyses by SEM-EDS indicate that Fe contents range from 2 to 3 wt.%, and Si and Al in kaolinite seem to be replaced by Fe. The pre-Edge analyses of XANES indicate that Fe in M01 and M07 are ferric iron. The EXAFS of M01 indicates that Fe is in octahedral sites and the second nearest neighbor is Fe, which suggest Fe-Fe bonding. In contrast, the EXAFS of M07 indicates that Fe is also in octahedral sites, but the second nearest neighbour is not Fe. The results of XAFS analyses suggest that ferrihydrite or similar materials exists in the kaolin clay of M01, but no ferrihydrite contribution to the kaolin clay of M07.

Fe-bearing kaolinite has been reported from soils under tropical environments and laterite [2,3]. Those kaolinite precipitated under strongly Fe-rich and oxidized environments. However, in the case of the Seto district, the host granitic rocks are not Fe-rich, and kaolinization did not occur on/near the surface but beneath fluvial or lacustrine sediments. The fluvial and lacustrine sediments have been generally in kaolin-stable acidic and anoxic conditions due to the existence of organic matter. The original Fe in arkose sediments was leached out and infiltrated into granitic rocks during kaolinization. Thus, we can interpret that the carrier of Fe would be organic acid solution, and the leached Fe reacted with kaolinite in green saprolite. The mineralogical difference between M01 and M07 might be attributed to the difference in the degree of reactions.

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PRELIMINARY MINERALOGICAL AND GEOCHEMICAL RECORDS FROM A SERIES OF SEDIMENT CORES FROM RINCÓN DEL MUERTO WETLAND (CÓRDOBA PROVINCE, S SPAIN)

Concepción Jiménez de Cisneros (1)*, María Dolores Rodríguez (2), Bartolomé Andreo (3), José Manuel Gil-Márquez (3), Matías Mudarra (3)

(1) Instituto Andaluz de Ciencias de la Tierra (CSIC-UGR), Avda. de las Palmeras 4, 18100 Armilla, Granada, Spain,
(2) Departamento de Química Inorgánica de la Universidad de Málaga, 29071, Campus de Teatinos, Málaga, Spain, (3) Departamento de Ecología y Geología y Centro de Hidrogeología de la Universidad de Málaga, 29071, Campus de Teatinos, Málaga, Spain
*concepcion.cisneros@csic.es

Climate variability is the main factor involved in the control of water level variations in wetlands [1]. A mineralogical and geochemical study of sediments cores from Rincón del Muerto wetland (Cordoba Province, S Spain) has been performed to provide information on limnology records and paleoclimate in southern Spain during the Holocene. In general, this area presents a poorly defined drainage network related to karstification processes affecting subjacent evaporite rocks. These endorheic depressions can be flood temporarily or even permanently. Synsedimentary processes and diagenesis result in local cementation, desiccation, and reworking of these deposits, particularly along the margins of the wetland. The results of XRD show that the dominant mineralogical composition corresponds to clay minerals (>50%), followed by quartz, calcite, gypsum, halite, dolomite and ankerite. The clay mineral associations consist of smectite (69%), illite (7%), kaolinite (3%), chlorite (<1%) and illite/smectite (I/S) mixed layers (24%). The XRF data and chemical ratios have been used as indicators of different processes that occurred in the pilot wetland area. Thus, the upper sediment levels of the cores are enriched in elements associated with alumino-silicates (Al, K, Ti, Fe), characterized by the presence of clay minerals, quartz and detrital calcite, reflecting fresher conditions. On the contrary, higher values of Sr and S have been detected in the lower sedimentary levels, accordingly to precipitation of gypsum and halite (water evaporation) and to endogenic carbonate precipitation (with higher S/Al, Sr/Al ratios). In some levels, higher values of organic carbon content have been distinguished, highlighting anoxic conditions during periods with high organic productivity (elevated organic carbon content and high Mg/Ca and Fe/Mn ratios).

Geochemical indicators (Cu and Ni) also mark more recent periods of greater detrital input to the wetland, related probably to agricultural and human activities in the area [2]. This preliminary geochemical study provides evidences about the main depositional processes that have occurred in Rincón del Muerto wetland, from which variations in paleoclimatic conditions in this area has been inferred.

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CLAY SMEARING PROCESSES IN PLIO-PLEISTOCENE SOFT-ROCKS FROM THE BAZA FAULT ZONE (S SPAIN)

Juan Jimenez-Millan J. (1), Isabel Abad (1), Francisco Juan García-Tortosa (1), Daniel R. Faulkner (2), Ivan Martin-Rojas (3), Pedro Alfaro (3)

(1) Departamento de Geología y Centro de Estudios Avanzados en Ciencias de la Tierra, Unidad Asociada al Instituto Andaluz de Ciencias de la Tierra, Universidad de Jaén, Spain, (2) Rock Deformation Laboratory, Department of Earth and Oceanic Sciences, University of Liverpool, United Kingdom, (3) Departamento de Ciencias de la Tierra y del Medio Ambiente, Universidad de Alicante, Spain

Clay smearing processes can be identified in m to cm-scale displacement faults offsetting soft-rocks sequences of interbedded carbonate, marls, sands, silts, gypsum and clays from an excavated trench in the Baza fault (Spain). This 37-km long structure is an E-dipping active normal fault located in the Guadix-Baza Basin (Betic Cordillera) with a variable strike with N-S and NNW-SSE segments. The fault has associated instrumental and historical seismicity, the most important of which is the 1531 Baza earthquake, with more than 400 fatalities.

Clay smearing appears by deformation of clay-rich sediments (illite, smectite) producing bands with reorientation, flow, and extrusion of clay minerals. Striations and slip surfaces are also sometimes observed. Many of these deformation bands show subsequent precipitation of gypsum. Contrasting with clay smearing, disaggregation bands can also be observed at the coarser grain sized (50-200 µm) sediments of the trench made of quartz, calcite, dolomite and feldspars. These bands (up to 300 µm thick) are characterised by granular flow processes such as grain rolling and grain boundary sliding. Grain scale mixing with silt sediments also occurs along discrete bands. Local grain cracking, increasing grain angularity and decreasing grain size, can also be observed. Shear-induced rotation in sediments rich in coarse muscovite, paragonite and chlorite grains (up to 100 µm long) produce phyllosilicate alignment to form local fabric that can be considered as a particular type of disaggregation band where platy minerals promote frictional grain boundary sliding within the bands.

Our mineral and petrographic characterization of the soft-rocks of the fault zone exposed in a trench allows us to recognize particular microstructures and deformation mechanisms occurring during seismic deformation. These features suggest predominance of ductile deformation mechanisms in the studied fault soft rocks. Shearing of sands and silt sediments could involve granular flow or local proto-cataclasis of grains. Clay rich-sediments always present ductile deformation. The dominant deformation mechanism may be controlled by the mineral composition of the shear band and the water content. Incorporation of clays and water-rich sediments along shear bands may reduce shear strength.

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CHARACTERIZATION AND STUDY OF NATURAL AND MODIFIED ZEOLITE AS ADSORBENT ON AMMONIUM REMOVAL FROM WASTE WATER

Jmayai Amel (1)*, Mehrez Hermassi (2), Rabeh Alouani (1), Jose Louis Cortina (2),
Abdeslem ben Hadj Amara (1)

(1) Department of Physics, UR05/13-01: Laboratory of Physics of Lamellar Hybrid Materials and Nanomaterials, Faculty of Science of Bizerte, 7021 Zarzouna, Tunisia, (2) Department of Chemical Engineering, Universitat Politècnica de Catalunya-Barcelona Tech (UPC),08028 Barcelona, Spain

In this study three natural zeolite were obtained from different regions of Yamen were fully characterized by scanning electron microscopy (SEM), Energy-dispersive X-ray spectroscopy (EDS) technique, point charge zero (PZC), X-Ray diffraction (XRD) and X-Ray Fluorescence (XRF). Quantitative and qualitative mineralogical characterization indicated than the main minerals constituents are clinoptilolite and mordenite and trace of feldspars and biotite, (with an amorphous fraction) were also detected. In this study natural zeolite was used in ammonium removal, the kinetics and isotherms of ion exchange were also studied. Important parameters which affect the ion exchange, such as pH of solution, contact time, zeolite mass and initial ammonium concentration were investigated. The acid-base properties of the zeolites were characterized by acid-base titrations (pH_{PZC}=7.6 ±0.4). The ammonium maximum sorption capacity at pH 8 shown important values witch achieved 51.81 mg-N/g for Zeolite-3.

Modification of zeolite structure was also studied, and results show a hight power of zeolite as adsorbent of ammonium from waste water.

Keywords: Zeolite, clinoptinilite, isotherms, ammonium, sorption, kinetic.

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MATERIAL CHARACTERISTICS AND MANUFACTURING TECHNIQUE OF RAMMED EARTHWORK IN THE 13TH KOREAN RAMPARTS

Young Hoon Jo, Chan Hee Lee*

Dept. of Cultural Heritage Conservation Sciences, Kongju National University, Gongu, 32588, Republic of Korea
*chanlee@kongju.ac.kr

Interpreting a rammed earth technique of soil ramparts via material analysis is very important to identify traditional building techniques and to assume the utilization ability of raw materials (Silva *et al*., 2013; Milete *et al*., 2016). Furthermore, this helps us understand the technical and social levels (Niroumand *et al*., 2014). This study identified the quantitative and objective manufacturing technique for the rammed earthwork of the Ganghwa Jungseong Fortress, the 13th Korean ramparts, by analyzing its physical, mineralogical, granulometric, and geochemical characteristics. Furthermore, mutual homogeneity between the rammed earthwork and a host rock, topsoil, and subsoil collected around the fortress was interpreted.

The physical characteristics of soil samples were analyzed by the Munsell soil color chart, chromameter, and magnetic susceptibility measurement. Mineralogical characteristics were identified using stereoscopic and polarizing microscopes and X-ray diffraction analyses. Particle sizes were classified by wet sieving and a laser diffraction analyzer. Using an inductively coupled plasma spectrometer and a neutron activation detector, the geochemical compositions of major, minor, and rare earth elements were obtained. The results revealed that the rammed earthwork was used a genetically common soil regardless of layers and locations. However the rammed earthwork showed different careful selection according to the ground, foundation and body parts. The ground part comprised a loam-textured weathered soil showing low brightness and high redness. Considering the low SiO_2 and high Al_2O_3 and Fe_2O_3 contents, the soil is highly influenced by siallitization.

The five-layered foundation part exhibited various colors from red to brownish yellow, wide range of magnetic susceptibilities (ranging from 3.65 to 12.80×10^{-3} SI unit), and particle distributions from silty loam to sandy loam. This part was overall affected by low siallitization except for the lowest layer, and it showed a wide range of organic contents (4.19 to 8.08 wt%). In particular, the highest layer in the foundation part exhibited a pale yellow color, which is a distinct characteristic, signifying the high magnetic susceptibility of 12.08×10^{-3} SI unit, low siallitization, and organic contents (4.19 wt.%). In addition to the physical and geochemical characteristics, the soil texture was classified as mere loam because the layer had much higher sand contents than the other layers.

This soil is similar to saprolite, a chemically weathered rock, which is soft, earthy, typically clay-rich, thoroughly decomposed, and formed via chemical weathering of igneous, sedimentary, and metamorphic rocks. Owing to high sand contents, this soil forms the frame of the foundation part and improves its ventilation and drainage because of the widening of the pore space between the soil particles. Unlike the foundation part, the body part is composed of silty loam in the lower part and silty loam and loam from the middle part. The technique that alternately hardens soils with different particle sizes has the advantages of external shock absorption and crack prevention owing to temperature change during winter and summer seasons.

The rammed earthwork and soils around the fortress had similar magnetic susceptibilities, rock-forming minerals (quartz, alkali feldspar, plagioclase, mica, illite, kaolinite, and chlorite), and geochemical characteristics. The results indicate that the rammed earthwork and soils around the fortress have a genetically common source. Moreover, the rammed earthwork was built using the soil weathered from the banded gneiss because it was correlated to the banded gneiss that constituted the bedrock around the fortress.

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AN EVALUATION OF CHILEAN KAOLINS FOR INDUSTRIAL APPLICATIONS

MANUEL M. JORDÁN (1)*, FRANCISCO PARDO (2), DAVID BLANCO (3)

(1) Miguel Hernández University of Elche, Department of Agrochemistry and the Environment (GEA-UMH), Avda.de la Universidad, s/n,03202 Elche (Alicante), Spain, (2) CEU Cardenal Herrera University. Department of Science Education. C/ Grecia 31 (Ciudad del Transporte II) 12006. Castellón, Spain, (3) Universidad Tecnológica Metropolitana. Department of Building Sciences. C/ Dieciocho 390, Santiago de Chile (Chile)

Ceramic products play a very important role in Chilean society. Ceramic products are considered primarily products. This is also one of the reasons for their wide usage (bathrooms, kitchens, laboratories, schools, etc). Residual deposits of kaolins are known in Chile, products from the meteorization of granodioritic to dioritic rocks, which form plastic clays with high kaolinite contents, in addition to illite, along with residual quartz. There are different types of kaolins in Chile distributed in deposits, specifically in the central and south-central sectors of the country [1]. These sedimentary plastic kaolins are found along both the eastern and western slopes of the Chilean Coast Range. However, neither the extension, potential, nor technological behaviour of this sedimentary sequence were adequately studied. Meseguer et al. (2011) carried out a preliminary study about kaolin deposits in the Maule Region (Chile). These authors have assessed the application of these non-exploited clays to the local ceramic industry. The main objective was to determine the technological properties and composition of these raw materials in order to evaluate their ceramic behaviour and applicability [2].

The kaolins studied were selected in the areas of San Miguel (A and B) and Las Juntas (C and D), both located in Cauquenes Province (Maule Region, Chile).The chemical and mineralogical composition was determined by X-ray fluorescence (XRF) and X-ray diffraction (XRD). Kaolins were moistened until homogeneous agglomerates with 5% of water were obtained. They were pressed (300 kg/cm^2, 80 x 40 x 5 mm). The pieces were finally heated. The mineralogical analysis of the fired bodies was carried out by XRD at the following temperatures 835, 980, 1080 and 1160 ºC. Ceramic bodies have been heated in a ceramic kiln following a standard heating cycle for ceramic bodies, after being dried in a stove. The usual industry sector firing cycles were designed (0-500 ºC: 2 h; 500-650 ºC: 2 h; 650-Tmax: 2 h; Tmax: 4 h), and maximum temperatures (Tmax) of 835, 980, 1080 and 1160 °C were reached. Mineralogical analysis of the ceramic bodies was performed by X-ray diffraction. Thermodilatometric analysis (TDA) was carried out using a horizontal pushrod dilatometer Bähr model DIL 804 with a heating rate of 10 ºK min-1 with α-Al2O3 as inert substance. Also, the plasticity index (PI) was measured for each sample. Linear contraction (LC), water absorption capacity (WAC) were done to characterize the fired clays.

Results show the presence of quartz, mullite, spinel, orthoclase, albite, hematite, enstatite, ferrosilite, augite and forsterite for A samples. Quartz, trydimite, anorthite, orthoclase, hematite, corundum, fayalite, ferrosilite and hercynite were present in B samples. Quartz, anorthite, albite, hematite, mullite, microcline, augite and enstatite were present in C kaolin samples. Quartz, mullite, spinel, orthoclase, trydimite, enstatite and olivine were present in D samples. The persistence of illite at least at 835 ºC is shown in all samples. At 1080 ºC mullite is formed in A, C and D series. In these series mullite content is high at 1160 ºC. A considerable decrease in the WAC coinciding with the beginning of vitrification was observed. At 1160 °C, the porosity of the tile bodies decreased significantly. The samples studied are easily adaptable to ceramic processes (pottery, sanitary, structural ceramic, bricks, etc).

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THE USE OF BIOSOLIDS AND MARBLE SLUDGE IN THE MANUFACTURE OF CERAMIC TILE BODIES

Manuel M. Jordán (1)*, Francisco Pardo (2), David Blanco (3)

(1) Miguel Hernández University of Elche, Department of Agrochemistry and the Environment (GEA-UMH), Avda. de la Universidad, s/n,03202 Elche (Alicante), Spain, (2) CEU Cardenal Herrera University. Department of Science Education. C/ Grecia 31 (Ciudad del Transporte II) 12006. Castellón, Spain, (3) Universidad Tecnológica Metropolitana. Department of Building Sciences. C/ Dieciocho 390, Santiago de Chile (Chile)

Due to determinant environmental factors, water treatment and purification processes have been generalised worldwide, especially in countries with increasing scarcity of water resources. There are several water purification processes, and waste denominated as biosolid is generated in every case and treatment type [1]. On the other hand, about 70% of the processing waste in the Spanish natural stone industry is disposed of locally. Marble dusts are usually dumped into riverbeds and this poses a major environmental concern [2]. The substitution of clayey raw materials for other wastes, in this case biosolids and marble sludge, in the production of traditional ceramics could be cost effective from the utilisation and recycling of these wastes as a secondary raw material. At the same time, it can be helpful in tempering the environmental problems associated with such wastes. A standard ceramic clay(52% SiO_2, 18% Al_2O_3, 11% CaO, 7% Fe_2O_3, 4% MgO), and three sewage sludge samples coming from three different sewage plants were selected. Soluble SO_4^{-2} and Cl^- were analyzed by gravimetry and titration, respectively. The total organic matter was determined by calcination at 500 ºC while the loss of mass was determined by calcination to 1000 ºC. The $CaCO_3$ content was determined by calcimetry. The content of heavy metals and trace elements were analyzed by X-ray fluorescence in all the samples. The mineralogical analysis of the clay samples was carried out by XRD on oriented aggregates (normal, heated to 550 ºC during 2 hours and treated with ethylenglycol) using a Siemens D-500 with Bragg-Bretano geometry. A representative sample of a residue rich in calcium carbonate (sludge) was selected from different marble plants of the natural stone industry of Alicante province (Spain). Chemical characterization of the residue employed was done by X-ray fluorescence (XRF) with a PW2400 X-ray spectrometer with rhodium target X-ray tube, controlled by SuperQ/Quantitative version 1.1 software. Some experimental tests were carried out with the ceramic clay, biosolids and the marble residue. Such tests consisted of the preparation of mixtures with the following biosolid contents: 0 (control), 1, 2, 3, 4, 5 and 10 (mass. %) and 0 (control), 15, 20, 25, 30 and 35% of marble sludge, respectively. The test bodies were pressed with a laboratory Mignon-S Nanetti uniaxial press, at 40 MPa, and shaped on discs of 20 mm diameter, 5 mm thick and approximate weights of 3.5 g. The usual industry sector firing cycles were designed (0-500 ºC: 2h; 500-650 ºC: 2 h; 650-Tmax: 2 h; Tmax: 4h), and maximum temperatures (Tmax) of 975, 1000, 1025 and 1050 °C were reached. The mineralogical analysis of the fired test bodies was carried out by XRD using the usual conditions and techniques. The mineral phases present in the fired test bodies were quartz, plagioclase, augite, gehlenite, wollastonite, orthoclase, spinel and hematites. To evaluate the ceramic properties of the obtained material, several processing and product properties (linear contraction, water absorption, bending strength) were determined. With regard to the technological properties of the final ceramic bodies, there does not seem to be any clear relation between the linear contraction values and the content of residue. However, the increase in water absorption along with the increase in the residue content is evident. The addition of residue decreased the bending strength. The selection of the adequate content of sludge to be added to the ceramic body will be controlled by the usual standards applied to construction materials.

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EFFECT OF PHYSICO-CHEMICAL PROPERTIES OF HALLOYSITE TOWARD PORPHYRINS INTERACTIONS

Lajm iAmira (1,3), Joussein Emmanuel (1)*, Leroy-Lhez Stephanie (2), Soubrand Marilyne (1), Riou Catherine (2), Medhioub Mounir (3)

(1) Université de Limoges, GRESE "Groupement de Recherche Eau Sol Environnement", Limoges, France, (2) Université de Limoges, LCSN "laboratoire de Chimie des Substances Naturelles", Limoges, France, (3) Université de Sfax, Sfax, Tunisie

Clay minerals represent natural and interesting host and guest organic chromophores components inducing the formation of dye molecular assemblies. Halloysite is a natural nanosized tubular clay (HNT) mineral that has many potentially important uses in different industrial fields. Particularly, it can be used as a support for loading and controlled-release of guests. Since the last decade, large of literature have been reported onto the HNT and their potentiality use (e.g. [1]). Indeed, HNT often varies in morphology, porosity, as well as in physical chemical properties. Photofunctional properties (photophysical and photochemical reactions) are one of the most promising properties of dye molecular systems (various applications such as molecular devices for optics, phytoremediation, lasers, photodynamic therapy of cancer, etc.). Then, it was proposed to understand the interactions of halloysite nanotubes with porphyrins. Various HNT which differs in term of morphology, physical-chemical reactivity, or hydration state were used to interact with cationic porphyrins (such as Tetra (N-methylpyridyl) porphyrin) in aqueous diluted media. Samples were study by XRD, IRTF, Raman, UV-Visible and fluorescence spectroscopy in the way to follow the interactions (surface or interlayer), as well as their orientations in relation to the properties of each HNT. Previous results give evidence that sample does not react in the same way with various surface charge from zeta potential. Moreover, the interactions are dominant in the case of surface whereas hydrated interlayer seems to be lower reactive. Discussion about the porphyrins interactions toward the surface and the lumen will be realized as well as the role of physical chemical properties of HNT.

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THE REMOVAL OF NICOTINE FROM AQUEOUS SOLUTION BY ADSORPTION ONTO MONTMORILLONITE

Nataša Jović-Jovičić*, Aleksandra Milutinović-Nikolić, Predrag Banković, Zorica Mojović, Irena Ilić, Marija Ajduković, Dušan Jovanović

University of Belgrade - Institute of Chemistry, Technology and Metallurgy, Centre for Catalysis and Chemical Engineering, Njegoševa 12, 11000 Belgrade, Republic of Serbia

Wastewaters polluted with nicotine have been classified as toxic and hazardous by European Union Regulations [1]. Using montmorillonite as nicotine adsorbent has several advantage to other methods and/or adsorbents since montmorillonite is an efficient adsorbent and at the same time natural, widely available at relatively low cost. In this work montmorillonite (SWy-2 purchased from The Source Clays Repository - The Clay Minerals Society) was used for nicotine adsorption experiments. UV-Vis spectroscopy (λ_{max}=261 nm) was used for measuring the nicotine concentration and adsorption was carried out at pH=9.26. The estimated equilibrium time was 60 min. The adsorption obeyed the pseudo-second-order-kinetics. The adsorption isotherms were obtained for initial concentration range of nicotine from 1×10^{-4} to 2×10^{-3} mol dm^{-3} and temperature range was between from 25 and 55 ºC. The obtained isotherms were fitted with Langmuir, Freundlich and Sips' models. For all investigated temperatures the results were best described with Sips' model indicating that adsorption occurred on heterogeneous surface with defined number of active sites [2]. The Gibbs free energy (ΔG) values calculated for the experimental data suggested that adsorption of nicotine onto montmorillonite was spontaneous, while the value of ΔH=19.0 kJ mol^{-1} was associated with endothermic process [3]. The result obtained for maximum adsorption capacity of SWy-2 in this study (Q_{max}=0.275 mmol g^{-1}) is comparable with data referred in literature [4], while at optimal pH=6 the Q_{max} of 0.713 mmol g^{-1} was achieved. The obtained results suggest that montmorillonite can be regarded as promising adsorbent for nicotine removal from aqueous solutions.

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CONTROLLED ANTIBACTERIAL ACTIVITY OF ANTIBIOTIC-NANOCLAY HYBRID COATED FILM

Jin-Song Jung*, Hyoung-Junkim, Jae-Min Oh

Department of Chemistry and Medical Chemistry, College of Science and Technology, Yonsei University, Wonju
Gangwondo, 26493, Republic of Korea
jaemin.oh@yonsei.ac.kr

The antibiotic coating was usually performed to prevent medical devices from infection by bacteria. However, coated antibiotics can be easily detached from surface of medical device without proper immobilization. In order to provide strong immobilization of antibiotics on coating surface, we utilized layered double hydroxide (LDH) and montmorillonite (MMT) as supporter. Two kinds of antibiotics, anionic levofloxacin (LFC) and cationic gentamicin (GTM), were respectively intercalated into LDH and MMT by ion-exchange reaction. From X-ray diffraction pattern, both clays showed lattice expansion along crystallographic c-axis, suggesting the existence of antibiotic molecules in the interlayer space of nanoclays. The infrared spectroscopy revealed that the intact structure of antibiotic molecules were well preserved after intercalation into nanoclays. Through the scanning electron microscope, it was proven that the size and shape of nanohybrids were maintained compared with pristine LDH and clay. The intercalated amounts of antibiotics quantified by CHNS elemental anlysis and thermogravimetry were comparable to the theoretical loading amount in terms of anionic exchange capacity of LDH and cationic exchange capacity of MMT. Antibiotic-nanoclay hybrids, LFC-LDH and GTM-MMT, and antibiotics only were coated on polyurethane film through drop-casting or dip-coating methods utilizing aqueous urethane binder To evaluate the controlled antibacterial activity by nanoclay immobilization, the polyurethane film coated with hybrid or antibiotic itself were immersed in simulated body fluid. After designated time points during 30 days, the antibacterial efficiency was monitored through bacterial colony forming inhibition assay.

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GENESIS OF SEPIOLITE AND PALYGORSKITE IN LACUSTRINE CARBONATE SEDIMENTS OF THE SAKARYA FORMATION (LOWER PLIOCENE) IN THE SİVRİHİSAR AND YUNUSEMRE REGIONS (ESKİŞEHİR), WEST CENTRAL ANATOLIA, TURKEY

Selahattin Kadir (1)*, Muhsin Eren (2), Taner İrkeç (3), Hülya Erkoyun (1), Tacit Külah (1), Nergis Önalgil (1), Jennifer Hugget (4)

(1) Eskişehir Osmangazi University, Department of Geological Engineering, TR-26480 Eskişehir, Turkey, (2) Mersin University, Department of Geological Engineering, TR-33343, Mersin, Turkey, (3) Consultant Geologist, TR-06810, Ankara, Turkey, (4) Natural History Museum, Department of Earth Sciences, London, UK
skadir.euroclay@gmail.com, m_eren@yahoo.com, tanerirkec@yahoo.com, hlerkoyun08@gmail.com, tacitkulah@gmail.com, onalgil_05290218@hotmail.com, info@petroclays.com

The Neogene lacustrine sediments in the Sivrihisar and Yunusemre regions, located at the eastern part of Eskişehir province are composed of claystone rich in sepiolite and palygorskite, argillaceous carbonates, and gypsum. Brown sepiolite and palygorskite with organic material content characterizes deposition in a swampy environment of the lake whereas dolomitic sepiolite and sepiolitic dolomite without organic content suggest deposition in the ponds mostly at the marginal zones, and indicate influence of freshwater and fluctuations in the lake-water level. The claystone and associated rock samples were examined using polarized-light microscopy, X-ray diffraction, scanning electron microscopy, and chemical and isotopic analysis methods. Dolomite and calcite are associated with sepiolite, palygorskite, smectite, chlorite, illite, quartz, amorphous silica, feldspar and amphibole within the sediments. Petrographic examination revealed that the dolomite samples are predominantly micrite, and partly recrystallized to dolomicrosparite and dolosparite in areas close to *desiccation* fractures. Presence of ostracods and dacycladecean algae in the carbonate samples reflects a restricted depositional environment. In argillaceous carbonates, sepiolite and palygorskite fibers appear either in knitted or scattered forms; which may envelope the relict carbonate crystals or may form bridges between them due to occasional changes in physico-chemical conditions provided by fluctuations in lake water level and influence of ground water in relation to climatic changes during and after dolomite precipitation and diagenesis. Dolomite samples are characterized by high MgO+CaO content as expected, with high ignition loss. On the other hand, sepiolite and/or palygorskite-dominated clay samples reflect high SiO_2+MgO (+Al_2O_3+Fe_2O_3) for sepiolite and SiO_2+Al_2O_3 (+MgO +Fe_2O_3) for palygorskite, with lesser ignition loss. Octahedral substitution of Fe^{3+} is not uncommon, especially in the crystal structure of palygorskite in the area. High Sr and Ba values in both carbonate and argillaceous carbonate are due to alteration of feldspar and hornblende in the metamorphic and volcanic units. Gypsum in the older rocks is probably another source for Sr. Enrichment of Ni and Cr is related to weathering of olivine and pyroxene in the ophiolitic basement units. Plot of SiO_2 vs. Al_2O_3+K_2O+Na_2O in sediments also suggests deposition under the arid conditions. The Ni/Co and V/(V+Ni) ratios of the sediments indicate anoxic to dysoxic conditions. A slight enrichment of δ^{13}C and δ^{18}O values of dolomite respect to calcite is probably due to evaporation rate in different parts of the lake environment. The δ^{34}S and δ^{18}O values for gypsum ranging from 15.7 to 22.3‰ and from 9.4 to 19.4‰, respectively suggest a progressive evaporitic lacustrine environment. A shift to lower values in δ^{18}O of anhydrite may reflect effect of evaporation. The ^{87}Sr/^{86}Sr isotope ratios of gypsum range from 0.707579 to 0.708203, and suggest a non-marine evaporitic source for precipitation. Changes in physico-chemical conditions resulted in periodic precipitation of sepiolite, palygorskite, and dolomite in the environment. The Si, Mg and Al required for sepiolite and palygorskite formation were supplied in solution(s) from the Paleozoic metamorphic and Upper Cretaceous ophiolitic rocks, and locally the Late Miocene-Early Pliocene volcanic, and volcaniclastic rocks.

Keywords: Argillaceous carbonate, dolomite, gypsum, sepiolite, palygorskite, Sivrihisar, Turkey.

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LIQUID CRYSTAL PHASES FORMED IN THE MIXTURE OF NANOSHEETS AND MICROTUBULES

Riki Kato (1), Nobuyoshi Miyamoto (1)*, Akira Kakugo (2)*

(1) Department of Life, Environment and Materials Science, Graduate School of Fukuoka Institute of Technology, 3-30-1, Wajirohigashi, Higashiku, Fukuoka 811-0295, Japan, (2) Department of Chemistry Faculty of Science, Hokkaido University, Kita 8, Nishi 5, Kita-ku, Sapporo, Hokkaido 060-0808, Japan

Inorganic nanosheets of around 1 nm thickness and large lateral surface are obtained by exfoliation of inorganic layered materials and they form liquid crystal (LC) phase in a solvent [1]. While tuning of the properties and structure of nanosheet LCs have been investigated by changing nanosheet and salt concentration and applying external field, mixing the nanosheets with other materials is another intriguing way. Here we focus on the mixing of nanosheets with microtubules (MTs) [2-4] which are known as important bio-matter in cell division and movement. MTs are rigid hollow tubes with the diameter of 25 nm and persistence length of several mm. They are consist of polymerized tubulin proteins at 37 ºC, while they are reversibly depolymerized by cooling.

Fluorohectorite (FHT) supplied from Topy Industry was purified by centrifugation, to obtain LC nanosheet colloid. MT was obtained by incubating tublin extracted from pig brain at 37 ºC for 30 min in a polymerization buffer with 1 mM GTP and 5% DMSO. The mixture of MT and FHT solution were characterized with polarized optical microscopy (POM) and small angle X-ray scattering (SAXS).

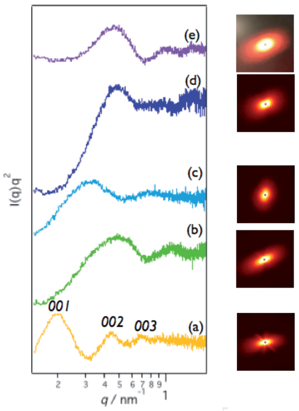

Fig. 1 SAXS patterns of the aqueous solutions of (a) nanosheets, (b)-(d) nanosheet/MT mixture and (e) MT measured at (a)(b)(d)(e) 37 ºC and (c) 5 ºC.

MT solution showed weak birefringence at 37 °C, while it became isotropic phase at 4 °C. Nanosheets/MT mixture showed stronger birefringence than each component. In the SAXS measurements, the nanosheet colloid showed the peaks due to the lamellar structure with the basal spacing of 34.1 nm. MT solution showed the pattern ascribable to the form factor of MT [4] Nanosheets/MT mixture showed a board peak (d=13.1 nm) that is different from the nanosheets or MT alone. After cooling, the peak moved to lower *q* (d = 21.3 nm) and it was recovered to original position after heating again. Thus it is supposed that structure of the liquid crystal colloid of nanosheet/MT mixture reversibly changed by polymerization and depolymerization of MT as triggered by temperature change.

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PREPARATION OF GEOPOLYMER FROM A NATURAL ZEOLITE AS A STARTING MATERIAL

Yoshikazu Kameshima*, Hiroki Baba, Shunsuke Nishimoto, Michihiro Miyake

Department of Material and Energy Science, Graduate School of Environmental and Life Science, Okayama University, 3-1-1 Tsushima-naka, Kita-ku, Okayama 700-8530, Japan
*ykameshi@cc.okayama-u.ac.jp

Geopolymer is one of the three-dimensional aluminosilicate materials formed by condensation of amorphous aluminosilicate source under highly alkaline conditions [1]. Although dehydroxylated kaolinite (metakaoline) is a good source of geopolymer, industrial wastes such as fly ash and slags have attracted attention as geoplymer raw materials because of their lower cost and lower environmental impact. Zeolite is one of aluminosilicate materials and is used for ion exchange materials, molecular sieves and catalysts. Because most industrially utilized zeolites are synthetic products, natural zeolite is only used for deodorant material and moisture absorbent. In this paper, the possibility of using natural zeolite (mordenite), which was produced relatively abundantly in Japan, as raw material of geopolymer was investigated.

Starting natural zeolite was heated at 900 ^{o}C for 3 h and heated mordenite was obtained. The heated mordenite was mixed with a predetermined amount of deionized water, sodium hydroxide, or potassium hydroxide. The resulting slurry was placed in a plastic beaker, and aged in an electrical oven kept at 50 °C. And then, the obtained cured sample was dried in same oven for several days and geopolymer sample (Si/Al=5) was obtained. The Si/Al ratio of the resulting geopolymer was controlled by additives, i.e. sodium aluminate was used for the geopolymer with Si/Al=3 and sodium silicate was used for the geopolymer with Si/Al=7. The resulting geopolymers were characterized by XRD and TG-DTA, and were observed by SEM, and were analyzed by XRF and EDS. The porosity of the resulting geopolymer was measured by Archimedes method and nitrogen adsorption method (BET).

As the geopolymerization, in other word, the dehydration polycondensation, proceeded, the sample shrank and naturally peeled off from the plastic beaker. The peeling off was observed after 1 day and 3day for the sample of Si/Al=3 and Si/Al=5, respectively. On the other hand, the sample of Si/Al=7 did not show the peeling off. Since this sample failed to retain the shape when kept in water, it was appeared that the geopolymerizaton of the sample of Si/Al=7 was insufficient. The apparent density of the sample of Si/Al=3 and Si/Al=5 was 2.35(9) and 2.25(1) g/cm^3, respectively. Additionally, the open porosity of the sample of Si/Al=3 and Si/Al=5 was 21(8) and 23(3)%, respectively. These values were comparable to those of previously reported geopolymers prepared from metakaoline [2-4]. The bending strength of sample of Si/Al=5 was ca. 17 MPa. From the above results, it was suggested that natural zeolite (mordenite) could be used as raw material for the synthesis of geopolymer.

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INTERCALATION BEHAVIOR OF PICOLINIC ACID INTO LAYERED DOUBLE HYDROXIDE

Yoshikazu Kameshima*, Daiki Kawada, Shunsuke Nishimoto, Michihiro Miyake

Department of Material and Energy Science, Graduate School of Environmental and Life Science, Okayama University, 3-1-1 Tsushima-naka, Kita-ku, Okayama 700-8530, Japan
*ykameshi@cc.okayama-u.ac.jp

Layered double hydroxides (LDHs) are represented by the chemical formula $M^{2+}_{1-x}M^{3+}_{x}(OH)_2A^{n-}_{x/n}\cdot mH_2O$ and are composed of octahedral $M^{2+}(OH)_6$ brucite-like layers, which are positively charged by the partial substitution of M^{3+} for M^{2+}, and anions are intercalated into the interlayer to achieve charge neutrality [1]. Although LDHs show anion exchangeability, it has recently attracted attention that the ion exchange reaction of carbonate type LDH occurs in alcohol solvent [2]. The ion exchange reaction of organic compounds in alcoholic solvents by LDH is a very interesting phenomenon and numerous studies have been reported. For example, Kameshima *et al.* reported that acetylsalicylic acid can be intercalated into LDH most stably when *tert*-butanol is used as a solvent [3]. However, the mechanism of this reaction has not been fully revealed yet.

Picolinic acid (PA) is an organic compound with the formula $C_5H_4N(COOH)$. PA consists of a pyridine ring with a carboxylic acid substituent at the 2-position. PA is used as an intermediate product of medicines, and metal salts are used as supplements. PA dissolves well in alcohol, but it is difficult to dissolve in water, therefore, the ion-exchange reaction in an alcohol solution is suitable for obtaining the PA/LDH composite. In this paper, the intercalation behaviour of PA to interlayer of LDH was investigated in various alcohol solvents to synthesize PA/LDH composites.

A commercially available LDH (DHT-6, Kyowa Kagaku Kogyo Co., Ltd.) was employed as the starting LDH (Mg/Al=3, CO_3 type). PA alcohol solutions of 50 mM were prepared using methanol, ethanol, 2-propanol, 2-butanol and *tert*-butanol as solvent. The starting LDH (0.2 g) was added to the PA solution (100 mL) and reacted with the solution under stirring for 0.5 - 72 h at 30 - 80 °C. After then, the solid was separated by centrifugation and washed three times with each solvent. The resulting solid was dried at 50 °C overnight in an oven. The obtained sample was characterized by XRD, FT-IR and TG-DTA.

PA intercalation to the interlayer of LDH did not occur in the case of using methanol and ethanol as solvent. In both solutions, LDH phase dissolved partially and unknown phase was observed in the case of ethanol. On the other hand, PA were successfully intercalated into the interlayer of LDH in the case of using 2-propanol, 2-butanol and *tert*-butanol as solvent. Although unknown phase was also observed in the case of 2-propanol and *tert*-butanol, no unknown phase was observed in the case of 2-butanol. Therefore, the most suitable solvent for synthesis of PA/LDH composite is considered to be 2-butanol.

About 2-butanol as a solvent, the ion exchange reaction progressed when a solution above 40 °C was used. When a solution at 40 to 60 °C was used, no ion exchange reaction occurred immediately after LDH dispersion. This phenomenon suggests that PA first undergoes deformation into a form suitable for ion exchange in solvent and then the ion exchange reaction proceeds. After a predetermined period of time, the intercalation of PA occurred. On the other hand, no initial period in which no ion exchange occurred was observed when a solution of 80 °C was used. The intercalated amount of PA increased with reaction time. As the reaction time got too long, an unknown phase was observed when a solution at 60 to 80 °C was used.

As a result, ion exchange at 80 °C for 3 h using a 50 mM picolinic acid solution of 2-butanol resulted in a PA/LDH composite with the least unreacted LDH and no unknown impurity phase.

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QUANTIFICATION OF OCTAHEDRAL IRON AND INTERLAYER POTASSIUM USING BASAL REFLECTIONS OF ILLITE

Il-Mo Kang (1)*, Hi-Soo Moon (2), Yungoo Song (2), Myung-Hun Kim (3)

(1) Advanced Geo-materials Department, Korea Institute of Geoscience and Mineral Resources (KIGAM) Pohang branch, 905, Yeongilman-daero, Heunghae-eup, Buk-gu, Pohang-si, Gyeongsangbuk-do 37559, Korea, (2) Department of Earth System Sciences, Yonsei University, 134, Sinchon-dong, Seodaemunku, Seoul, 120-749, Korea, (3) Department of Chemistry, Yonsei University, 134, Sinchon-dong, Seodaemunku, Seoul, 120-749, Korea

X-ray powder diffraction (XRD) was used as a basic tool for illite identification/quantification, expandability, polytype, and coherent scattering domain characterization [1]. However, XRD has not been extensively employed to evaluate chemical components of illite, even though XRD has economical and operational advantages as compared with chemical analyses. Because X-ray scattering efficiencies of Si, Al, and Mg are similar, XRD intensities of illite are heavily dependent on Fe and K coordinated in octahedral and interlayer sites, respectively. This phenomenon allows us to use XRD for Fe and K estimations. The goal of this study is to derive convenient equations for quantifying octahedral Fe and interlayer K using relative intensities of the illite basal reflections. For doing it, we adopted 002/005 and 003/005 ratios of illite according to three reasons. First, the 001 reflection is affected significantly by XRD instrumental geometries and preferred orientation. Second, the 004 reflection is too small to be compared with other reflections. Third, peak broadening originated from the Ka radiation doublet is dominant at higher order reflections than the 005 reflection. The layer structure factors of illite were computed for $0 \leq Fe \leq 0.4$ and $0.5 \leq K \leq 1.0$ atoms per half-unit cell using CALCLPG2, a sub-program of MudMaster [2]. Atomic coordinates and temperature correction of atomic scattering factors followed the one-dimensional modelling scheme of Moore and Reynolds (1997) [1]. The Lorentz-polarization factor for random powders and the CuKα radiation (0.15418 nm) were employed for computational simplification. As a result, the following equations were derived by regressing the data set of illite basal reflections.

$$C_{Fe}=(\ln I_{002/005}-1.807\ln I_{003/005}+1.29)/(1.241\ln I_{003/005}-3.843)$$

$$C_{K}=-(\ln I_{002/005}+0.121\ln I_{003/005}-2.592)/(1.308\ln I_{003/005}+1.984)$$

The equations could be used to quickly estimate the contents of octahedral Fe (C_{Fe}) and interlayer K (C_K) within *ca.* ±0.05 atoms per half-unit cell, respectively, if incident radiation loss is minimized and basal reflection modification caused by expandable layers is eliminated. More details are described in Kang et al. (2004) [3].

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EFFECT OF BENTONITE AND CALCIUM CARBONATE ON LEAD UPTAKE BY MAIZE GROWN IN A COARSE TEXTURED SOIL

Bocar A. Diallo, Antoine Karam*

Département des sols et de génie agroalimentaire, Université Laval, Québec, QC, Canada

The excessive concentration of lead (Pb) in contaminated soils poses a serious threat to the environment. The phytoavailability of Pb in polluted sandy soils increases under acidic conditions. Mineral amendment such as clay minerals and calcium carbonate may mitigate Pb phytoavailability and toxicity. The aim of this study was to evaluate maize (*Zea mays* L.) uptake of Pb from a sandy soil spiked with lead nitrate (100 mg/kg) and treated with bentonite (0, 10, 20, 30 and 40 g/kg) and calcium carbonate (0, 10, 20 and 30 g/kg). The treatments were studied in a complete randomized design with three replications. The results were analysed by ANOVA and the standard error of differences was used to separate the means. Regression analysis was used to establish relationships between measured parameters. After corn harvest, soil pH ranged from 5.4 (without amendment) to 7.8 (highest bentonite and calcium carbonate rate). Shoot dry matter yield (stems or leaves) and Pb uptake were significantly affected by additions of bentonite and calcium carbonate. Compared with the control, the amendment rates generally decreased the contents of Pb in the aboveground biomass. Tissue Pb concentrations ranged from 22.1 (soil without amendment) to 5.1 mg/kg in stems and from 18.3 (soil without amendment) to 6.3 mg/kg in leaves. Bioaccumulation ratio for Pb in stem biomass ($[Pb]_{\text{stem biomass}}/[Pb]_{\text{soil}}$) ranged from 0.31 in soil without amendment to 0.16 in soil treated with bentonite alone (highest rate) and to 0.09 in soil treated with calcium carbonate alone (highest rate). All treatments considered, the main effect of calcium carbonate rates on Pb uptake was more important than that of bentonite. A significant interaction on Pb uptake was obtained with bentonite and calcium carbonate rates. Concentration of Pb in stems was negatively correlated ($p \leq 0.001$) with soil pH (r=-0.628) and concentration of Ca in stems (r=-0.620). Bentonite can supply nutrients such as calcium, magnesium and potassium to the plant, and also provide sorption sites that have a strong affinity for Pb. The results suggest that bentonite and calcium carbonate added to metal-contaminated sandy soil before plant seedling decreased the phytoextraction efficiency of Pb.

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DELAMINATION KINETICS OF KAOLINITE BY DFT CALCULATIONS

Anton Kasprzhitskii, Georgy Lazorenko*, Victor Yavna, Yakov Ermolov, Kirill Ermolov

Department of Physics, Rostov State Transport University, Narodnogo Opolcheniya sq., 344038, Rostov-on-Don, Russia
akasprzhitsky@yandex.ru

Intercalation of clays, such as kaolinite, has been of considerable interest to develop materials with different rheological, surface and structural properties. Kaolinite intercalation and its application in polymer-based functional composites have attracted much attention, both in industry and in academia. It is explained by the fact that these materials frequently demonstrate remarkable improvements in desired properties as compared to the virgin polymer or conventional micro and macro-composites [1]. A variety of inorganic and organic species can be used for intercalation of interlayer spaces of Kaolinite, including formamide [2,3], dimethylsulfoxide [4], methanol [5,6], urea [7], potassium acetate [8], aniline [9], and hydrazine [10]. Intercalation of small molecules into interlayer spaces of Kaolinite can be used as a preliminary expansion step permitting insertion of large-sized, non-reactive molecules by displacement intercalation methods.

Lately, some studies have been conducted with the use of molecular simulation method to assess the intercalation of simple molecules in Kaolinite [11-13]. Simulation is useful because it allows a more detailed interpretation of experimental results, as well as it provides findings that cannot easily be derived from strictly experimental data. In the majority of cases, experimental observations alone cannot provide a clear picture of mechanism of molecular intercalation process, or influences of intercalation on clay structure. On the other hand, quantum-chemical simulations can contribute to gaining information about intercalation phenomena on microscopic level. Despite previous studies exact organization and structure of molecular complexes in interlayer space and on the edges of Kaolinite in the process of delamination demands further studies. Nevertheless, application of DFT-simulation will enable to gain additional information on the character of chemical bonds and structural organization of the complex “Kaolinite - polar molecule”.

The paper considers studies of delamination processes of Kaolinite under its intercalation by polar organic compounds. Structural and spectral characteristics of simple organic molecules under their adsorption on basal surfaces and edges of Kaolinite and in interlayer space have been studied by DFT simulation methods. Types of adsorption centers and character of chemical bonds in the system “Kaolinite-polar molecule” have been stated. Allocated positions of polar molecules determined by the peculiarities of basal surfaces of Kaolinite and presence of edge faults have been disclosed. Besides, conditions under which process of delamination of Kaolinite have been established.

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RHEOLOGICAL PROPERTIES AND STRUCTURE OF LIQUID CRYSTALLINE MONTMORILLONITE COLLOID

Riki Kato*, Nobuyoshi Miyamoto

Department of Life, Environment and Materials Science, Fukuoka Institute of Technology, Fukuoka 811-0295, Japan
miyamoto@fit.ac.jp

Inorganic nanosheets obtained by exfoliation of a layered crystal have been attracting keen interest as novel nanomaterial due to the anisotropic morphology with the thickness of 1 nm, maximum lateral width of several hundred μm. Recently, nanosheets dispersed in a solvent was found to show liquid crystal (LC) phase, which is called nanosheet liquid crystal (LC) [1]. Nanosheet LCs are potentially applicable for optical devices and composite materials with regulated structures. For the future applications, structural control of the LC phase in macroscopic to nanoscopic scales and the control of viscoelastic property are important. Although several nanosheet LCs have been reported so far, development of new materials of nanosheet LCs is important to further clarify the fundamental aspects and future applications.

Among several nanosheet LCs, clay minerals are rich in resources, environmental friendly, harmless and biocompatibile. Although clay minerals have been investigated for many kinds of applications for long time, there had been few reports on liquid crystal phases until the recent reports [2,3]. In this study, the LC phase of a natural clay mineral montmorillomnite (MMT) was identified and its viscoelastic property and structure was investigated by dynamic mechanical analysis (DMA) and small angle X-ray scattering (SAXS).

MMT nanosheets with the thickness of 0.9 nm and the average lateral size D of 540 nm, measured by dynamic light scattering, were obtained by dispersing the MMT powder (Kunipia-F from Tsukinuno, Japan) in water and removing impurity. Exfoliation into single layers was confirmed by atomic force microscope (AFM). MMT colloid showed LC phase with huge oriented domains of several cm at 2 wt%. The formation of large domain is highlighted as an important feature of the present system, distinguished from other clay and oxide nanosheet LCs already reported. At 3 wt% and above, the domain size was reduced and the colloid became a physical gel. In DMA analysis of the 3 wt% sample, G' (storage elastic modulus) was larger than G'' (loss elastic modulus) when strain is smaller than 160%, indicating that the sample is physical gel but it flows with large mechanical strain. At below 2 wt%, $G'<G''$ even at small strain, indicating the sample is always flowing. The 2 wt% sample shows intermediate behavior. In the SAXS analysis, peaks due to highly regulated lamellar structure with the basal spacing d = 60.0 nm were observed at 2 wt%. The structure order decreased at more than 3wt% and the d value decreased to 56.6 nm at 3 wt% and 35.0 nm at 4 wt%. The isotropic sample (1 wt%) also showed the peaks at d = 82 nm, indicating that the structural order is present only very locally.

In order to investigate the influence of particle size of the nanosheets, samples with average particle sizes D = 420 and 370 nm were also prepared by ultrasonication of the colloid for different duration. The critical concentration for isotropic to LC phase transition was 3 wt% for D = 370 nm, while it was 2 wt% for D = 540 and 420 nm. The threshold concentration for the formation of huge orientation domain and sol-gel transition also increased. In DMA analyses, the viscosity decreased as the particle size decreased, and the strain for sol-gel transition also decreases. In the SAXS analysis at 2 wt% and below, basal spacing increased as the particle size decreased for the samples. In contrast, the basal spacing did not depend on the size at 3 wt% and above. In addition, structure order also increased as particle size decreased. With the average particle size of 370 nm at 4 wt%, higher order peak up to seventh one was observable, indicating very highly ordered structure. Michot et al. [4] have already investigated the LC phase and rheological properties of the colloid of natural montmorillonite from Wyoming with the average size of 410 nm. While the sol-gel transition concentration is almost consistent, isotropic-LC phase transition concentration is higher (3 wt%) than the present system. The effect of chemical composition and other factors is worth investigated in detail.

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THE ROLE OF MOLECULAR INTERACTIONS ON THE MACROSCALE PROPERTIES OF SWELLING CLAYS: A MULTISCALE MODELING APPROACH

R. Katti Dinesh*, S. Katti Kalpana

North Dakota State University, Fargo, North Dakota, 58108, United States of America
*dinesh.katti@ndsu.edu

Swelling clays or expansive clays are found in various parts of the world. Due to swelling action and the related swelling pressure when constrained, these clays can cause enormous damage to the infrastructure, which is estimated to be between 13 and 20 million dollars in the United States alone. These clays are also used as barrier materials for environmental engineering applications, as drilling muds in petroleum extraction and as drug delivery carriers in the pharmaceutical industry. The predominant clay minerals in swelling clays are typically Smectite group of clay minerals with montmorillonite clay mineral being very common.

In our research, multiscale modeling and experimental approaches are used to bridge the molecular interactions between Na-montmorillonite clay and fluids to the evolution of the clay microstructure and the macroscale properties of the clay. This paper describes the significant role of molecular interactions on the macroscopic properties of swelling clays.

The authors have developed a multiscale approach that includes molecular dynamics, steered molecular dynamics and discrete element modeling tightly integrated with experiments at various length scales to elucidate the key mechanisms that influence macroscale properties of swelling clays that include swelling, swelling pressure, permeability, compressibility, etc. The molecular models of Na-montmorillonite clay developed and used in our studies mimic SWy-2 from the Clay Minerals Society and correspond to the clay used in the experiments [1,2,3]. The molecular dynamics simulations are used to evaluate the mechanical response of the clay with various levels of hydration and the relationships between binding interaction energies [4], interlayer swelling, and exfoliation. Long molecular dynamics simulations are used to evaluate fluid flow into the interlayer and for identifying the associated mechanisms [5]. Discrete element modeling simulations describe the role of particle breakdown on swelling and swelling pressure [6]. Molecular dynamics simulations of clay with fluids with a wide range of dielectric constants [7] along with experiments further illustrate the key role of molecular interactions between clay and fluids on the macroscale properties [8]. Our results indicate that the molecular interactions alter the clay microstructure. The molecular interactions between the clay and fluids along with the altered microstructure influence the macroscale properties of swelling clays.

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BIOMINERALIZATION INSIDE NANOCLAY GALLERIES: OPPORTUNITIES IN REGENERATIVE MEDICINE AND CANCER THERAPY

Kalpana S. Katti*, Dinesh R. Katti, Md Shahjahan Molla, Sumanta Kar

Department of Civil and Environmental Engineering, North Dakota State University, Fargo, 58105, ND, USA

Use of tissue engineered scaffolds has shown much promise in regenerative medicine, in particular for development of tissues and organs. Extensive materials and scaffolds design and manufacturing routes are undertaken for filling small and large defects. Tissue engineered approaches are particularly promising for large bone defect rehabilitation. Smectite clays have been used in biomedical applications for wound healing. We have made use nanoclays for tissue engineering applications for bone regeneration [1]. We have developed novel nanoclay based polymer nanocomposites using amino acid modification of the nanoclay [2]. This nanocomposite scaffold system presents an environment for bone cells and mesenchymal stem cells to grow and proliferate [3]. The nanoclay galleries in montmorillonite nanoclay are modified with amino valeric acid. This amino acid nanoclay is further used to mineralize hydroxyapatite. The mineralization of hydroxyapatite assisted by amino acids was found to be biomimetic, with characteristics of biomineralization, as indicated by morphology and mineralogy of the mineralized hydroxyapatite. In addition, on seeding the scaffolds made using the nanoclay with biomineralized hydroxyapatite and polycaprolactone, with human mesenchymal stem cells, we observe vesicular delivery of mineral packets to extracellular space initiating the biomineralization of hydroxyapatite and formation of mineralized collagen in the extracellular matrix [4]. In addition, the stoichiometry of the observed hydroxyapatite inside the vesicles is found to be fetal bone-like indicated by Ca/P rations much less than those seen for mature bone. This our material system and scaffold design using modified nanoclays is an excellent system for bone development.

Interestingly, many cancers metastasize to bone and the unique bone microenvironment represents a very attractive niche for cancer cells to migrate to and proliferate. During cancer progression, cancer cells often invade into and migrate to distant organs and form 3D organized colonies through mechanisms of metastasis. Prostate and breast cancer cells are specifically inclined to metastasize to bone. The process occurs in two unique steps. The first involving an epithelial to mesenchymal transition causing cancers to enter into blood stream. The second stage involves a mesenchymal to epithelial transition with cancer cells reaching a remote location, such as bone and colonizing there. The nanoclay based tissue engineered scaffolds and the humanoid bone creation on these scaffolds using human mesenchymal stem cells is used to culture prostate and breast cancer cells [5]. A new sequential culture method is presented wherein, human mesenchymal stem cells differentiate and create bone-like tissue which is used to culture human prostate and human breast cancer cells. The metastasis stage of cancer progression is thus enabled *in vitro* using tissue engineering regenerative medicine approaches. We observe formation of tight tumoroids on the scaffolds We report detailed microstructural, spectroscopic and gene analysis of the tumors. The various stages of metastasis are often well marked by over and under expression of specific genes. Gene expression studies o indicate genetic changes to cancer cells from qRT-PCR experiments suggest the development of the mesenchymal to epithelial transition, or the second stage of metastasis of cancer development in the tumors formed. Biomineralization in the nanoclay galleries is thus used to develop the unique microenvironment of bone that draws cancer cells to it. The biomimetic nanoclay based scaffold system presented here represents an excellent bone-mimetic environment for study of tumor formation and cancer metastasis to bone.

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CORROSION AT THE BENTONITE IRON INTERFACE

Stephan Kaufhold (1), Reiner Dohrmann (1,2), Achim Walter Hassel (3)

(1) LBEG, Hannover, Germany, (2) BGR, Hannover, Germany, (3) Johannes Kepler University Linz, Austria

Bentonites will be used as so called geotechnical barrier surrounding metal canisters containing high-level radioactive waste (HLRW). They should isolate the canister from the host rock and hence be as stable as possible. The metal canister will be hot which accelerates chemical and mineralogical reactions taking place in the bentonite. Moreover, bentonite was found to play a role concerning the corrosion of the metal canister which is one of the most important barriers in these waste repository concepts. The interaction of bentonite and iron was, therefore, investigated systematically, based on 38 well characterised bentonites (Kaufhold et al., 2015). The bentonites were used both in their natural state (natural cation population) and after saturation with Na and Ca, respectively. All bentonite samples were contacted with a precisely weighed iron pellet at 60 °C in a glove box. Bentonite and iron pellet were separated after 5 months. The extent of the corrosion was quantified by measuring the weight loss of the iron pellets. Most of the samples showed greenish colour after terminating the test which can be probably related to the formation of iron-silicates. Various studies reported on the formation of berthierine (the Fe analogue of kaolinite) or chlorites at higher temperatures. The formation of a 1:1 phase was confirmed in a separate test especially designed to produce significant amounts of the corrosion product (Kaufhold et al., 2015).

The extent of the corrosion of the pellets was compared with the bentonite properties. First of all the role of the type of counterion was identified. Most of the Ca/Mg dominated bentonites showed slightly more corrosion (weight loss of the pellets) as compared to most of the Na dominated bentonites. This can be explained by the density of the gels which formed in the laboratory test reactors. Ca bentonites mixed with water yield comparably dense gels which results in a larger number of smectite particles at the iron bentonite interface. This effect, however, has to be elucidated further. The most interesting and relevant result was found when considering Na bentonites and Ca/Mg bentonites separately. Both samples sets revealed the role of the layer charge density (determined by the alkylammonium method; Fig. 1). In conclusion, low layer charge densities lead to increased corrosion. Intermediate to high charged smectites can be used to decrease the corrosion rate.

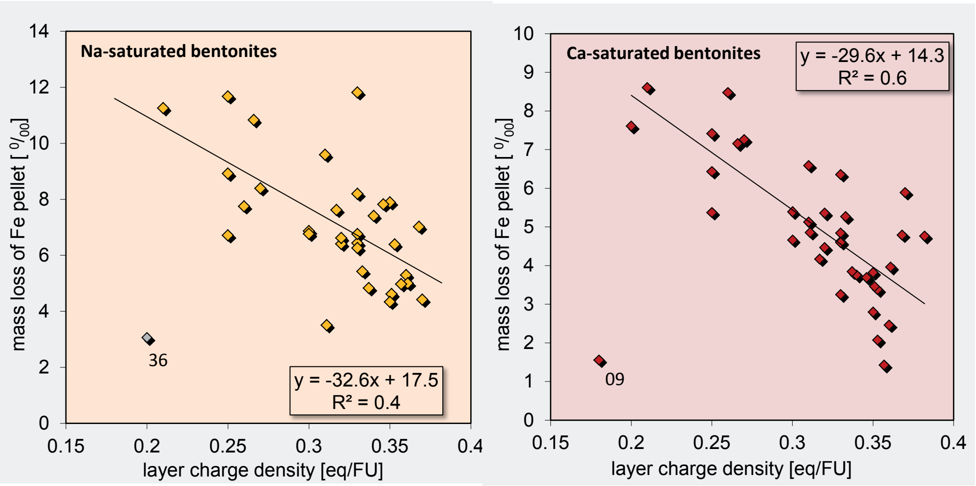

Fig. 1. Comparison of the layer charge density with the mass loss of the iron pellets of the Na-bentonite series (left) and of the Ca-bentonite series (right), Kaufhold et al. (2015).

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TRIOCTHADRALISATION OF DIOCTAHEDRAL SMECTITES

Stephan Kaufhold (1), Reiner Dohrmann (1,2), Kristian Ufer (1)

(1) BGR, Hannover, Germany, (2) LBEG, Hannover, Germany

Large scale deposition tests are conducted to identify possible bentonite alteration mechanisms and to be able to assess the long term behaviour of bentonites in geotechnical barrier systems. Bentonite is mostly used in combination with granite or other crystalline host rocks to prevent fluid migration. Such systems were and are tested in the underground laboratories in Äspö (Sweden) and Grimsel (Switzerland). In most of the large or even real scale tests Mg accumulation was found at the contact to the heater. Both infrared and X-ray diffraction revealed a certain extent of trioctahedralisation. Neither the mechanism nor the reasons for the existence of this reaction are understood so far. Notably, this reaction has been observed both at the bentonite-Fe and bentonite-Cu interface. For modelling the long term performance of bentonite in HLRW repository systems this reaction has to be understood. In principle two different reactions could lead to the trioctahedralisation. On the one hand dioctahedral smectites could dissolve and precipitate as triocthaedral smectites - a process which would be driven by a larger formation energy of saponite compared with montmorillonite/beidellite. On the other hand Mg could be added to the smectite structure similar to the process described by Hofmann & Klemen [1] and Greene-Kelly [2]. A dehydrated cation can migrate through the tetrahedral sheet finally residing in the vacancies of the octahedral sheet.

Many such studies were conducted with Li but Mg was rarely taken into account. Therefore, Kaufhold et al. [3] compared the interaction of different bentonites/smectites with Li and Mg under various conditions. A set of eight samples with varying portion of tetrahedral charge were saturated with both Li and Mg, respectively. The samples were stored at different temperatures for different times in both dry and wet environments. The CEC was determined before and after cation saturation and after storing at varying conditions. A significant CEC decrease was found for Li- and Mg saturated samples after heating at 250 °C under dry conditions. This CEC reduction depended on the portion of tetrahedral charge and was smaller for Mg samples compared with Li samples. This result demonstrated that it is much more difficult for Mg to enter the octahedral vacancies compared to Li. This can be explained by the larger hydration energy and/or slightly larger radius. However, a positive relation of the CEC reduction with the portion of tetrahedral charge was found in both cases (Li and Mg) which indicated a similar process behind the CEC reduction. Mg residing at the bottom of the pseudohexagonal holes would not explain this relation. The important result with respect to understanding HLRW bentonite performance is that i) Mg fixation can occur apart from dissolution/precipitation processes, ii) Mg fixation only occurs under dry conditions and iii) that Mg fixation can act as a sink for Mg hence leading to Mg diffusion towards the heater. The results of the present study, however, do no explain different extents of Mg accumulation and trioctahedralisation observed in the different deposition tests. Accordingly further laboratory studies are required to identify all relevant parameters. As an example, dissolution/precipitation processes could occur along with the above discussed solid state reaction.

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EFFECT OF AMMONIUM ION ON EXPANDABILITY OF MONTMORILLONITE

Ryohei Kawakita (1)*, Akito Saito (1), Hiroshi Sakuma (2), Sohtaro Anraku (3), Chie Oda (3), Morihiro Mihara (3), Tsutomu Sato (4)

(1) Graduate school of engineering, Hokkaido University, Sapporo, 060-8628, Japan, (2) National Institute for Materials Science, Tsukuba, 305-0047, Japan, (3) Radioactive Waste Processing and Disposal Research Department, Japan Atomic Energy Agency, Tokai, 319-1194, Japan, (4) Faculty of engineering, Hokkaido University, Sapporo, 060-8628, Japan
*sanigo325@eis.hokudai.ac.jp

Bentonite has been used as a barrier material in waste disposal due to the high swelling and cation exchange capacity of montmorillonite (MMT), which is the main component mineral. Sodium type bentonite is expected to be used in the geologic disposal of radioactive waste. Replacement of the interlayer Na^+ by other cations, however, induces change in the swelling behaviour of MMT. In the both ordinal and radioactive waste disposal, NH_4^+ would be respectively produced by protein degradation and nitrate reduction and may contact with Na-MMT. NH_4^+ would replace the interlayer Na^+ in Na-MMT to form NH_4-MMT, but swelling behaviour of NH_4-MMT has not been well known.

To understand the swelling behaviour of NH_4-MMT, the expandability of monovalent homoionic MMTs such as Na-, K-, Cs-, Rb- and NH_4-MMTs were investigated by XRD under controlled relative humidity (RH). Molecular dynamics (MD) calculations were also conducted to compare their expansion behaviours.

At low RH (0-20%), Na- and K-MMTs kept phase without water layer, although NH_4-, Cs- and Rb-MMTs expanded to one-water layer with larger basal spacing. Traditionally, the expansion behaviours are almost explained based on ionic radius and hydration energy of interlayer cation. However, the difference in expansion behaviour between NH_4- and K-MMTs could not be explained because ionic radius and hydration energy of NH_4^+ and K^+ are almost same.

To clarify the difference, the classical MD simulation was conducted to describe the mixing enthalpy of MMT / water molecules system by including the number of interlayer water molecules as a variable. The potential functions and parameters of MMT and water molecules proposed by Nakano & Kawamura (2006) and Suzuki & Kawamura (2004) were employed in this study. Parameters on NH_4^+ were determined to reproduce NH_4Cl structure based on the distance between nitrogen and hydrogen atoms by IR spectrum. The mixing enthalpy was used as an index to evaluate the swelling state stability. To consider the RH effect, the mixing enthalpy (H_{mix}) was calculated by $H_{mix} = H_{(MMT + nH2O)} - (H_{MMT} + n\mu_{H2O})$, where the chemical potential of water, μ_{H2O}, includes the effect of RH by $\mu_{H2O} = \mu^0 + RT\ln(P/P_0)$ (μ^0: standard chemical potential, R: gas constant, T: temperature, P/P_0: partial pressure of water). In this study, $n = 0$ to 20 water molecules were added to homoionic MMT to understand the different expansion behaviour of each monovalent homoionic MMT under different RH conditions. Series of calculated mixing enthalpy can explain the difference in expansion behaviour of different homoiconic MMT.

In the NH_4-MMT system, the hydrogen bond between hydrogen in NH_4^+ and surface oxygen on MMT was confirmed. These hydrogen bonds make large basal spacing of NH_4-MMT rather than that of K-MMT at dehydrated condition. This difference leads hydration of NH_4-MMT at low RH condition, because the expansion of MMT occurs when hydration of interlayer cation exceeds the electrostatic attraction between silicate layer and interlayer cation. Therefore, there is difference in the expandability between NH_4- and K-MMTs at low RH.

This study was partly funded by the Ministry of Economy, Trade and Industry of Japan through “The project for validating assessment methodology in geological disposal system” in JFY 2016.

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DIELECTRIC PROPERTIES OF POLYVINYLCHLORIDE-PRISTINE BENTONITE COMPOSITES

Ahmet Ugur Kaya (1)*, Selahaddi̇n Guner (2), Emi̇ne Can (3), Fatma Gozuak (3)

(1) Kocaeli University Faculty of Art&Science, Department of Physic, Kocaeli, Turkey, (2) Kocaeli University Faculty of Art&Science, Department of Chemistry, Kocaeli, Turkey, (3) Istanbul Medeniyet University, Department of Physics Engineering, İstanbul, Turkey
*ugurk@kocaeli.edu.tr

In this study, dielectric properties of polyvinylchloride (PVC)-Pristine Bentonite composites were investigated as a function of PVC loading. The composites were prepared by solution mixing technique with 1 g of bentonite suspension in 30 mL of chloroform solution, by adding PVC dissolved in 20 mL of chloroform. The resulting PVC-Pristine Bentonite mixture was filtered, the solid portion was allowed to stand at room temperature vacuum drying. Dielectric spectroscopy was carried out 1Hz-1MHz. It was observed that reel permittivities (ε') of samples were decreased with increase of PVC loading. Loss factor ($\tan\delta$) was shifted to the low frequencies according to Pristine Bentonite. Infrared spectra of samples were measured and results were supported by infrared spectroscopy. As a result, at low PVC loading, clay-PVC interaction increased and dielectric permittivities of composites decreased relative to pure bentonite.

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CLAY PHASES IN TAILINGS: HERITAGE OF PAST ORE EXTRACTION AND PROCESSING - TWO CHILEAN EXAMPLES

Manuel Humeres, Ursula Kelm*, Enrique Saez

Instituto de Geología Económica Aplicada (GEA), Universidad de Concepción, Concepción, Chile

The reprocessing of tailings is often undertaken for recovery of elements not part of former ore treatment, and at the same time to relocate tailings in an environmentally more acceptable location complying with ever more stringent environmental regulations. As opposed to the original ore deposits, secondary tailings “ore bodies” may represent very reactive environments with mineral degradation still ongoing several decades after their deposition. In order to understand this reactivity it is important to understand any comportment of ore and gangue distinct from the primary deposit mineralogy, to examine historic processing records, mine exploitation registers and mineralogy, as well as to understand impoundment operation together with its climatic and hydrologic conditions. These records are often incomplete, in particular for sites in operation well over half a century ago.

Here, mineralogical (including clay size fractions) and granulometric characterization is presented of two historic tailings deposits generated from a Cu-Mo porphyry copper and a polymetallic skarn deposit, processed over eight and two decades ago respectively. Characterizations are part of a study to evaluate element mobilization within the impoundments and early stage identification of potential mineralogical differences with respect to primary ore flotation or leaching. Sampling was carried out on drill cores or purpose cut excavations.

For the porphyry copper tailings, unimodal grain size distributions correspond to the finest tailings sediments with P80 of average 24 µm, 130 µm for bimodal and 207 µm for trimodal distributions; the latter <5% of the samples. Undamaged core samples have clay contents (<2 µm content) of 11%, whereas disintegrated core sections contain on averages <7% clay fraction. Clay phases, illite/muscovite, biotite, chlorite are present throughout the cores whereas smectite and kaolinite are predominantly found in the deepest parts of the impoundment corresponding to extraction points once located in secondary sulphide mineralization, now almost completely exploited. Biotite-vermiculite interlayered phases are likely to come from the ore deposit and do not respond to secondary alteration. Changes in flotation conditions (acid-alkaline flotation) can be monitored by pyrite content. Presence of molybdenite in the <2 µm fraction is enhanced by ultrasound treatment of clay size fraction samples. Chalcanthite and jarosite are the dominant secondary minerals together with newly formed gypsum.

For the skarn tailings similar observations apply with respect the grain size distribution as for the porphyry copper tailings, however clay phases (illite-muscovite, biotite, chlorite, chlorite-biotite regular mixed layer, smectite, kaolinite, minor pyrophyllite) do not no represent any vertical stratification but rather reflect the blending of several ores and market dependent processing by selective flotation. Iron-hardpan formation occurred in the upper parts of the tailings. Climatic conditions, such as high wind speeds result in fast drying of tailings once deposited, thus secondary phases like jarosite are best preserved in microenvironments of sediment agglomerates protected from fast drying.

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CLAY MINERAL DATING OF THE SRONLAIRIG FAULT, SCOTTISH HIGHLANDS

Simon Kemp (1)*, Martin Gillespie (2), Graham Leslie (2), Horst Zwingmann (3), Diarmad Campbell (2)

(1) British Geological Survey, Nottingham, NG12 5GG, UK, (2) British Geological Survey, Edinburgh, EH14 4AP, UK, (3) Kyoto University, Kyoto, Japan
*sjk@bgs.ac.uk

The Glendoe Hydro Scheme, above Loch Ness in the Highlands of Scotland, represents the UKs first major hydroelectric scheme in more than 50 years and generates ~180 GWh electricity/year. Temporary excavations during the project construction, at the southern end of the dam plinth, exposed a homogeneous red/green clay-rich fault gougein a host-rock of Dalradian psammite locally veined with granite. Those excavations coincidedwith the mapped trace of the subvertical Sronlairig Fault, a featurerelated in part to the Great Glen and Ericht-Laidon faults, andwhich is understoodto result from brittle deformation during the Caledonian orogeny in late Silurian to Devonian times (c. 420-390 Ma). These large-scale NE-SW to NNE-SSW-trending faults offset and modified the pre-existing ductile structures, lithostratigraphy and post-tectonic granitic intrusions and locally control the orientation of the valleys and lochs [1]. The Sronlairig Fault is interpreted as a major synthetic R-type shear that branches off the Glen Buck Fault, exhibits a clear sinistral offset, and displaces the Eilrig Shear Zone by 5 km [2].

Numerous recent studies have highlighted the potential to constrain the timing of fault gouge formation by the isotopic dating of authigenic clay minerals [3]. Three samples of the fault gouge were collected. Quantitative powder and <2 µm oriented mountX-ray diffraction (XRD)analysis indicate mica-dominated assemblages, suitable for K-Ar dating techniques. In order to constrain the timingof fault formation, a series of fine size-separates (2-0.2, 0.2-0.1, 0.1-0.05 and <0.05 µm) were isolated prior to K-Ar analysis and further, detailed XRD analysis to distinguish and quantify different mica polytypes. Novel, capillary encapsulation and analysis in a high intensity, parallel X-ray beam was employed to identify diagnostic peak positions, intensities and widths.

Coarser size-fractions are composed of greater proportions of $2M_1$, detrital illite. Finer size-fractions show increasing proportions of 1M, authigenic illite with no evidence of detrital $2M_1$ polytypes in the finest fractions. A range of approaches were trialled to quantify the illite polytypes including WILDFIRE-modelling. However, corrected peak area measurements following the guidelines of [4] proved most effective. A series of Illite Age Analysis Plots [5] were produced, plotting the proportion of the $2M_1$ polytype (±5% error bars) against the function $\exp^{(\lambda t)-1}$. Excellent R^2 values of >0.97 were obtained with a predicted mean authigenic mica/illite age of 145 Ma (Jurassic/Cretaceous boundary) and a detrital mica/illite age of 296 Ma (Carboniferous/Permian boundary).

The Carboniferous/Permian boundary age for the detrital illite suggests that the Sronlairig Fault is responding with other structures in this region to the WNW(NW)-ESE(SE) extension which becomes important for basin development and oil migration in the Pentland and Moray Firth regions [6]. The Jurassic/Cretaceous boundaryage for the authigenic illite corresponds with basin development in the Moray Firth Basin and where the Great Glen Fault and related structures may act to partition active extension in the Moray Firth region from relative inactivity in the Pentland Firth area [6,7]. These new age dates record the long-lived activity on the Great Glen Fault Zone, particularly so in post-Caledonian times with no isotopic evidence for younger tectonic overprints.

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IRON UPTAKE CHARACTERIZATION OF CLAY MINERALS COMBINING *AB INITIO* CALCULATIONS AND XAFS SPECTROSCOPY STUDIES

Annamária Kéri (1,2)*, Rainer Dähn (1), Matthias Krack (1), Sergey Churakov (1,2)

(1) Paul Scherrer Institute, Villigen PSI, Switzerland, (2) Institute for Geological Sciences, University of Bern, Bern, Switzerland
*annamaria.keri@psi.ch

Clay minerals can irreversibly bind metals in waste and soil matrices under mildly acidic to basic pH conditions. Their ability to retain radionuclides is extensively used in various concepts for the geological disposal of high level radioactive waste (HLW). In the Swiss concept for HLW, for example, spent fuel and vitrified radioactive waste will be encapsulated in thick walled steel containers (0.25 m) surrounded by compacted bentonite which contains ~75 wt.% montmorillonite. It is expected that the corrosion of the steel disposal casks under anoxic conditions will start after the re-saturation of the bentonite buffer. It is estimated that after about 10'000 years of the post disposal canisters will corrode through and a slow process of radionuclides release will start. Due to corrosion, large quantities of Fe will be present in the repository near field that might influence the in situ repository conditions and the retardation of radionuclides. It has been shown experimentally that the presence of ferrous iron in the system reduces the uptake of the radionuclides on montmorillonite due to sorption competition [1]. Additionally, the sorption of Fe itself at clay minerals can substantially be enhanced by structural ferric iron due to redox processes [2]. Therefore, a comprehensive knowledge of the processes at the clay-water interface is required [3].

It has been demonstrated that the combination of X-ray absorption fine structure (XAFS) spectroscopy techniques and ab initio calculations is a promising tool for the investigation of complex environmental systems at the atomistic level. The data analysis of XAFS spectra allow in the best cases determining the nature of the surface complexes formed at clay mineral edge sites. Molecular simulations based on density functional theory are suitable to ascertain the preferential occupation sites of the clay particles and to serve as the basis for the interpretation of XAFS data analysis [4].

In this study, Fe K-edge XAFS measurements on Fe-bearing montmorillonite was interpreted applying ab initio calculations to gain insights of the structural environment of iron present in different oxidation states and at distinct crystallographic sites in montmorillonite. Such information is essential for understanding the mechanism of the oxidative uptake of iron ($Fe^{2+}_{aq} \rightarrow Fe^{3+}_{surf}$) by clay minerals. The calculated extended X-ray absorption fine structure (EXAFS) and X-ray absorption near edge structure (XANES) spectra of structural Fe^{3+} and Fe^{2+} in montmorillonite were obtained on the basis of the ab initio molecular dynamics simulations. The calculated spectra were compared with the spectroscopic measurements. The comparison confirmed that montmorillonite incorporates iron in Fe3+ state. The analyses of the lattice energies of the substituted Fe in montmorillonite suggested that $Fe^{2+} \rightarrow Fe^{3+}$ redox reaction may occur between the Fe atoms adsorbed on the surface and incorporated structurally into the bulk.

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KAOLINITE AND BENTONITE AS AMENDMENTS IN STABILIZATION/ SOLIDIFICATION OF POLLUTED SEDIMENT - LONG-TERM ASSESMENT

Djurdja Kerkez, Dunja Radjenovic, Dragana Tomasevic Pilipovic*, Milena Becelic-Tomin, Natasa Slijepcevic, Srdjan Roncevic, Bozo Dalmacija

University of Novi Sad, Faculty of Sciences, Department for Chemistry, Biochemistry and Environmental Protection, 21000 Novi Sad, Serbia

Clays and modified clays, as aluminosilicate agents, can be used for the treatment of wastes as they contain additives to control hydration. Chemical stabilization is caused by adsorption, chemisorption or incorporation of contaminants into the crystal structure of mineral agents.

This method is commonly used for the treatment of wastes with high water content. Similar to the application of cement, clay binds water and creates a solid form. This method is applicable to wastes containing high concentration of dissolved salts and organic contaminants. The physical characteristics of the waste treated this way are suitable for compact storage and maximum utilization of space in the landfill. In this research kaolinite and bentonite, together with a certain proportion of lime, were used for stabilization/solidification (S/S) treatment of sediment polluted with toxic metals.

These originate from Great Backa Canal which is considered as one of the most polluted reservoirs in Europe.

Samples were created using 30% of clay (both kaolinite and bentonite) and 10% of lime (K30L10 and B30L10). After compaction and mixing, samples were withdrawn for testing metal leaching after 7 and 28 days (period of maturing), and after 7 years. Leaching of metals was examined using the toxicity characteristic leaching procedure (TCLP test) [1] and the German standard leaching test-(DIN 3841-4 S4) [2].

X-ray diffraction (XRD) and scanning electron microscope (SEM) analyses were also performed on the prepared monolithic matrices.

Results indicated successful S/S treatment using both clays and lime, from the aspect of all tested metals. None of the metal concentrations, for all three time periods exceeded proposed regulatory limits. However, metal concentrations in theleachate were not uniform due to variable pH and aging. Differences were also noticed between different clay treatments, possibly due to differences in their structure and physical-chemical properties. Structural microanalysis indicated the formation of dense matrices over time, with thepresence of micro cracks over long period of time. Overall our results indicated that clays, in this kind of remediation procedure can be considered successful for environmental applications.

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ALKALI ACTIVATION OF PURE CALCINED MONTMORILLONITE

Ahmed Z. Khalifa (1)*, Yiannis Pontikes (2), Jan Elsen (3), Özlem Cizer (1)

(1) KU Leuven, Department of Civil Engineering, Kasteelpark Arenberg 40, 3001 Leuven, Belgium, (2) KU Leuven, Department of Materials Engineering, Kasteelpark Arenberg 44, 3001 Leuven, Belgium, (3) KU Leuven, Department of Earth and Environmental Sciences, Celestijnenlaan 200C, B-3001 Heverlee, Belgium

One of the promising routes to make the cement-based materials eco-friendly is to use alkali-activated materials. In general, any material that has certain amount of reactive silica and alumina can be alkali activated; yet, the process and resulting material properties are dependent on the composition of the solid precursor. There is a wide range of reactive aluminosilicate materials, which can be used for the synthesis of alkali activated materials, calcined clay being the most abundant and widespread aluminosilicate source. The reactivity of the calcined clay depends on the type and the content of the clay mineral. Metakaolin, which is the dehydroxylated form of kaolinite, is one of the most frequently used precursors in alkali activation, due to its amorphous phase and high reactivity. However, other clay minerals such as 2:1 clays, which are found in natural clay deposits, have been rarely studied for the synthesis of alkali activated materials probably due to their complexity of mineralogy and structure, presence of interlayer cations and isomorphic substitution.

This study investigates the reactivity of thermally treated pure 2:1 clay minerals such as Ca- and Na- montmorillonite through alkali activation. The aim of this study is to understand the influence of the pure clay type and the influence of the interlayer cations on the activation potential and early age reaction mechanism and kinetics of montmorillonite. Three pure natural calcined clays were used: kaolinite (>95 wt%) as a reference material, as well as Ca- and Na- montmorillonite (>90-100 wt%). The two-montmorillonite clays were subjected to a purification process using the Jackson-treatment method in order to remove the residual impurities and to separate the fraction less than 2 µm, which will be used in this investigation. Afterwards, the kaolinite and montmorillonite were thermally activated at 600 °C and 800 °C respectively.

The presence of 2:1 clay minerals yields a Si/Al ratio >2, which limits the use of silicate solution as alkaline activator. A series of sodium hydroxide activated calcined montmorillonite with different solution/binder and Na_2O/Al_2O_3 molar ratios were used. Reaction mechanism and products were characterized using a series of analytical techniques such as X-ray diffraction, Thermogravimetric analysis (TGA), Brunauer-Emmett-Teller (BET) method, and ICP-OES, isothermal conduction calorimetry and scanning electron microscopy (SEM).

Keywords: alkali activation, thermally activated clays, montmorillonite.

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ADSORPTION BEHAVIOUR OF CHROMATE ON SCHWERTMANNITE

Khandala Khamphila (1)*, Keisuke Fukushi (2), Tsutomu Sato (3)

(1) Graduate school of Engineering, Hokkaido University, Hokkaido, Japan, (2) Institute of Nature and Environmental Technology, Kakuma, Kanazawa, Ishikawa, 920-1192, Japan, (3) Faculty of Engineering, Hokkaido University, Hokkaido, Japan

Nature of adsorbed oxyanions species on iron oxides are important for their adsorption behaviour under a very wide range of pH values, ionic strengths and electrolyte compositions. Among toxic oxyanions, chromate oxyanions are difficult to remove from the contaminated water, because of the presence of coexisting oxyanions in the natural systems. Iron hydroxide minerals, such as ferrihydrite and schwertmannite, are excellent adsorbents for arsenate and phosphate by formation of inner-sphere complexation. There are several published studies on surface complexation modelling of oxyanions adsorption on ferrihydrite. However, such information is lacking for the adsorption of oxyanions onto schwertmannite. In this context, the present study was undertaken to study chromate adsorption behaviour onto schwertmannite. Adsorption experiments were conducted by using synthesized ferrihydrite and schwertmannite as adsorbents and the adsorption behaviour of chromate on schwertmannite was compared with those of other oxyanions such as arsenate, phosphate, and sulfate. The adsorption experiments were conducted using several initial concentrations (0.6 mM and 1 mM) of anions included arsenate, phosphate, chromate and sulfate, with wide range of pH (3-12) and different ionic strength (0.01-0.1M, $NaNO_3$) of background solutions. Anions adsorption fractions were changed as function of pH and ionic strength. Ferrihydrite and schwertmannite showed similar adsorption capacity and selectivity for oxyanions in the following order: $H_2AsO_4^- > H_2PO_4^- > HCrO_4^- > SO_4^{2-}$. Zeta potential measurements were undertaken to understand the adsorption mechanism of oxyanions. The difference in the point of zero charge (PZC) of adsorbents before and after adsorption was larger in the following order: $H_2AsO_4^- > H_2PO_4^- > HCrO_4^- > SO_4^{2-}$. The anions showing a larger difference in the PZC indicates a strong interaction with the surface of adsorbents and thus the modification of surface charge property is large after adsorption. The difference in the PZC for chromate suggests an intermediate complex between inner and outer-sphere complex on schwertmannite. Zeta potential measurements for SO_4 sorbed ferrihydrite and schwertmannite were similar, which indicate a similar SO_4 adsorption mechanism onto ferrihydrite and schwertmannite. Therefore, an extend triple layer modelling (ETLM) of SO_4^{2-} adsorption for schwertmannite is allowed by referring that for ferrihydrite in a similar way, ETLM of chromate anion for schwertmannite was carried out by referring ETLM for SO_4^{2-}-ferrihydrite. In this study, chromate reaction equation can be represented by the both formation of inner-sphere species and outer-sphere (H-bonded) species. The ETLM of chromate adsorption for schwertmannite was setting by using the data basis of ferrihydrite ETLM. In this presentation, the ETLM results for chromate would be shown as a trial for explain the difference in adsorption behaviour of chromate from those of arsenate, phosphate and sulphate anions.

Keyword: Chromate, adsorption and schwertmannite.

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BISPYRIBAC NANOPESTICIDES FROM ANIONIC AND ALKYLAMMONIUM CATIONIC CLAYS FOR MINIMIZING WATER ENVIRONMENTAL RISKS

Rachid Khatem (1), Rafael Celis (2), Abdullah Bakthi (1), Juan Cornejo (2), Miguel Real (2), M. Carmen Hermosin (2)*

(1) Laboratory of Biodiversity and Conservation of Soil and Water.University of AbdelhamidIbnBadis, Mostaganem, Algeria,
(2) Environmental Agrochemistry, Instituto de Recursos Naturales y Agrobiologia de Sevilla, CSIC, Sevilla, Spain

The development of new formulations based on clays as smart delivery systems or nanopesticides has become an interesting strategy for decreasing the environmental impact of pesticides [1-3]. Layered double hydroxides (LDHs) or anionic clays are especially convenient as host materials for anionic or acid pesticides to decreasetheir soil leaching losses, which areoftenvery high for this type of pesticides, particularly if they have high water solubility [4]. Alkylammonium cationic clays have also been shown as good carriers for pesticides in controlled release formulations [3,5]. We prepared and compared nanopesticide formulations of a very water soluble anionic herbicide, bispyribac (BIS), as LDH and as alkylammonium clay complexes, whose water and soil behaviour were lab-tested, as smart deliverysystemsto minimize their surface and ground water impact.

The initial materials were LDH, lab-synthesized andcalcined at 500ºC (LDH500), and alkylammonium Cloisite10A (Clo10A) from BYK and supply by Comindex SA. The adsorption of bispyribac onLDH500 and Clo10A was firstly assayed. The LDH-BIS complex was prepared by regeneration of LDH500 in aqueous solution containing herbicide. The Clo-BIS complexes (20% w/w) were prepared in three ways: (i) ground mixing (GM); (ii) weak complex (WC) and (iii) strong complex (SC)^3. The characterization of the LDH-BIS and Clo-BIS complexes were done by XRD, SEM and FTIR spectroscopy. The bispyribac slow release in water and the bispyribac leaching out from the soil column experiments were designed to compare the diverse nanopesticide complexes versus its technical and commercial products (Nominee 400SC).

The L-type is othermsshowed that bispyribac adsorbed on both clays by specific mechanism and fitting to Langmuir model rendered a monolayer capacity much larger for LDH500 (Qm=1.3mmol/g) than for Clo10A (Qm=0.2 mmol/g). The XRD of LDH-BIS complex showed that layered structure was recovered and herbicidewas mainly in the interlayer with a basal spacing of 22.4 Å asan anion(~25% of AEC), besides some carbonate and nitrate, as revealed by FT-IR. The XRD of Clo-BIS complexes showed that GM displayed an unchanged Clo10A (19 Å) basal spacing, whereas the other WC and SC complexes showed an increase and broadening of d_{001} around 21 Å indicating a disordered with different interlayering grade of bispyribac. The FT-IR spectra confirmed the presence of bispyribac as anion in all the complexes. The water release profiles showed the technical product and the Clo10A-BIS GM released immediately 98% and 100% of their initialherbicide content, whereas the LDH-BIS, and Clo10A-BIS SC and WC released immediately 18, 23 and 65% reaching, after 120 h 68, 25 and 75%, thus displaying slow release profiles. The SC complex Clo10A-BIS could not be appropriated because of its very low final release. The soil column leaching studies revealed important differences among the diverse nanopesticides and with technical and commercial products. Those differences, as the corresponding water release profiles, were related with structure and interaction mechanism of bispyribac in the complexes. These results show that, combining aselection of carriers with diverse preparation modes, the resulting nanopesticides can offer a wide range of leaching risk minimization strategies.

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COMPOSITIONAL AND TECHNICAL EVALUATION OF SOME TUNISIAN AND EURO-MEDITERRANEAN COSMETICS PRODUCTS BASED ON CLAY

Khiari Imen (1)*, Sanchez Espejo Rita (2), Cerezo Pilar (3), Aguzzi Carola (3), López-Galindo Alberto (2), Viseras Iborra César (2,3), Jamoussi Fakher (1)

(1) Laboratory of Georesources, CERTE, Technopole Borj Cedria, BP273, 8020 Soliman, Tunisia, (2) Andalusian Institute of Earth Sciences (IACT), CSIC-University of Granada, Avda. Palmeras 4, Armilla (Granada), Spain, (3) Department of Pharmacy and Pharmaceutical Technology. University of Granada. Granada, Spain
*khiari_imen@yahoo.fr

Most of Mediterranean countries including Tunisia, commercialize clay based cosmetic products. In some cases, however, they could even be harmful to human health as a result of the presence of impurities, including heavy metals, quartz and other non-suitable associated phases. The presence of these impurities should be controlled and if necessary the material must be treated to eliminate them or even discarded. The final goal should always to suggest a product that can be safely applied to the patient. For these reasons, information about the mineralogy, chemistry and technical characteristics of these materials must be provided by factories or sellers, even if these substances probably vary widely in composition, texture and crystallinity, with significant effects on their properties and consequently should be controlled.

Aim of this work, was to characterize bought clayey samples of various Tunisian and some Mediterranean stores, in order to determine their suitability in therapeutic preparation of mud and/or homemade or marketed cosmetic product.

Study of these clayey samples has required a multitude of analyzes of physic-chemical characterization such as: mineralogical analysis by XRD, chemical analysis by XRF, electronic scan microscopy (MEB), thermo gravimetric analysis, cation exchange capacity (CEC), pH and cooling kinetics, permeability and rheology.

Considerable compositional and technical differences between studied clays were found. These differences should be put in consideration because they affect directly the effectiveness of final mud. With regard to the distributions and textures of particle dimensions, substantial differences were also found. Consequently, the corresponding technical properties differ considerably between samples which have similar uses and effectiveness. Most studied samples showed similar mineralogical composition (mainly constituted by smectite, with illite, kaolinite, gypsum, carbonates as calcite and dolomite, and quartz as impurities).

Smectitic clays are characterized by smoothness of their particles, which constitutes a real advantage for their possible application in geomedecine.

The most advised clays must have a high CEC, a very important specific surface (high absorption and adsorption), a pH ranging between 8.5 and 10.5; this basic character supports the exfoliating clay capacity and allows the elimination of the dead cells.

Agreeing with parameters traditionally used in pelotherapy, Tunisian clays were in agreement with the European and American standards of pharmacopeia.

On the basis of these results, and by comparison between these clays, we can conclude that they apply well to an external use as curative or cosmetic mud (low content of elements traces). In some cases, they need purification from different impurities.

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Keywords: clay based cosmetic products, clayey samples, therapeutic preparation of mud and/or homemade Clays, pelotherapy, pharmacopeia.

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ENHANCING HYDROCARBON BIODEGRADATION BY CLAY ADDING IN OIL DRILLING WASTE

Mohamed Khodja (1), Samia Haddadi (2), Hichem Chaker (1), Narimene Moudjahed (2), Khadidja Guellil (2)

(1) Sonatrach /Direction Centrale Recherche et Développement-Division Recherche et Développement Amont, Avenue du 1er novembre 35000, Boumerdès, Algeria, (2) Sonatrach/Direction Centrale Recherche et Développement-Division Technologies et Développement, Avenue du 1er novembre 35000, Boumerdès, Algeria

In the oil industry, contamination by hydrocarbons is the main cause of pollution. The selection of contaminated soils technologies is highly dependent on: geographic conditions, hydrogeology, drilling fluid composition, climate of the drill sites and environment regulations. The great problem for oil companies regarding the environmental protection issue is to know what can be perform effectively without generating anovercost that may affect competitiveness. Land farming presents satisfactory economic, scientific and environmental issues. In Arid area, soil behaviour is very sensitive comparatively to humid zone because of the limited water availability and low biodiversity. So, underthese difficult conditions, the bioremediation treatment can be improved by in-situ addition of clay minerals, especially hydrated bentonite.

The main objective of this study wasto enhance the activity of indigenous microorganisms activity. The experimental work was conducted for several months. Firstly, by using soil model to study soil-hydrocarbon adsorption with each mineral that is presentin the reserve pit (quartz, clay, carbonate and barite). Secondly, follow theautochthons microorganism population development and identify microflora performance (high biodegradation rate) present in reserve pits. The total petroleum hydrocarbon (TPH) variation in soil sample was monitored by gas chromatography, distillation, SARA analysis, total organic carbon(TOC) and coupled to microflora growth. Biodegradation stimulation was carried out byadding manure, surfactants and water. Pit Analysis showedthe presence of several microorganisms including *Pseudomonas, Enterobacter, Citrobacter, Micrococcus, Acinetobacter, Staphylococcus, Corynebacterium and Bacillus.*

The first results showedthat: (i) each mineral exhibits a specific behaviour to hydrocarbons compounds due to the difference in surface properties; (ii) oils waste amended with bentonite improved the hydrocarbons reduction until 35% (TPH) after one month of ageing; (iii) bentonite-hydrocarbons-microorganisms-water system simulated natural micro bioreactor due to bacteria immobilization on clay surface, water availability, which allows organic pollutants mobility, bioavailability and consequently increasing hydrocarbon biodegradation. Microorganisms grown in hydrated bentonite clay showed enhanced numbers in colony forming units (CFU) and prolonged survival. This beneficial effect is attributed to the sustainable supply of cationic nutrients, organic carbon, the buffering capacity of clays, and their large surface areas that accumulate nutrients, serve as attachment sites and adsorb pollutants. In perspective, further investigation will be performed with adding environmentally friendly additives to accelerate the pollutant elimination and optimize the oil waste management.

Keywords: drilling waste, biodegradation, hydrocarbon, bentonite, microorganism.

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MINERALOGY AND CHEMISTRY OF BIOTITE IN THE WEATHERING PROFILE OF GRANITIC ROCKS IN THE EASTERN PART OF FUKUSHIMA PREFECTURE, JAPAN

Ryosuke Kikuchi (1)*, Hiroki Mukai (1), Koji Ichimura (1), Toshihiro Kogure (1), Yoshio Takahashi (1), Yoichi Sakai (2)

(1) Department of Earth and Planetary Sciences, Graduate School of Sciences, The University of Tokyo, Tokyo, 113-0033, Japan, (2) Department of Chemistry, Daido University, Nagoya, 457-8530, Japan
*rkikuchi@eps.s.u-tokyo.ac.jp

Weathering and dissolution of biotite in granitic rocks play an important role in the element transport at the Earth's surface because it is a dominant source of K in soils, Mg and Fe in groundwater. Moreover, biotite limits the migration of various elements in rocks and soils due to its high sorption capacity. For example, radioactive caesium emitted by the accident of Fukushima Daiichi Nuclear Power Plant (FDNPP) have been adhered at the surface soil in Fukushima, and partially-vermiculitized biotite was the major material in the radioactive fine particles of the contaminated soil in Fukushima [1]. Although there have been many investigation of biotite alternation in other natural granitic/granodioritic environments [2,3], microscopic mechanism of biotite weathering is still unclear yet due to its heterogeneity in chemical composition among grain-to-grain scale and/or inside each grain. This study investigated mineralogical and chemical properties of biotite in the natural weathering granitic environment in the eastern part of Fukushima Prefecture in Japan, focusing on spatial distributions of constituent elements at intra-grain scale. The eastern part of Fukushima Prefecture in Japan is mainly covered by Abukuma granitic rocks formed in Cretaceous period. Our sampling point locates about 40 km southwest from FDNPP, and its geological setting is very similar to that of radioactive contaminated areas. The annual air temperature and precipitation are 10.5 ˚C and 1245 mm. The weathering profile showing from granodiorite core-stones to reddish-brown soils was exposed in steep walls recently formed by stone quarrying. Pinkish-coloured clay veins found in some part of the wall contain intensively weathered biotite. The underlying fresh rock was composed of plagioclase, quartz, K-feldspar, biotite, hornblende and accessory minerals such as apatite, zircon and ilmenite. Several weathered samples were taken from progressively weathered shells around fresh core-stones. Biotite grains of 1-5 mm in diameter were separated by sieving and hand sorting. The grains were ground into powder for Mössbauer spectroscopy and X-ray diffractometry (XRD). Several grains were impregnated in epoxy resin and cross-sectioned perpendicular to basal planes, to prepare polished cross-sections for Field-Emission Electron Probe Microanalysis (FE-EPMA) and Field-Emission Scanning Electron Microscopy (FE-SEM). Based on sample occurrence, chemical composition and crystallography, weathering states of biotite were classified into roughly two stages: (1) early weathering stage and (2) later weathering stage. (1) The early weathered biotite were found on the surface of exposed core-stones, retaining original colour of fresh rocks but being disintegrated. XRD profiles of oriented specimens showed two sharp peaks of biotite (10 Å) and vermiculite (14-15 Å), corresponding to segregated interstratified structures not physical mixing. 060 reflections of randomly oriented specimens showed a linear decrease of the *b*-axis along with an increase of $Fe^{3+}/\Sigma Fe$ ratio, owing to the decrease of ionic radii of Fe. Electron microscopy visualized K-rich-Ca-low (biotite-like) packets and K-low-Ca-rich (Ca-vermiculite-like) packets of several micrometer in width in grains. This is consistent with the XRD patterns indicating segregated interstratification. On the contrary, constituent elements of the silicate layer were conserved from original biotite. (2) The later weathered biotite were found from the slightly coloured, disintegrated rock layer to the top of soil layer. XRD profiles showed randomly interstratified structure of biotite and vermiculite, while 14-15 Å peak from vermiculite packets decreased as weathering proceed. Fe oxidation was almost completed ($Fe^{3+}/\Sigma Fe \sim 95$-100%), and the *b*-axis decreased after the completion of Fe oxidation, probably owing to the ejection of octahedral cations. FE-EPMA and FE-SEM showed heterogeneous elemental distribution, including constituent elements of silicate layers. The segregation of Ca-vermiculite and biotite was obscure. In conclusion, cation release of biotite was controlled by Fe oxidation and interlayer cation exchange in the early weathering stage, and by decomposition of silicate layers in the later weathering stage.

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MONITORING SPECIFIC SURFACE AREA AND POROSITY OF LAYERED DOUBLE HYDROXIDES ACCORDING TO SYNTHESIS METHOD AND CALCINATION CONDITION

Bo-Kyung Kim*, Gyeong-Hyeon Gwak, Jae-Min Oh

Department of Chemistry and Medical Chemistry, College of Science and Technology, Yonsei University, Wonju,
Gangwondo, 26493, Republic of Korea
jaemin.oh@yonsei.ac.kr

We investigated specific surface area and porosity of layered double hydroxides (LDHs) which were synthesized through various routes, calcined at different temperature to obtaine layered double oxides (LDOs) and reconstructed to original LDH structure. Four different synthesis methods were utilized to obtain MgAl-CO_3-LDHs: 1) coprecipitation of metal cations with sodium hydroxide (LDH-C), 2) coprecipitation followed by hydrothermal reaction (LDH-CH), 3) coprecipitation of metal cations with homogeneous urea hydrolysis (LDH-U) and 4) hydrothermal reaction after urea hydrolysis (LDH-UH). All the samples showed typical hydrotalcite structure in powder X-ray diffraction patterns with different crystallinity with respect to synthesis method. The primary particle sizes determined by scanning electron microscopy were 22, 160, 2150 and 2420 nm for LDH-C, LDH-CH, LDH-U and LDH-UH, respectively. The specific surface area of LDH samples calculated from nitrogen adsorption-desorption isotherm were highly dependent on their primary particle size: smaller particle tended to have larger specific surface area and pore volume (between LDH-C and LDH-CH) and plate like LDHs (LDH-U and LDH-UH) had larger specific surface area. All the LDHs were calcined at different temperature - 400 °C, 500 °C and 600 °C - for 10 h, showing phase transformation to periclase, a typical phase of LDO. The particle sizes and morphologies of LDOs were almost maintained compared to corresponding LDHs. However, their specific surface area and pore volume enhanced significantly, and the gap was the largest in LDH-CH sample, suggesting the effect of particle size and morphology in specific surface area and porosity. The LDOs were completely reconstructed to LDH phase in the presence of water and bicarbonate anion. The particle size, morphology and specifc surface area and porosity of reconstructed LDHs (R-LDHs) were evaluated with scanning electron microscopy and nitrogen adsorption-desorption isotherm. The chemical environment of LDH, LDO and R-LDH around aluminum was evaluated with solid state aluminum nuclear magnetic resonance spectroscopy.

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CANRINITE-TYPE ZEOLITE SYNTHESIZED FROM CA-TYPE BENTONITE USING HYDROTHERMAL METHOD

Daeyoung Kim (1), Sung Man Seo (2)*, Ki-Min Roh (1,2), Il-Mo Kang (2)

(1) Department of Nanomaterials Science and Engineering, University of Science and Technology, Daejeon 34113, Korea, (2) Advanced Geo-materials R&D Department, Pohang Branch, Korea Institute of Geoscience and Mineral Resources, Pohang 37559, Korea

Bentonite has been used in medication or cosmetic industries. However, about 80% bentonites are abandoned during the purification processes. In this study, we researched efficient use of bentonite sludge by the hydrothermal method.

Cancrinite-type zeolite was synthesized from Ca-bentonite by the hydrothermal method using aqueous Na^+ without adding any extra silica and alumina sources. The acid treated bentonite mixture slowly added to the Na^+ solution with various concentrations by vigorous stirring at room temperature. The final mixtures were placed in a convention oven at 368 K for 24 h. The final products were filtered and washed with deionized water, and then the products were dried at high temperature in an oven prior to characterization. The synthesized products were characterized by X-ray powder diffraction (XRD), scanning electron microscopy (SEM), and N_2 adsorption-desorption.

The crystallographic composition of the products was determined by XRD. The crystalline phases were identified as cancrinite-type zeolite. The high crystalline cancrinites were synthesized using high concentration Na^+ solution. The surface area of synthesized cancrinites and bentonite sludge were 50.67 m^2/g and 129.42 m^2/g, respectively, analyzed by Brunauer-Emmett-Teller method. This study showed that the activated bentonite sludge solution was converted to pure cancrinite with high crystallinity at optimized conditions. Based on the characterization results, alkali metal concentration is important key to synthesize open porous material from bentonite as layered one.

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ANTI-BIOFOULING PROPERTY OF MONTMORILLONITE COATED POLYURETHANE FILM

Hyouhg-Jun Kim (1)*, Jun Jeong Choi (2), Jae-Min Oh (1)

(1) Department of Chemistry and Medical Chemistry, College of Science and Technology, Yonsei University, Wonju, Gangwondo 220-710, South Korea, (2) College of Pharmacy, Yonsei Institute of Pharmaceutical Sciences, Yonsei University, Incheon, South Korea
jaemin.oh@yonsei.ac.kr

The biofouling on medical products can not only cause secondary infection but also reduce their performance. In order to provide anti-biofouling property to polyurethane, which are often utilized in medical product for bronchial tissue, we introduced montmorillonite coating expecting increased surface roughness and decreased surface energy. Medical grade montmorillonite (VEEGUM®R EP) and urethane binder were chosen, as they showed high biocompatibility on human bronchial epithelial BEAS-2B cell culture lines, with IC50 of 135.9 μg/mL and 3212 μg/mL, respectively. Polyurethane film was coated with aqueous suspension containing 1% montmorillonite and 35% urethane through dip-coating at 0.05 mm/s speed. The coating was hardened at 100 °C for 30 min resulting in 9μm thickness and 4B hardness by pencil standard. Through scanning electron microscopy, montmorillonite with ~ 3 μm size was found to be randomly distributed on the polyurethane film with slight agglomeration. Atomic force microscopy revealed that the surface roughness of polyurethane film enhanced from 3.8 nm to 7.5 nm upon montmorillonite coating. The water contact angle of film changed from 74.7° to 90.1° upon montmorillonite introduction, suggesting the decreased surface energy and increased hydrophobicity of polyurethane film. In order to evaluate anti-biofouling property, we exposed the film with and without clay coating to mucin and the amount of adhered mucin was quantified by Alcian blue staining assay.[1] It was revealed that anti-biofouling property of polyurethane on mucin enhanced 77% upon montmorillonite coating.

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PROTEIN ENCAPSULATION IN CLAYS FOR ENHANCED THERMAL STABILITY

Hyoung-Mi Kim*, Jae-Min Oh

Department of Chemistry and Medical Chemistry, College of Science and Technology, Yonsei University, Wonju, South Korea
jaemin.oh@yonsei.ac.kr

We encapsulated two kinds of proteins, bovine serum albumin (BSA) and hydrolysed keratin (KER), with clays such as montmorillonite (MMT), halloysite nanotube (HNT) and layered double hydroxide (LDH)to enhance thermal stability of proteins. Two kinds of clays, MMT and HNT, were utilized as purchased and LDH was synthesized by coprecipitating Mg^{2+} and Al^{3+} with sodium hydroxide solution. Protein encapsulation with MMT and HNT was carried out by simply mixing protein solution and clay suspension at room temperature with protein:clay weight ratio of 2:1. In order to encapsulate protein with LDH, reconstruction method was utilized; calcined LDH at 400 °C for 6 h was reacted with protein solution with protein:LDH weight ratio of 2:1. According to Bradford protein quantification assay and thermogravimetry, clays were determined to contain 30, 26 and 33 wt/wt% of BSA for MMT, HNT and LDH, respectively. From X-ray diffraction and infrared spectroscopy, protein encapsulating clays were determined to contain intact structured protein without significant structural modification of clays. The particle size and morphology of MMT and HNT were not significantly changed upon protein encapsulation showing various size and lamellar morphology for MMT and ~ 500 nm size and rod-like shape for HNT. The particle morphology of LDH was significantly changed by protein encapsulation showing rosette-like structure with partial agglomeration after protein encapsulation. The protein adsorption kinetic and isotherm depending on clay type were studied with Bradford assay to elucidate encapsulation mechanism. The thermal stability of protein with or without clay encapsulation was investigated by monitoring secondary structure change after exposure on various temperature.

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REACTIVE EXPERIMENTS AND GEOCHEMICAL MODELING OF CO2-CAPROCK-WATER INTERACTION IN THE POTENTIAL STORAGE SITE

Seon-Ok Kim (1)*, Sookyun Wang (1), Minhee Lee (2), Jeongpil An (2)

(1) Pukyong National University, Dept. of Energy Resources Engineering, Busan 48513, Republic of Korea, (2) Pukyong National University, Dept. of Earth Environmental Sciences, Busan 48513, Republic of Korea
*seonok@pknu.ac.kr

Caprocks with significant clay content are candidate seal layers for CO_2 geological storage. This study aims to identify the mineralogical and petrographical characteristics of caprock from drilling cores of Pohang basin as a potential CO2 storage site. Experiments and modeling were conducted in order to investigate the geochemical and mineralogical caprock effects of carbon dioxide. A series of autoclave experiments were conducted to simulate the interaction in the $scCO_2$-caprock-brine using a high pressure and temperature cell at 50 °C and 100 bar. Geochemical and mineralogical alterations after 15 days of scCO2-caprock-brine sample reactions were quantitatively examined by XRD, XRF, ICP-OES investigation. Results of mineralogical studies, together with petrographic data of caprock and data on the physicochemical parameters of brine were used for geochemical modeling. Modeling was carried out using the The Geochemist's Workbench 11.0.4 geochemical simulator. Results from XRD analysis for caprock sample showed that major compositional minerals are quartz, plagioclase, and K-feldspar, and muscovite, pyrite, siderite, calcite, kaolinite and montmorillonite were included on a small scale. Results from ICP-OES analysis for brine showed that concentration of Ca2+, Na+, K+ and Mg2+ increased due to dissolution of plagioclase, K-feldspar and muscovite. Results of modeling for the period of 100 years showed that the recrystallization of kaolinite, dawsonite and beidellite, at the expense of plagioclase and K-feldspar is characteristic. Volumes of newly precipitation minerals and minerals passing into brine were balanced, so the porosity remained nearly unchanged. Experimental and modeling results indicate the interaction between caprock and scCO2 during geologic carbon sequestration can exert significant impacts in brine pH and solubility/stability of minerals.

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CATALYTIC PERFORMANCE OF NIOBIUM OXIDE-PILLARED KENYAITE FOR VAPOR PHASE BECKMANN REARRANGEMENT OF CYCLOHEXANONE OXIME

Sun Jin Kim (1)*, Hun Jung (2), Kwang-Doeg Jung (2), Oh-Shim Joo (2)

(1) Center for Materials Architecturing, Korea Institute of Science and Technology, Hwarangno 14-gil 5, Seongbuk-gu, Seoul 02792, Korea, (2) Clean Energy Research Center, Korea Institute of Science and Technology, Hwarangno 14-gil 5, Seongbuk-gu, Seoul 02792, Korea
*skim@kist.re.kr

Pillared layered materials have attracted much attention for commercial application because of their catalytic and molecular sieving properties [1]. The layered materials pillared with inorganic clusters have pore structures, high thermal stability and high surface area like zeolites and molecular sieves. Layered silicates such as kenyaite ($Na_2Si_{20}O_{41}\cdot 11H_2O$), magadiite ($Na_2Si_{14}O_{29}\cdot 11H_2O$) and ilerite ($Na_2Si_8O_{17}\cdot xH_2O$) are known to be useful hosts for preparing pillared materials [2-4]. They have very similar properties to clay minerals [5] and the interlayer spaces are easily expanded by intercalation of long chain amines.

In this work, we have prepared niobium oxide-pillared kenyaite (Nb-Kenyaite) materials by intercalation method using octylamine as a layer-expansion agent and niobium ethoxide ($Nb(OC_2H_5)_5$) as metal precursor, respectively, and applied the pillared materials as catalysts for vapor phase Beckmann rearrangement of cyclohexanone oxime.

Nb-kenyaite materials exhibited larger surface area and basal spacing than those of H-kenyaite, which is used as a host, suggesting the formation of pillared materials with porosity. The results from NH_3-TPD and FT-IR measurements demonstrated that Nb-kenyaite materials possessed weak acid site and hydroxyl group which act as active sites in Beckmann rearrangement reaction.

For vapor phase Beckmann rearrangement of cyclohexanone oxime, Nb-kenyaite catalysts exhibited high catalytic performance. The oxime conversion reached 99.5% with lactam selectivity of 92.1% at 350 °C. The high catalytic performance of Nb-kenyaite catalysts for vapor phase Beckmann rearrangement of cyclohexanone oxime was due to the presence of porosity, acidity and hydroxyl groups formed by niobium pillaring into the layers of kenyaite.

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PREPARATION OF SIZE CONTROLLED LAYERED DOUBLE HYDROXIDE HAVING GADOLINIUM, GALLIUM AND SILVER MOIETY FOR COMPUTED TOMOGRAPHY CONTRASTING PROPERTY

Tae-Hyun Kim (1)*, Hyoung-Mi Kim (1), Dongju Seo (2), Jin Keun Park (2), Jae-Min Oh (1)

(1) Department of Chemistry and Medical Chemistry, College of Science and Technology, Yonsei University, Wonju 26493, Republic of Korea, (2) Department of Chemistry, Hankuk University of Foreign Studies, Yongin 17035, Republic of Korea
jaemin.oh@yonsei.ac.kr

Layered double hydroxide (LDH) nanoparticles containing heavy atoms such as gadolinium, gallium and silver, were prepared in order to take advantage of computed tomography (CT) contrasting ability of heavy elements. Considering the biocompatibility and effective cellular uptake, the particle size of LDH was controlled with reverse micelle method. MgAl-LDH was prepared by conventional coprecipitation method with or without reverse micelle consisting of sodium dodecyl sulfate, octane and butanol. From the scanning electron microscopy and dynamic light scattering analysis, it was revealed that the LDH synthesized with reverse micelle had average particle size of ~300 nm, without serious aggregation compared with coprecipiated LDHs. Gadolinium was introduced into LDH in the form of gadolinium diethylenetriaminepentaacetate (Gd-DTPA) which was intercalated into MgAl-LDH (GL). Gallium of silver was directly incorporated into LDH lattice during coprecipitation. In this way, GGL having both gadolinium and gallium and AGL with both gadolinium and silver moiety were obtained. The powder X-ray diffraction patterns showed all the LDHs had intended hydrotalcite structure with expanded interlayer distance upon Gd-DTPA intercalation. In order to evaluate CT contrasting property of heavy element introduced LDH, Hounsfield unit (HU), a quantitative scale of radiodensity, was measured with microCT imaging instrument. The obtained HU was 109, 144 and 212 for GL, GGL and AGL, respectively, suggesting that heavy element incorporation increased CT contrasting property of LDHs.

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IMPROVEMENT OF TISSUE REGENERATIVE POTENTIAL OF HUMAN BONE DRIVED EXTRACELLULAR MATRIX GELS BY USING CLAY NANO PARTICLES

Yang-Hee Kim (1)*, Jonathan James (1), Lisa White (2), Richard O. C. Oreffo (1), Jonathan Dawson (1)

(1) Bone and Joint Research Group, Centre for Human Development, Stem cell, and Regeneration, Faculty of Medicine, University of Southampton, Southampton, SO16 6YD, UK, (2) School of Pharmacy, University of Nottingham, Nottingham NG7 2RD, UK

Tissue regeneration can be accelerated by the use of biomaterials, which provide a biological environment and can facilitate the delivery of biomolecules to cells at sites of defected/damaged tissue. Laponite, a clay nano-particle, is particularly suitable for injection to a defect sites and, crucially, has the potential for osteo-induction for bone tissue regeneration. Laponite displays a capacity for the absorption of proteins, including growth factors, which can result in enhanced bone formation[1,2]. Extracellular matrix (ECM) gels derived from decellularized tissues contain native components and structures that can provide an appropriate environmental niche and signalling cues for cells and thus aid regeneration of damaged tissues [3,4]. However, the control and modulation of ECM physiochemical properties, such as its degradation rate, molecular incorporation, swelling, and gelation, in isolation are complex and challenging. To address these issues we combined human ECM gels with aqueous laponite suspensions and studied the resultant physiochemical properties and cell responses.

We mixed laponite (40 mg/ml) with human bone derived ECM gels (16 mg/ml) at various ratios, 25:75, 50:50, 75:25, and investigated gel stiffness, degradation, and morphology. We found that increasing the concentration of laponite improved both the formation of the gel and gel/ECM strength. To investigate gel degradation, we incubated the gels in phosphate buffered saline (PBS) for 24 hours, after which we added collagenase in PBS and incubated the gels for a further 24 hours. The addition of collagenase resulted in a rapid release profile from the ECM gels, however, an increase in the concentration of laponite in the gels resulted in reduction of ECM protein release. The results indicates that mixing laponite with ECM gels helps control the enzymatic degradation of the gels. To further understand cell behaviours on the ECM/laponite gels, human bone marrow derived marrow stromal cells (HBMSCs) were seeded on the constructs and cultured for 7 days. ECM gels lacking laponite dispersed in media resulting in cell attachment to the culture plate, a likely consequence of the fast degradation and weak gel conservation of ECM gels. In marked contrast, HBMSCs were observed on the surface of ECM gels with Laponite and examination of alkaline phosphate (ALP), to determine osteogenic differentiation potential, demonstrated high ALP activity of the cells on laponite-ECM gels. This study demonstrates the significant potential of laponite clay particles to harness the biological properties of ECM gels for tissue regeneration strategies.

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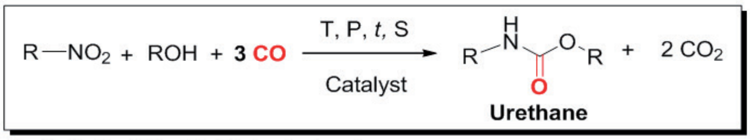
CLAY SUPPORTED METAL SELENIDES AS CATALYSTS FOR REDUCTIVE CARBONYLATION OF NITROBENZENE FOR GENERATING URETHANES

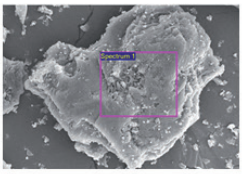
Yong Jin Kim (1)*, Vy Anh Tran (2), Thuy Tram Huynh Nguyen (2)

(1) Green Process Material Research Group, Korea Institute of Industrial Technology, Cheonan-si, 31056, Republic of Korea,
(2) Korea University of Science and Technology (UST), Daejeon, Republic of Korea

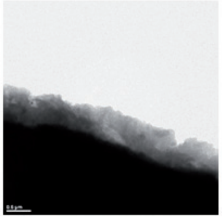
Carbamates have been widely used due to their versatilities such as intermediates in pharmaceuticals, pesticides, fertilizers or precursors of isocyanates. The conventional process for the production of carbamates involves the toxic usage of phosgene. The reductive of carbonylation of aromatic nitro compounds with carbon monoxide in the presence of alcohols has attracted much attention as a phosgene-free alternative route to carbamates.[1,2] In this study, first-row transition metal selenides (MSe_2, M = Cu, Fe, Mn, Co)/Supports (Support = Clay and Zeolites) have been synthesized and investigated as active heterogeneous catalyst for reductive carbonylation to produce urethanes (carbamates). The synthesized MSe_2/Support materials were characterized with SEM, TEM, and XPS.



R = Ph; R′ = Me; **MPC** = Methyl-*N*-phenyl carbamate

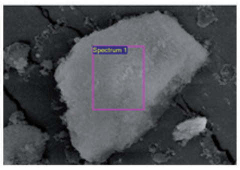


SEM Image of $CuSe_2$/MK-10

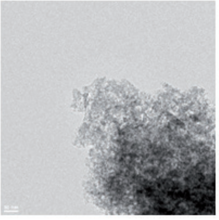


TEM Image of $CuSe_2$/FAPO

Cheap and highly active heterogeneous catalyst for carbonylation of aromatic nitro compounds to generate urethanes



TEM Image of $FeSe_2$/MK-10



TEM Image of $FeSe_2$/FAPO

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FWHM OF LOW-ANGLE BASAL PHYLLOSILICATE XRD REFLECTIONS: FITTED FUNCTIONS VERSUS DIFFRACTION TRACES

Hanan J. Kisch

Department of Geological and Environmental Sciences, Ben-Gurion University of the Negev, P.O.B. 653, Beer-Sheva 84105, Israel
kisch@bgu.ac.il

Kübler introduced the illite "crystallinity" using the half-height width or FWHM (full width at half maximum) of the XRD illite/mica reflection at 10-Å as a measure of incipient metamorphism of mica-rich rocks, measuring FWHM directly on the diffraction traces; this procedure has since been followed by the vast majority of workers. Although the FWHM values vary with the time constant for the "time width" of the receiving slit, receiving slit (°)/scan rate (°/sec) (Kisch 1990), these variations are known, have been tested on inter-laboratory standard slabs against tens of laboratories, and thus can be reliably predicted and corrected to a standard setting. However, in recent years some workers have measured FWHM of the fitted Pearson VII function rather than on the diffraction traces themselves, without ascertaining that the values thus obtained are comparable.

Comparison of the FWHM values of the Pearson VII function with those measured directly on the diffraction traces ($FWHM_{prof.}$) for more than 50 slides and slabs shows that, at least for low-angle diffraction peaks such as the illite/mica reflection at 10 Å, these show major differences: the former are *broader* by up to 0.05° Δ2Θ for $FWHM_{prof.}$ ≤0.2° 2Θ, up to 0.08° Δ2Θ (mostly 0.02-0.06° Δ2Θ) for peaks with $FWHM_{prof.}$0.21-0.42° 2Θ. and up to 0.12° Δ2Θ with $FWHM_{prof.}$ ca. 0.50° 2Θ. However, both the broadening of $FWHM_{P7}/FWHM_{prof.}$ and the reduction of the peak maxima I_{P7}/I_{prof} are more closely related to the fitting reliability R, the percentage broadening $\Delta FWHM_{P7}/FWHM_{prof}$ increasing from ≤12% for good fits with R ≥96%, through 13-22% for R = 93-95½% and 26-35% for poor fits with R = 90-92%, to up to 50% for the poorest fits with R < 90%, whileI_{P7}/I_{prof} approaches the reciprocal of $FWHM_{P7}/FWHM_{prof}$.

The Pearson VII function shows gentle curvature ("smoothening") atits tops and fast fading of the tails relative to virtually all 10-Å diffraction traces. Their broad $FWHM_{P7}$ results from the consequent lowering/"under-fitting" of the peak top sand the upper tails, and compensatory broadening/"over-fitting" of the intermediate peak flanks, most markedly for peaks with high tails *and* sharp tops. $FWHM_{P7}$ *contraction* (by up to 0.01° Δ2Θ or 14%) with respect to $FWHM_{prof.}$ is restricted to rare traces with relatively broad peak tops, with additional enhancement of the peak maximum only on traces of muscovite flakes, whose exceptionally low tails *and* relatively broad peak tops are both "over-fitted" by the Pearson VII function.

This broadening largely accounts for the high "FWHM" values in the inter-laboratory calibration curve of Warr & Rice (1994, Fig.2), and the resulting inordinately broad anchizone limits of these authors and Warr & Ferreiro-Mählmann (2015). The scatter of the points about their regression reflects the very different broadening percentage for the samples used. If the values reported were internal breadths rather than FWHM, they would be an additional 22% broader than FWHM of the Pearson VII functions.

The fitting reliabilities of the Cauchy function,94½-98½%, are almost invariably higher than those of the Pearson VII function (90½-97%) by 1-5%; their FWHM values are narrower by 0.01- 0.07° Δ2Θ or 5-17% for both the illite/mica 10-Å and the chlorite 7-Å reflections. Although they still differ somewhat from the FWHM values on the diffraction traces, predominantly still being slightly broader, they are much closer, usually within 0.02° Δ2Θ. This markedly lesser broadening of FWHM of the Cauchy relative to the Pearson VII function is the result of its stronger top curvature and notably faster tail fading (less "smoothening"). For higher-angle mica peaks, the FWHM values of the Pearson VII and Cauchy functions converge, usually differing only by 0.01-0.03° Δ2Θ for the 5-Å peak, and even less for the 3.3-Å peak.

It is therefore strongly recommended that FWHM values of the illite/mica 10-Å reflections be measured on the diffraction traces rather than on fitted functions. Where peak fitting is unavoidable, for instance in order to separate the contributions of adjoining partly resolved or unresolved reflections such as 9.66-Å paragonite or 9.2-Å pyrophyllite from the 10-Å illite/mica reflection on broadened 10-Å reflections, Cauchy rather than Pearson VII functions should be used.

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EXFOLIATED KAOLINITES AS POTENTIAL PHOTOCATALYSTS

János Kistóf (1)*, Erzsébet Horváth (2), Balázs Zsirka (2), Péter Szabó (1), Dávid Fertig (2)

(1) University of Pannonia, Department of Analytical Chemistry, P.O.Box 158, Veszprém, 8201 HUNGARY, (2) University of Pannonia, Institute of Environmental Engineering, P.O.Box 158, Veszprém, 8201 HUNGARY
*kristof@almos.vein.hu

Based on their bandgap values, kaolins can have semiconductive and photocatalytic properties enabling them to be used as potential photocatalysts.

Kaolinite nanostructures and silver-coated kaolinite nanohybrids were made from ordered (Hinkley Index, HI=1.4) and disordered (HI=0.3) kaolins via intercalation/deintercalation. The book-type kaolin built up from tetrahedral(T)-octahedral(O) double layers has very low photocatalytic activity. At the same time, the nanostructures made of individual TO layers show photochemical activity in spite of the fact that their bandgap values are comparable to those of the book-type ones. The presence of Ag on the surface significantly reduced the bandgap and shifted the excitation wavelength towards the visible range. This phenomenon supports the supposition that kaolinite has some semiconductive character. This work presents the connection between photocatalytic activity and morphology.

The surface activity of kaolinite nanostructures and their Ag-hybrids was studied through the decomposition of sodium-benzenesulfonate (BS) test compound with attenuated total reflection Fourier transform infrared spectroscopy (FT-IR/ATR). BS decomposition can be detected on the nano-kaolinite surface but with low efficiency. The presence of silver can significantly improve the mineralization efficiency.

No correlation was found between the activity and the quantity of Ti and Fe contaminants and the amount of Ag on the surface. However, the activity could be correlated with the order-dependent morphology (mixture of semi-hexagonal and nanoscroll-type structures), the pore size and with the increase of the surface coverage.

Kaolins are natural, cheap and abundant raw materials. On the one hand, revealing the parameters influencing their photochemical activity can contribute to the cost optimization of environmental technologies (e.g. water treatment processes). On the other, understanding the physico-chemical background of the catalytic properties is of importance from environmental points of view contributing to the understanding of the role of clay minerals in the purification of natural waters.

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TALE OF THE UNEXPECTED: HOW HALLOYSITE PREDISPOSES FLOW SLIDING

Max O. Kluger (1)*, Vicki G. Moon (2), Stefan Kreiter (1), David J. Lowe (2), G. Jock Churchman (3), Daniel A. Hepp (1), Tobias Mörz (1)

(1) MARUM-Center for Marine Environmental Sciences, University of Bremen, Leobener Straße, 28359 Bremen, Germany, (2) School of Science, University of Waikato, Private Bag 3105, Hamilton 3240, New Zealand, (3) School of Agriculture, Food and Wine, University of Adelaide, Adelaide, SA 5005, Australia

In many regions around the world, tephras from volcanic eruptions cover wide areas of the landscape. With time, the primary constituents of tephras may alter to the low-activity clay mineral halloysite, which has often been associated with layers that are susceptible to damaging and unpredictable flow slides. However, the precise role of halloysite in the development of the high mobility during landsliding is unknown. In this study [1], a succession of altered tephras was analysed, having been involved in a recent flow slide in North Island, New Zealand. We found a new open-sided spheroidal halloysite particle shape in the form of "mushroom caps" that apparently governed the development of high mobility in the failure zone during landsliding. We suggest that the rearrangement in the halloysite texture during the failure process reduced the attractions between the particles at nanoscale dimensions and thus predisposed flow sliding. Our findings contribute to an improved understanding of the mechanisms of flow sliding in altered tephras rich in halloysite.

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TWO TYPES OF CHLORITE TRANSFORMED FROM BIOTITE BY HYDROTHERMAL ALTERATION OF GRANITE

Toshihiro Kogure (1)*, Takahiro Ishii (1), Ryosuke Kikuchi (1), Ritsuro Miyawaki (2), Takashi Yuguchi (3)

(1) Department of Earth and Planetary Sciences, Graduate School of Sciences, The University of Tokyo, Tokyo, 113-0033, Japan, (2) National Museum of Nature and Science, Tsukuba, 305-0005, Japan, (3) Department of Earth and Environmental Sciences, Undergraduate and Graduate School, Yamagata University, Yamagata, 990-8560, Japan
*kogure@eps.s.u-tokyo.ac.jp

Chlorite commonly forms by hydrothermal alteration of biotite in granitic rocks. This "chloritization" mechanism of biotite has been paid attention and investigated for a long time to understand alteration history of granitic rock which is one of the most common lithofacies. However, it looks that previous studies have focused either crystallographic [1,2] or chemical aspect [3] of the chloritization, not both. This study investigated the chloritization process of biotite, by analysing both the crystal structures and chemical compositions of the chlorite. As a result, a new insight for the chloritization, simultaneous occurrence of the two transformation mechanisms, is proposed.

The rock investigated was Toki granite, distributed in Central Japan. The sample was collected from the borehole in the Mizunami Underground Research Laboratory; in the altitude range from -274 m to -314 m above sea level [3]. Observation of the petrographic thin sections revealed that the granite contains biotite with various stages of chloritization. Generally biotite grains of various chloritization are homogeneously distributed in a thin section. X-ray diffraction (XRD) patterns obtained using a Gandolfi camera confirmed that the dominant polytype of unaltered biotite is 1*M* and the polytypic group of the emerald-like coloured chlorite grains is II*bb*. Electron microprobe analysis revealed that emerald-like coloured, completely chloritized grains contain no titanium (Ti) which is a constituent element of biotite in granite ("Ti-free chlorite"). On the other hand, element mapping of partially chloritized biotite grains indicated that the grains contain thin regions with no potassium (namely no biotite component) but with a certain amount of Ti. Considering existence of other elements, these thin regions are also considered to be chlorite ("Ti-bearing chlorite"). Quantitative analysis of these Ti-free and Ti-bearing chlorite showed different Al contents and Mg/Fe ratios between them, beside the amount of Ti. Investigation using TEM confirmed that both Ti-free and Ti-bearing chlorites are really "chlorite", from electron diffraction and high-resolution imaging.

This compositional difference can be ascribed to different chloritization mechanisms; Ti-bearing chlorite took over the 2:1 layer from biotite, and Ti-free chlorite was formed via dissolution-recrystallization process. In biotite, Ti is expected to locate in the octahedral sheet of the 2:1 layer. Hence, chlorite transformed from biotite must contain Ti, if the 2:1 layer was inherited from biotite without significant cation diffusion. On the contrary, chlorite can be Ti-free, if the 2:1 layer was once dissolved and new 2:1 layers formed from the hydrothermal fluid. In this case, Ti formed titanite, $CaTiSiO_5$, which is common within chloritized grains, with calcium and silicon transported via the fluid. In TEM, Ti-bearing chlorite showed a diffraction pattern indicating a mixture of different polytypic groups, indicating structural discontinuity with completely chloritized grains which were II*bb* from XRD. II*bb* is considered to be the most stable polytypic group and expected to form if chlorite was formed from solution. However, if chlorite was transformed from biotite via a solid-to-solid pathway inheriting the 2:1 layer, complete II*bb* stacking may not be expected owing to the difference of the interlayer structures between biotite and chlorite [2]. Finally high-resolution imaging support that Ti-bearing chlorite inherited the 2:1 layer from biotite, because this chlorite has 2:1 layers whose orientation is uniform, which is the same characteristic as biotite-1*M*. On the other hand, Ti-bearing chlorite consists of 2:1 layers whose orientation is considerably disordered.

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CESIUM-DESORPTION BEHAVIOR OF WEATHERED BIOTITE TO UNDERSTAND THE DYNAMICS OF RADIOACTIVE CESIUM CONTAMINATING FUKUSHIMA SOILS

Hiroki Mukai (1), Toshihiro Kogure (1)*, Yoshio Takahashi (1), Kenji Tamura (2), Tsuyoshi Yaita (3)

(1) Department of Earth and Planetary Science, Graduate School of Science, The University of Tokyo, Tokyo, 113-0033, Japan, (2) National Institute for Materials Science, Tsukuba, Ibaraki 305-0044, Japan, (3) Quantum Beam Science Center, Japan Atomic Energy Agency, Sayo, Hyogo 679-5148, Japan
*kogure@eps.s.u-tokyo.ac.jp

As six years has passed after March 2011, ^{137}Cs is now the main source of the radiation in Fukushima, due to its abundance and relatively long half-life. Hence, the state and dynamics of ^{137}Cs in the contaminated soil should be investigated in detail for the solution of the radioactive pollution. We reported, using autoradiography with micro-processed imaging plates (IPs) and various electron microscopic techniques, that partially-vermiculitized biotite which is termed weathered biotite (WB) in this study, is a major adsorbent of radioactive cesium in the actual soil collected from Fukushima [1]. Furthermore, from the sorption experiments using very dilute ^{137}Cs radioisotope solutions which were comparable to the actual contamination level in Fukushima, it was demonstrated that WB sorbed Cs far more than other clay minerals [2]. After these findings, we have investigated Cs-desorption properties of WB to understand the dynamics of radioactive cesium in Fukushima.

Radioactive cesium (^{137}Cs) was sorbed to WB with the concentration comparable to that in the actual WB collected from Fukushima, and desorption ratio for individual mineral particles was estimated by IP autoradiography [1]. ^{137}Cs sorbed to WB by immersing the mineral particles in the ^{137}Cs solution for one day was hardly desorbed by immersing in solutions of KNO_3 (1 M), $CsNO_3$ (1 M) and NH_4NO_3 (1 M), but mostly desorbed by $NaNO_3$ (1 M), $LiNO_3$ (1 M), HCl (0.1 M) and HNO_3 (0.1 M). ^{137}Cs was hardly desorbed from the WB by natural seawater in spite of abundant Na^+ (0.47 M). The desorption experiments with NaCl + KCl solution indicated that K^+ inhibited ^{137}Cs desorption from WB in the seawater. Such dependence of the desorption behavior of WB on the electrolyte solutions was found to be corresponding to the collapse of the hydrated interlayer by K^+, Cs^+ and NH_4^+, from X-ray diffraction analyses. Desorption of ^{137}Cs by HCl and HNO_3 is probably by the dissolution of the surface biotite layers where ^{137}Cs was trapped. In case of ferruginous smectite which also sorbs Cs efficiently, the sorbed ^{137}Cs was almost desorbed by natural seawater.

If the duration for the sorption was longer than around one week, ^{137}Cs in WB became hardly desorbed even by the treatment with the solutions of $NaNO_3$ and $LiNO_3$, suggesting that Cs sorbed in WB became more stable with time. Probably Cs sorbed in WB has migrated with time, to find more attractive interlayer sites in WB. These results imply that radioactive cesium sorbed in the granitic soil in Fukushima is very stable and almost difficult to be desorbed by electrolyte solutions including seawater, as almost six years have passed after the accident.

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IMAGING OF EXTREMELY BEAM-SENSITIVE CLAY MINERALS USING A HIGH-RESOLUTION AND HIGH-SPEED CMOS CAMERA

Toshihiro Kogure (1)*, Fumihiko Uesugi (2), Masaki Takeguchi (2)

(1) Department of Earth and Planetary Science, Graduate School of Science, The University of Tokyo, Tokyo, 113-0033, Japan, (2) TEM station, National Institute for Materials Science (NIMS) TEM Station, Tsukuba, Ibaraki 305-0047, Japan
*kogure@eps.s.u-tokyo.ac.jp

Although recent transmission electron microscopy has attained a resolution less than one angstrom, it is often difficult to demonstrate such performance for beam-sensitive clay minerals. On the other hand, high-resolution (HR) imaging with high-quality to obtain the information for stacking sequence, cation distribution, planar defects, interstratification, etc. in clay minerals is still demanding. One of the authors has been struggling against this problem for about two decades. Although it is not a quantitative result, electron energy does not influence the degradation speed of clay minerals significantly. Although rise of the specimen temperature by radiation definitely accelerates the radiation damage, specimen cooling using a cold-stage holder was not effective, probably due to a low heat conductivity of clay minerals.

A successful way to obtain HR images from beam-sensitive clay minerals is to reduce electron dose on the specimen and record the images before amorphization. Kogure et al. [1] succeeded for the first time in recording HR images of tubular halloysite, which is extremely beam-sensitive among clay minerals, using a new TEM with computer-assisted minimal dose system [2]. In the system, electron pre-dose before recording images was minimized by a factor of ~ 100 compared to the experiments using conventional TEMs.

Very recently a new CMOS type camera with a high performance, Gatan OneView, has been commercialized. This high sensitivity camera can acquire images of 4K x 4K pixels with a rate of ~ 25fps. Using the camera, HR images can be recorded continuously like “video”. By moving the TEM stage carrying dispersed clay minerals during video recording, HR images can be obtained without electron pre-dose, if we encounter grains with proper crystal orientation and specimen height. Such opportunity is sufficiently expected for specimens such as halloysite with a tubular form.

This figure is an example of the successful images using OneView camera. The TEM used was a JEOL ARM-200F with a cold-type field emission gun operated at 200 kV and a CEOS hexapole Cs-corrector for the image-forming lens. Five continuous images were accumulated to improve the S/N ratio. Two-dimensional lattice contrast similar to our previous work [1] is clearly visible.

This work was supported by NIMS microstructural characterization platform as a program of “Nanotechnology Platform” of the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan.

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TOPOTACTIC CONVERSION OF LAYERED SILICATE RUB-15 TO SILICA SODALITE THROUGH INTERLAYER CONDENSATION IN *N*-METHYLFORMAMIDE

Masakazu Koike (1)*, Yusuke Asakura (1), Yoshiyuki Kuroda (2), Hidehiro Tsuzura (1), Hiroaki Wada (1), Atsushi Shimojima (1), Kazuyuki Kuroda (1,3)

(1) Department of Applied Chemistry, Faculty of Science and Engineering, Waseda University, Tokyo, 169-8555, Japan, (2) Waseda Institute for Advanced Study, Waseda University, Tokyo, 169-8050, Japan, (3) Kagami Memorial Research Institute for Materials Science and Technology, Waseda University, Tokyo, 169-0051, Japan.
kuroda@waseda.jp

Topotactic conversion of layered silicates through interlayer condensation has attracted much attention as an alternative route to the synthesis of zeolites [1]. The conversion of layered silicates into zeolites is advantageous to obtain unique frameworks, new compositions, and morphologies. In many cases, the control of the stacking sequence of silicate layers by intercalation of organic compounds is essential for interlayer condensation [1]. But, this method suffers from the formation of defects in the products caused by gradual elimination of interlayer organic compounds during calcination. Recently, we have reported that refluxing of layered octosilicate intercalating organic compounds in *N*-methylformamide (NMF) is effective to interlayer condensation without the elimination of the interlayer organic compounds [2]. The residual organic compounds were removed by calcination after the interlayer condensation. However, the applicability of this method to other layered silicates has not been fully understood. Layered silicate RUB-15 ($[(CH_3)_4N]_8[H_8Si_{24}O_{56}]\cdot 20H_2O$) is converted to SOD-type zeolite (sodalite) by intercalation of acetic acid and calcination, though the resultant silica sodalite contains a small amount of defects and an amorphous phase [3,4]. In this study, we focus on the application of the refluxing method for the topotactic conversion of RUB-15 to silica sodalite with less defects. RUB-15 was stirred in 6 M acetic acid for 3 h for the exchange of interlayer cation ($(CH_3)_4N^+$) with acetic acid (denoted as Ac-RUB-15) according to the previous reports [3,4]. Ac-RUB-15 was then refluxed in NMF at 180 °C for 1 h for interlayer condensation (denoted as NMF(180rf)-Ac-RUB-15). The residual organic compounds were removed by calcination at 800 °C for 5 h (denoted as cal-NMF(180rf)-Ac-RUB-15). The powder XRD pattern of Ac-RUB-15 shows that the basal spacing of Ac-RUB-15 largely decreases from that of RUB-15 by 0.64 nm, and the CHN data show that the amounts of N decreased, indicating that interlayer cation was mostly exchanged with acetic acid. The conversion of Ac-RUB-15 into sodalite through refluxing in NMF was confirmed from the powder XRD pattern of NMF(180rf)-Ac-RUB-15. The ^{29}Si MAS NMR spectrum of NMF(180rf)-Ac-RUB-15 shows Q^4 signal at -115 ppm, and the substantial decrease in the intensity of Q^3 signals; thus, most of the interlayer Si-OH groups were condensed between the layers. The SEM images show that the platelike morphology was retained after refluxing, indicating that RUB-15 was topotactically converted to silica sodalite. In addition, the FT-IR spectrum of NMF(180rf)-Ac-RUB-15 shows the absorption bands due to C=O and N-H, originating from the organic compounds present inside the sodalite framework. After calcination, all XRD peaks of cal-NMF(180rf)-Ac-RUB-15 assignable to sodalite were fully retained. The removal of the residual organic compounds such as NMF, acetic acid, and their decomposed products was confirmed from the CHN results. The ^{29}Si MAS NMR spectrum of cal-NMF(180rf)-Ac-RUB-15 shows that the intensity of the broad Q^3 signal substantially decreased, if compared with those of the other calcined samples (that prepared by direct calcination of Ac-RUB-15 as previously reported [3,4], and that prepared by intercalation of NMF at room temperature with stirring and subsequent calcination). These results indicate that silica sodalite with lesser amounts of defects was obtained. In conclusion, silica sodalite was successfully prepared by refluxing layered silicate RUB-15 intercalating acetic acid, in NMF. The refluxing method is quite useful for interlayer condensation of RUB-15 without elimination of interlayer organic compounds, which leads to the formation of lesser amounts of defects, if compared with the conventional calcination method.

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RHEOLOGICAL PROPERTIES AND MODEL DESCRIPTION OF DIFFERENT ORIGIN CLAYS USED IN DRILLING FLUIDS

Mustafa Versan Kok

Dept. of Petroleum and Natural Gas Engineering, Middle East Technical University, 06800, Ankara-Turkey
kok@metu.edu.tr

In this research, X-ray diffraction, scanning electron microscopy (SEM), thermogravimetry (TGA) and variable Fann viscometer was used in order to identify and determine the physical properties of drilling fluids those composed of different origin clay samples. All the drilling fluid formulations was prepared according to the API RP-13B.

The XRD analysis of bentonite samples showed that the major clay mineral constituents comprise smectite and montmorillonite. Quartz, kaolinite, mica, cristobilite, and illitewas also present at minor amounts. The bentonite samples also included minor amounts of mixed-layer illite-smectite and chlorite. In the scanning electron microscopy (SEM), it was observed that the quartz grains were covered with clay mineral layers and aggregated by thin chains of clay mineral particles. In the thermogravimetric analysis (TG/DTG) of different clay samples, distinct weight loss regions were observed in different heating rates. The weight loss region between 20-80 °C is attributed to the loss of physically bonded water from the exchange layer. The second weight loss region was attributed mainly to the loss of structural water (lattice water).

Six different (600, 300, 200, 100, 6, and 3) readings at standard Fann viscometer speeds were determined in order to estimate the rheological model parameters of drilling fluids The concepts involving shear stress and shear rate and their measurements enable to identify the mathematical description of the flow of drilling fluids. The amount of force applied to a fluid determines the shear rate; on the other hand, drilling fluid behavior resistance of the fluid to the applied rate of shear or force is called the shear stress. Most drilling fluids do not confirm exactly to any of the proposed models, but drilling fluid behavior can be predicted with accuracy sufficient for practical purposes by one or more of them. There are many proposed models in the literature, some of them are widely used and accepted, while use of some are very limited. Four different rheological models known as Bingham Plastic, Power-Law, Hershel-Bulkley, and Robertson-Stiff was used by explicitly solving the required number of equations simultaneously [1-2].

Different statistical techniques (variance, standard deviation, coefficient of variation, mean and sum square error, skew, mean and median) were also used in order to see how calculated shear stress values was closed to the observed values. It was observed that Power Law model best represented this relationship.

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CATALYTIC EFFECT OF CLAY IN CRUDE OIL COMBUSTION

Mustafa Versan Kok

Dept. of Petroleum and Natural Gas Engineering, Middle East Technical University, 06800, Ankara-Turkey
kok@metu.edu.tr

In this research, the effect of heating rate and different clay concentrations on heavy crude oils in limestone matrix was investigated by differential scanning calorimeter (DSC) in which the heat flow rate of the samples as functions of temperature were recorded continuously. DSC experiments were performed at three different heating rates (3, 5 and 10 K min^{-1}) under an air flow rate of 50 ml min^{-1}. Prior to experiments, temperature calibrations of the differential scanning calorimeter (DSC) were performed using indium as reference. Reproducibility of the experiments was acceptable and the experimental data presented corresponds to the different operating conditions are the mean values of the runs carried out twice within the experimental error of less than ±0.5%.

Two different reaction mechanism were observed known as low temperature oxidation (LTO) and high temperature oxidation (HTO) reactions. These two reaction regions involve quite different chemical reactions, but occur across overlapping temperature ranges. With the addition of clay concentrations (10 and 20 wt.%) the reaction regions, temperature intervals and the corresponding peak temperatures are shifted to lower temperatures regions. This is the indication that the addition of clay to porous matrix significantly affects the fuel deposition and high temperature oxidation regions.

In the kinetic analysis two different methods were used. For both models, divergences appeared in the activation energy values that can be explained with the different equation parameters and assumptions that those models are based on. It was observed that as the clay content in the porous matrix increased from 10 to 20 wt%, activation energy values are decreased in the same order.

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LIESKOVEC BENTONITE - CHARACTEIZATION AND PROPERTIES

Peter Komadel (1)*, Jana Madejova (1), Slavka Andrejkovicova (2), Reiner Dohrmann (3) Ivan Janotka (4)

(1) Institute of Inorganic Chemistry, Slovak Academy of Sciences, Bratislava, SK-845 36 Slovakia, (2) Planetary Environments Laboratory, NASA Goddard Space Flight Center, Greenbelt, CRESST/USRA, Columbia, MD, USA, (3) BGR, Bundesanstalt für Geowissenschaften und Rohstoffe, D-30655 Hannover, Germany, (4) Building Testing and Research Institute, SK-821 04 Bratislava, Slovakia

This contribution will be a summary of our extensive investigation of Lieskovec bentonite (Central Slovakia) and its fine fractions. This bentonite was developed from andesitic pyroclastics and redeposited after a short distance transport, which added quartz to the bentonite [1]. Greater iron content in bentonites affects the clay colour, frequently making it yellowish or even brownish. This is often the consequence of having a part of total iron extraneous to smectite layers, bound in iron oxides or oxohydroxides, typically in goethite. From systematically sampled Lieskovec deposit the clay samples show an iron-rich montmorillonite as the main mineral, whereas the admixtures present in all samples include kaolinite, quartz, cristobalite and plagioclase, while muscovite and orthoclase appear in most samples. The bentonite is relatively homogeneous as is demonstrated by chemical composition and quantitative analysis using Rietveld refinement. Total Fe_2O_3 content (5-9 wt.%) in Lieskovec samples is higher than in most other Slovak bentonites. Mössbauer spectroscopy shows that Fe(II) covers less than 5 wt.% of total Fe. Goethite and/or hematite are not present in all clay fractions separated from the raw bentonite and they contain up to 26 wt.% of total Fe. Low tetrahedral Al and octahedral Mg substitutions cause that the smectite is of lower charge than montmorillonite separated from the better known Slovak bentonite Stará Kremnička - Jelšový potok. This is in accord with the absence of the AlMgOH bending vibration in the IR spectra of the Lieskovec samples.

Enhancement of geotechnical parameters of Fe-rich bentonite of lower smectite content (L = Lieskovec, 29-56% montmorillonite) by addition of an Al-rich bentonite of higher smectite content (JP = Jelšový potok, 64% montmorillonite) was on materials with L:JP mass ratios of 65:35, 75:25 and 85:15. Addition of more expensive Ca^{2+}-JP to Ca^{2+}-L bentonite caused increase in some geotechnical properties, such as liquid limit (w_L) by 20% and water adsorption measured by Enslin test (E_S) by 50% compared to raw Ca^{2+}-L samples; however, the parameters were still insufficient for applications of Ca^{2+}-blends for sealing purposes. After natrification of the blends with soda ash the geotechnical parameters markedly improved. The primary factor affecting the geotechnical properties of the blends in this series was smectite content in L bentonite along with the L:JP ratio. Higher smectite and higher JP contents caused increased liquid limit and water adsorption by Enslin test values and decreased permeability coefficients. The highest w_L and E_S values for the Na-L11/JP blend resulted from the highest smectite content in L11 (56%) while low values for Na-L5/JP blend were the consequence of the lowest smectite content in L5 (29%). Natrification of Ca^{2+}-L samples to their Na^+-counterparts resulted in increased liquid limit values by 95% in comparison with the Ca^{2+}-forms and water adsorption by Enslin test by 65%. Permeability coefficients of the order of 10^{-11} m.s^{-11} for all the blends were sufficiently low. The liquid limit and water absorption values of the blend containing 65 mass % of Na^+-L and 35 mass % of Na^+-JP bentonites fulfilled all the requirements on geotechnical parameters of bentonites used in GCLs, the details are available [3] and will be discussed in the presentation.

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KANEMITE AS A PRECURSOR FOR THE SYNTHESIS OF PHOTOACVTIVE LAYERED MATERIALS

Anna Koteja*, Karolina Góra, Jakub Matusik

AGH University of Science and Technology, Faculty of Geology, Geophysics and Environmental Protection, Department of Mineralogy, Petrography and Geochemistry, al. Mickiewicza 30 30-059 Kraków, Poland
*akoteja@agh.edu.pl

Kanemite is a layered sodium silicate ($NaHSi_2O_5 \cdot 3H_2O$), that possesses the ability to exchange its interlayer cations [1]. Thus the intercalation of the mineral with cationic surfactants is relatively easy and is done through the ion-exchange process. The organo-kanemite is an excellent precursor for further modifications leading to a material with novel and functional properties. Photoactive layered materials are produced through the combination of a layered structure and a photoactive organic compound such as azobenzene (Az). Az molecule in normal conditions occurs in the form of a stable *trans*-isomer. UV radiation induces the conformational change of Az into the metastable *cis*-isomer and the reaction is reversible [2]. The isomerization of Az molecules intercalated into the interlayer space of a layered mineral influences the whole organo-mineral complex. Appropriately designed photoactive complexes may serve as unique devices controlled remotely with light at nanoscale. The research objective was to synthesize a kanemite-azobenzene material that performs UV induced basal spacing shifts.

The kanemite synthesis was based on the procedures proposed in previous reports [3,4]. The obtained mineral was ion-exchanged with alkylammonium surfactants: alkyltrimethylammonium - C_n and alkylbenzyldimethylammonium - BC_n ions, where n stands for the number of carbon atoms in the alkyl chain and is equal to 12,14, and 16. Subsequently the organo-kanemite samples were ground with Az at 0.2 weight ratio and the mixture was heated at 80 °C for 24 h. The modified samples were characterized with XRD, FTIR and CHN elemental analysis. The Az-kanemites were treated with UV light (365 nm, 10 mW/cm^2) for 0.5 h and immediately after that the XRD patterns were collected.

The ammonium salts intercalation resulted in the d_{001} basal spacing increase. The d_{001} values were equal to ~25 Å for C_{16} and BC_{16}, ~27 Å for BC_{14} and BC_{12} and ~34 Å for C_{14} and C_{12}. This values suggested a paraffin type arrangement of the molecules. The FTIR spectra revealed bands attributed to the C-H group vibration at 3000-2800 cm^{-1} and ~1500 cm^{-1} regions. Also the CHN elemental analysis confirmed the presence of organic molecules, as the content of the elements increased significantly. From the nitrogen content the molar content of surfactants was calculated. It varied between 1.83 and 3.52 mmol/g of kanemite and was highest for C_{14} and BC_{14} intercalates. Reaction with Az induced further increase of the basal spacing by additional 2.0 to 5.5 Å. The largest d_{001} increase was observed for the C_{16} - 5.5 Å, for BC_{16} - 3.9 Å and C_{14} intercalates - 3.4. The BC_{14} and BC_{12} derivatives showed a ~2 Å increase, while for C_{12} no change occurred. The elemental analysis showed a relatively low amount of intercalated azobenzene molecules. The largest Az content was intercalated into the C_{14} and C_{16} derivatives: 0.32 and 0.38 mmol/g, respectively. For BC_n samples it varied from 0.11 to 0.18 mmol/g. For C_{12} no increase of CHN elements was observed, which is consistent with the XRD results and suggested unsuccessful Az intercalation. Upon exposure to UV light the Az intercalated kanemites showed slight but evident d_{001} decrease from 0.3 Å up to 1.2 Å. The magnitude of the photoresponse effect depended mainly on the type of pre-intercalated surfactant - the alkyl chain length and the presence of benzyl ring at the ammonium head.

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UV TRIGGERED BASAL SPACING SHIFTS IN SMECTITE INTERCALATES

Anna Koteja*, Jakub Matusik

AGH University of Science and Technology, Faculty of Geology, Geophysics and Environmental Protection, Department of Mineralogy, Petrography and Geochemistry, al. Mickiewicza 30 30-059 Kraków, Poland
*akoteja@agh.edu.pl

Photoactive layered materials are derived from the combination of a layered inorganic structure (e.g. clay mineral) and the organic photoactive compound. Among the latter, the azobenzene derivatives attract much attention in many fields of science connected with photochemistry. The azobenzene molecule normally occurs in a *trans*-isomer form which isomerizes into the metastable *cis*-isomer upon UV radiation. This is accompanied with change of the molecule shape and dimensions. The reverse *cis* to *trans* reaction occurs spontaneously and it may be accelerated with Vis light or heat [1]. The immobilization of azobenzene in a solid structure leads to a novel and functional material with properties controlled remotely with light, at the atomic scale [2]. The research goal was to synthesize a hybrid organo-smectite material that exhibits d_{001} basal spacing shifts upon the UV light.

SWy smectite from Wyoming deposit (USA) and BId beidellite from Idaho deposit (USA) were ion-exchanged with a series of akylammonium surfactants. These included: C_n - alkyltrimethyl ammonium ions and BC_n - alkylbenzyldimethyl ammonium ions, where n = 12, 14, and 16, indicates the number of carbon atoms in the alkyl chain. The resultant organo-smectites were reacted with azobenzene (Az) in 120 °C for 24 h at 0.2 Az/organo-smectite weight ratio. The products were characterized with XRD, FTIR, and CHN analysis. In order to investigate the photoresponsive behaviour the Az-smectites were treated with UV light (365 nm, 15 mW/cm^2) for 1 h and the changes were monitored with the XRD and FTIR analysis.

The first modification step resulted in the increase of the basal spacing for both the SWy and the BId ion-exchanged samples. The d_{001} values varied from 16 to 26 Å, depending on the alkyl chain length, which corresponded to the bilayer to pseudotrimolecular arrangement of the surfactant molecules. The C-H stretching and bending vibration bands appeared respectively in the 3000-2800 cm^{-1} and 1500-1400 cm^{-1} regions of the FTIR spectra. The elemental analysis revealed an increasing number of intercalated molecules along with the increasing alkyl chain. The intercalated surfactants fully balanced the CEC of smectite. The Az co-intercalation induced further changes of the XRD pattern. The BId derivatives, regardless of the pre-intercalated salt, showed high d_{001} values between 30 and 33 Å and an integral series of 2nd and 3rd order reflections. Similar results were observed for SWy-C_{16}, -BC_{14}, and BC_{16} intercalates. Whereas no or insignificant changes of d-value appeared for the SWy-C_{12}, -C_{14} and BC_{12}. Even though, the presence of Az was confirmed in all samples by the FTIR spectra, which revealed new bands mainly in the 820-760 cm^{-1} region. From the elemental analysis the Az/organic cation molar ratio was calculated as ~1.0 for SWy and ~1-2 for BId intercalates.

UV radiation induced the basal spacing shifts in the Az intercalated smectites. In case of the SWy samples the shifts were relatively small and irregular, while all the BId derivatives showed significant decrease of d_{001} upon UV. The photoresponses varied between 0.4 and 2.1 Å. The largest effects were observed for the intercalates with short alkyl chains (C_{12} and BC_{12}) and they decreased with the increasing alkyl chain length. The photoresponsive reaction was reversible after two cycles of alternating UV and Vis radiation. The isomerization of Az was confirmed in the FTIR spectra as the reaction affects the intensity of 760 cm^{-1} band, which is sensitive to the presence of *trans* or *cis* Az form. Summarizing the results it may be concluded that the principal factors influencing the effective photoresponses are the location and magnitude of layer charge, as these are the main differences between SWy and BId minerals. Also the low occupation of the interlayer space with surfactants promoted larger photoresponses, probably because it provided more space for Az isomerization.

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ASSESSMENT AND UPGRADE OF MEDIUM-LOW GRADE BENTONITES FROM CHIOS AND SAMOS ISLANDS AND WESTERN THRACE, GREECE

E. Koutsopoulou (1)*, I. Marantos (2), G. E. Christidis (3)

(1) University of Patras, Department of Geology, 26500 Rio, Patras, Greece, (2) Institute of Geological and Mineral Exploration (IGME), Spyrou Loui 1, 13677 Acharnes, Greece, (3) Technical University of Crete, Department of Mineral Resources Engineering, 73100 Chania, Greece
*ekoutsop@upatras.gr

Bentonites are important industrial clays rich in smectite with unique intrinsic properties such as high cation exchange capacity, swelling behavior, adsorption properties and large surface area. Organically modified smectites have attracted intense research interest because they allow the development of high added value materials with novel applications in a variety of uses. Recently, medium-low grade bentonite deposits from the islands of Chios and Samos, eastern Aegean and from areas of Thrace (Skaloma, Feres, Sappes), NE Greece have been assessed for their mineralogical and geochemical characteristics and for their potential use in traditional industrial applications [1]. The bentonite samples were classified according to the layer charge of the smectites present, following the characterization scheme of Christidis et al. (2006) [2]. The smectites in Chios and Samos bentonites are medium-high charge montmorillonites whereas their Thracian counterparts contain montmorillonites with more variable compositions and Fe-rich beidellites [1].

Surface modification of the montmorillonite present in the different bentonite samples with alkylammonium salts has produced a series of organophilic end-products. Na-activated montmorillonite was treated with dodecylamine (DDA) and hexadecylamine (HDA) as organo-surfactants each with concentrations of 200%, 100% and 50% of the CEC. Double-layer configuration was developed in both DDA and HDA for the concentrations of 200% and 100% of the CEC whereas monolayer arrangement was observed for the 50% of CEC. Nevertheless, all samples were rendered organophilic even at the lowest alkylammonium concentrations, thus making them suitable for a number of industrial applications. The mean layer charge of the smectites calculated from the structural formula is larger than the layer charge determined after alkylammonium exchange.

In addition the bentonite samples were acid activated with 3N H_2SO_4 at ~70 °C and a solid liquid ratio 1:10. In bentonites from Thrace, acid treatment resulted in almost total dissolution of the clay structure which led to a significant decrease in the d(001), the disappearance of the d(003) reflection, and an increase in the background between 20° and 30° 2θ due to the deposition of amorphous silica caused after the attack on the octahedral sheet during acid treatment. The Samos and Chios bentonites were partially dissolved with a decrease in the d(001) reflection and its progression to lower d-spacing values. Preliminary tests showed that they are suitable for crude oil clarification.

Finally, the montmorillonites treated with DDA were used for the preparation of clay/polymer nanocomposites with Diglycidyl ether bisphenol A (DGEBA, RenLam CY-219 epoxy resin), and a mixture of polyamines namely polyoxypropylenediamine, isophorone diamine, trimethylhexamethylenediamine, 4,4'-isopropyl-hexamethylene-diamine and benzyl alcohol (Ren HY 5161, hardener). Upon DGEBA intercalation into the montmorillonite interlayer all nanocomposites showed d-spacings determined by the initial d-spacing of the organically modified montmorillonite. As a next step, the nanocomposites will be fully characterized and their mechanical strength will be determined. The results of the present study show that these medium-low grade bentonites could be used in high added-value applications after processing.

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MULTISCALE MODELING OF KAOLINITE AGGREGATION IN AQUEOUS ELECTROLYTE SOLUTIONS AND IN NON-AQUEOUS MEDIA

Andriy Kovalenko (1,2)*, Stepan Hlushak (2), Rola Mansa (3), Guy B. Ngassa (3), Christian Detellier (3)

(1) National Institute for Nanotechnology, National Research Council, Edmonton, Alberta, Canada T6G2M9, (2) Department of Mechanical Engineering, University of Alberta, Edmonton, Alberta, Canada T6G 1H9, (3) Department of Chemistry and Biomolecular Sciences and Centre for Catalysis Research and Innovation, University of Ottawa, Ontario, Canada K1N6N4

Clay minerals have specific adhesion and adsorption properties of dramatic importance for scientific problems and technological applications. They range from DNA adsorption on clay minerals to biomedical applications for absorption of toxic compounds and heavy metals, filtration, wastewater treatment, and sustainable catalysts for organic reactions, to polymer-clay nanocomposites for membranes, functional, and building materials. Critical is understanding of molecular forces driving adsorption of molecules and nanoparticles on clays in different complex solvent environments. This provides access to optimization and design of new clay based materials and processes, in particular, overcoming a conceptual gap in the understanding of their behaviour and characteristics in non-aqueous environment. Theoretical understanding of molecular mechanisms governing the behaviour of clays in aqueous and non-aqueous solutions gives a fundamental insight into their functioning and reveals perspectives in building new highly efficient clay based systems for control of materials.

Towards these goals, we have been studying in particular the behaviour of organic polymers such as ethyl cellulose in water and in a mixture of cyclohexane and toluene organic solvents at the surface of kaolinite and illite nanoparticles. The calculation shows the dependence of the polymerization degree on the properties of the organic solvents and the temperature and pressure change considerably shifting the polymerization degree. The calculations predict that kaolinite platelets aggregate due to face-to-face, edge-to-face, and edge-to-edge interactions, and reveal the effect of the change in the solution temperature and pressure conditions on the platelets aggregation behavior. These phenomena have strong effect on bioadsorption on clays and on flocculation of clay nanoparticles in non-aqueous as well as aqueous electrolyte solutions with polymeric additives. This also has substantial effect on the morphology of clay assemblies in dispersion in aqueous and non-aqueous solvent mixtures.

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MOLECULAR MODELLING OF ORGANOCLAYS AND OTHER MATERIALS

Petr Kovář (1)*, Miroslav Pospíšil (1), Jan Demel (2), Rosa Torres (3)

(1) Charles University, Faculty of Mathematics and Physics, Ke Karlovu 3, 12116 Prague, Czech Republic, (2) Institute of Inorganic Chemistry of the Czech Academy of Sciences, v.v.i., Husinec-Řež 1001, 250 68 Řež, CZ, (3) CETMIC-CONICET-CCT La Plata-CICBA. Camino Centenario y 506, 1897 M. B. Gonnet, La Plata, Argentina
*kovar@karlov.mff.cuni.cz

Molecular modelling calculations based on empirical force fields can be used for structure characterization of a wide range of organo-inorganic hybrid materials. In combination with X-ray diffraction, FTIR spectroscopy and TG analysis they can provide a detailed view on the structure arrangement of the guests in the interlayer space and can explain the relationship between the structure and observed properties of investigated materials. We report the results on the following organo-inorganic structures:

i) Adsorption of thiabendazole on Na-montmorillonite (Mt) and two organomodified montmorillonites. The different interactions of the fungicide thiabendazole (TBZ) on montmorillonite clay and two organo-clays (phosphatidylcholine (DSPC) and octadecyl trimethylammonium (ODTMA) bromide) were deeper investigated in order to use these systems in water remediation, where adsorption was the driving mechanism. The simulations provided a detailed view on the orientation of TBZ and by comparing the interaction energies in the models we were able to determine which form of TBZ(TBZ^0 or $TBZH^+$) was likely present in the investigated samples. The interaction energies between TBZ (TBZ^0 and $TBZH^+$) and Mt surface or organically modified Mt surface were related to desorption properties of investigated samples. In case of Wy-TBZ strong electrostatic interactions (-240 kcal/mol) prevented $TBZH^+$ from desorbing out of Mt surface. In case of WyODTMA there were weak van der Waals interactions (-7 kcal/mol) between TBZ^0 and the organic surface formed by ODTMA cations. TBZ^0 was located only organic surface, and a small amount of $TBZH^+$ was located on Mt surface, which can explain 82% desorption of TBZ. Lower desorption (53%) of TBZ in case of WyDSPC-TBZ can be ascribed to the fact that part of TBZ^0 molecules was immersed among DSPC chains and exhibited stronger attractive interactions (-37 kcal/mol) with the surfactants. It led to a more difficult release than in the case where TBZ^0 is located only on the surface formed by head groups of DSPC and has weaker interactions (-16 kcal/mol) with the surfactants.

ii) Simulations of metal organic framework (PCN - 222) modified with diphenylphosphinic acid (DPPA). The aim was to describe the structure and energy characteristics of the system. Experimental measurements revealed that every SBU unit contained 2 - 3 DPPA. The DPPA molecule can be bonded to SBU unit in a chelate or bridging coordination. In order to distinguish if the bridging or the chelate coordination of DPPA molecule is more probable, we compared total energy of calculated models. One could see that the bridging coordination exhibited significantly lower energy values with respect to the chelate one indicating that a bridging coordination could be favoured to a chelate coordination. The value of total energy depended also on the number of DPPA molecules bonded to SBU units. The total energy was higher for the models with 3 DPPA molecules in comparison to the models containing only 2 DPPA molecules. This is consistent with the results of elemental analysis. In the sample with 2 DPPA molecules per SBU unit there was a fast binding of DPPA molecules to SBU units (DPPA molecules in the models aimed to the MOF pore) while in the sample with 3 DPPA molecules per SBU units 10 times higher concentration of DPPA was necessary for binding due to a steric hindrance.

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METHODOLOGICAL ASPECTS OF K-Ar DATING IN APPLICATION TO SEDIMENTARY BASINS THERMAL HISTORY RECONSTRUCTION

Sylwia Kowalska (1)*, Stanisław Hałas (2), Artur Wójtowicz (2), Klaus Wemmer (3), Zbyszek Mikołajewski (4)

(1) Oil and Gas Institute - National Research Institute, Kraków, Poland, (2) Mass Spectrometry Laboratory, Institute of Physics, Maria Curie-Skłodowska University, Lublin, Poland, (3) Isotope Geology Division, Geoscience Center, University of Göttingen, Göttingen, Germany, (4) PGNiG SA, Geology and Hydrocarbon Production Branch, Poland
*kowalska@inig.pl

K-Ar dating of maximum diagenesis is widely used in geology for thermal history reconstruction in sedimentary basins. Various research centers give different sizes measurement error (from 1 to 10 Ma), which should be taken for the results. Usually the reported measurement bias responds only to standard operating procedure of an individual laboratory and is estimated by that laboratory. The main aim of this study was to find out what the real error should be taken into account as the real error when interpreting geological K-Ar dating results. For this purpose an interlaboratory comparison with the participation of four well-known laboratories was organized. Free of them are performing measurements by K-Ar method and one by Ar-Ar method with the use of the capsule technique specially adapted for very fine clay materials. Following scientists took part in the interlaboratory comparison: Stanislaw Hałas and Artur Wojtowicz from the University in Lublin (K-Ar), Klaus Wemmer from the University of Göttingen (K-Ar), Yakov Kapusta from ACTLAB laboratory in Canada (K-Ar) and Chris Hall from the University of Michigan in the USA (Ar-Ar). Test samples was previously analysed by Jan Środoń and Michał Banaś from Institute of Geological Science of Polish Academy of Sciences - Research Center in Krakow in Poland (Kowalska, 2008).

The research material consisted of Silurian and Ordovician bentonites from the polish part of the East European Platform. Samples come from different boreholes drilled lately by PGNiG S.A. during intensive shale gas exploration in Poland. Silurian and Ordovition strata in that region are very reach in volcaniclastic layers, which shows also different thicknesses from millimetres to more than 3 m.

Interlaboratory comparison was carried out on three test samples. From each test sample four different grain fractions <0.02, 0.02-0.05, 0.05-0.2 and 0.2-2 μm were separated at the Institute of Geological Sciences in Krakow. Samples were splited by quartering, encrypted and sent to the laboratories participating in the comparison.

All laboratories (despite of the Środoń and Banaś Lab) obtained very similar results for the three finest fractions. The fraction 0.2-2 μm gave distinctly older ages, which proves an admixture of detrital material. The results of K-Ar and Ar-Ar dating, show that dating of diagenetic age is possible for a fraction less than 0.2 μm. Based on the results of interlaboratory comparison, it is also clearly visible that the most difficulties arise from the determination of potassium as for this element greater dispersion of results was achieved.

Comparison of the results achieved from laboratories taking part in the research clearly indicates that the actual measurement errors range up to +/- 10 Ma. Significantly younger ages obtained with the Ar-Ar method confirm the large influence of the Ar escape effect from the very fine grained samples, the so called “recoil effect” (e.g. Hall, 2013).

The above observations were confirmed by further studies carried out simultaneously for 60 bentonite samples from 10 other boreholes using only less than 2 μm fraction. It was also proved that in case of the Silurian and Ordovitian complex in Poland the thickness of bentonite layer do not influence the K-Ar results and all of them are suitable to date the maximum of thermo diagenesis. Very consistent results were achieved for the whole range of bentonites thicknesses.

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CLAY MINERALS IN THE CARBONIFEROUS SANDSTONES IN THE SOUTH-EASTERN PART OF THE LUBLIN BASIN (POLAND)

Kozłowska Aleksandra

Polish Geological Institute-National Research Institute, Rakowiecka 4, 00-975 Warsaw, Poland

The paper presents petrographical, mineralogical and geochemical results of clay minerals of the Carboniferous sandstones. The research materials came from seven boreholes. The following research methods were used: polarizing microscope, scanning electron microscope, X-ray, infrared analysis and K-Ar dating of authigenic illite. The analyzed sandstones represent deposits of the Visean - Bashkirian age. They were formed in the river and delta channels, river and delta flood plains and crevasse plays.

The sandstones are represented mainly by subarkosic, quartz and sublithic arenites and wackes. The sandstones are cemented by matrix and/or by cement. The matrix is mostly formed by detrital clay minerals or their mixture with a quartz dust. The cement is composed of the diagenetic minerals, among which clay minerals (kaolinite, dickit, illite, chlorites and mixed-layered illite/smectite) are the main components besides quartz and carbonates.

Kaolinite is the main clay mineral of the Carboniferous sandstones. Two types of morphological kaolinite, vermiform and blocky can be observed in the whole profile. The infrared analysis revealed the presence of kaolinite, kaolinite with dickite intergrowths and dickite.

Illite occurs in the form of very small plates, resembling elongated laths, needles and fibers. The X-ray analysis identifed two illite polytypes: the variety 1M - which is attributed to diagenetic origin and the variety 2M1 indicating a detrital origin. The K-Ar age of illite crystallization were determined in two samples and the data indicate the beginning of the crystallization age of diagenetic illite in the Permian about 260 My ago.

Most of chlorites usually occur in dispersed form in the rock cement and are known as allogenenic minerals. The authigenic chlorites create two forms: rims (Fe-chlorite) and a filling of pore space (Fe-chlorite and Mg-chlorite).

The illite/smectite mixed-layered minerals with a content of illite above 85% were identified in the X-ray research (the degree of illite/smectite order - $R = 3$ and $R \geq 3$).

In the diagenetic history of the Carboniferous sediments the chlorite rims and vermiform kaolinite formed in eodiagenesis in the temperature about 20-40 °C [2] and 25-50 °C [6], respectively. In mezodiagenesis, above 50 ºC crystallized: blocky kaolinite and dickite, illite/smectite mixed-layer minerals and fibrous illite. Blocky kaolinite formed in the temperature range from 50 to 80 °C [6]. Illite/smectite mixed-layered minerals suggest the temperature of about 160 °C which affected the rocks [7]. The transformation of kaolinite to dickite (about 120 °C) [1] and crystallization of fibrous illite (in range of 100-140 °C) [3] took place at the last stage of diagenesis.

The maximum temperature that affected the Carboniferous rocks during diagenesis is estimated at about 120 °C, based on clay minerals. The dating of fibrous illite about 260 My ago, suggesting the action of the diagenetic processes up to the Early Permian, because illite is the mineral which has formed as the last one in the diagenetic history [5]. The Permian age of the K-Ar data of diagenetic illite crystallization indicates a different diagenetic history of the Carboniferous sediments in the south-eastern part of the Lublin Basin when compared to the other Polish regions (the Upper Triassic - Middle Jurassic) [4]. Aiming at confirmation of the Permian age, a determination of deposition age from zircon diagenetic overgrowths from the sandstone by use of ion microprobe equipment - SHRIMP IIe/MC is planned.

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MECHANISM OF WATER FREEZING IN CLAY-WATER SYSTEM BETWEEN 225 AND 203 K

Tomasz Kozlowski

Kielce University of Technology, Kielce, 25-539, Poland

The widely known technique of DSC-based thermoporometry [1] allows to determine the pore size distribution curve from the data collected on cooling or warming a sample of a porous medium saturated with water or other liquid. Thermodynamic relationships, derived from the Gibbs-Thompson equation, link the radius of an ice crystal with its temperature of freezing or melting and then, under some assumption, the corresponding pore radius can be obtained. Parallelly, the quantity of ice undergoing the phase change at a given temperature can be calculated from the DSC (Differential Scanning Calorimetry) data and then transformed into the pore volume. However, the involved mass can be calculated from the heat of the phase change via the latent heat, i.e. the enthalpy change associated with the phase transition per unit of mass. Unfortunately, the temperature dependence of the latent heat of the phase transitions of the water in the restricted geometry has not yet been reliably determined and the used formulas may be taken as uncertain.

In the present study, a model of the montmorillonite-water system is assumed and a general empirical relationship enabling the prediction of the enthalpy change between 273 and 203 K is proposed. In the model, most of the micropores are slit-like in shape and the freezing process below 245 K involves the formation of flat "ice plates" with cylindrical interphase. Homoionic forms (Ca^{2+}, Na^+, and K^+) of montmorillonite were used as material in parallel DSC and BJH experiments. The total number of the low-temperature DSC peaks analyzed was 93. There were observed peaks of the average transition temperatures T_a in the range between 245.4 K and 200.2 K, yet their distribution was not uniform. The cluster analysis allowed the identification of four characteristic groups of peaks: #1 at $\Delta T = 33.35 \pm 1.84$ K (24 peaks), #2 at $\Delta T = 39.94 \pm 2.11$ K (37 peaks), #3 at $\Delta T = 46.37 \pm 1.74$ K (14 peaks), and #4 at $\Delta T = 62.25 \pm 3.69$ K (18 peaks). The first three clusters correspond to the component peaks resulting from the decomposition of the main complex DSC peak. The cluster #4 corresponds to the secondary low temperature peaks appearing at about $\Delta T = 58.8$ K. Strikingly, a gap between $\Delta T = 48$ K and $\Delta T = 58$ K is observed. The solidification heat associated with a DSC peak was related to the mass of the ice formed. The latter was calculated from the BJH differential curves measured for the same system. A good qualitative compatibility between the low temperature exothermic peaks and the peaks on the curves *dm/dT* obtained from the BJH data was observed. Statistical analysis of the enthalpy change values determined between 245 and 200 K showed an insignificance of the kind of homoionic form and sample parameters such as dry mass, water mass and water content. The mechanism of freezing in such a system has been proposed as follows. After breaking the supercooling (usually between 258 and 253 K), the crystallization process proceeds in the macro- and mesopores of a radius between several micrometers and 2 nm as the growth of ice crystals with a spherical interface ($dA/dV = 2/R$). At approximately 242 K, solidification involves the slit-shaped pores between the flat particles and the formation of flat "ice plates" with a cylindrical interphase ($dA/dV = 1/R$). The observed low temperature peaks are a manifestation of this secondary solidification process in the slit-shaped micropores of a width of between 4 and 0.5 nm.

In view of the present results, the solidification of the interlayer water would have to occur in the form of flat sheets of a thickness approximately equal to 0.8-0.9 nm ($= 2r_c$). Such a representation, however, is nothing but a rough simplification. The "sheet" may be an ice-like structure of a few distorted unit cells of low energy and entropy [2]. A serious problem is constituted by the location of the exchangeable cations in such a structure. The results of the molecular dynamics simulations presented by Skipper *et al.* [3] in a two-molecular layer Na-hectorite hydrate (being, as montmorillonite, the 2:1 type clay mineral) with a layer spacing of 1.5 nm at 300 K indicate a central positioning of Na counterions and a strongly layered surface water, with each molecule able to direct one hydrogen atom towards the surface. The counterions would be partially incorporated into the forming ice-like structure, most possibly in outer- or inner-sphere complexes with a solvation shell, the thickness of which depending on the valence and size of a cation [3].

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QUANTUM CHEMICAL MODELING OF Fe(III) OCTAHEDRAL SUBSTITUTIONS IN 2:1 CLAY MINERALS

Alena Kremleva (1), Sven Krüger (1), Stefan Kienzle (1), Notker Rösch (1,2)*

(1) Department Chemie, Technische Universität München, 85747 Garching, Germany, (2) Institute of High Performance Computing, Agency for Science, Technology and Research, 138632 Singapore, Singapore

Clays are mostly composed of phyllosilicate minerals. Due to their variable composition and properties they are widely used, e.g., in ceramics, as sorbents, in catalysis, and as technical barriers of waste repositories. The analysis of numerous experimental observations yields relationships between various properties of clays and their composition [1,2]. However, an explanation of these empirical correlations is often missing. Here computational studies on the atomic scale can shed some light.

We examined computationally how the structure and the composition of water-free clay minerals vary with the iron content [3]. To this end, we applied a spin-polarized version of density functional theory to suitable models, and we included a self-interaction correction for iron as well as van der Waals corrections (DFT+U+D3 approach) in combination with the plane-wave based projector augmented wave method as implemented in the program VASP. We added Fe^{3+} substitutions in the mineral models by introducing 1 or 2 Fe octahedral substitutions per 2×1 unit cell, which contains 8 octahedral cations in total. As a reference, we first explored the neutral mineral pyrophyllite.

Besides various positions of Fe substitutions with respect to each other, we also studied various relative spin orientations of the Fe ions. Fe-substituted pyrophyllite was found to prefer always low spin states. When two neighboring Fe substitutions are connected via an O/OH bridge, the structure with opposite spins is 2-3 kJ/mol per unit cell more favorable compared to the high-spin state structure. For non-adjacent Fe substitutions, opposite spins are favored by at most 1 kJ/mol per unit cell for several arrangements inspected. The interaction of two Fe octahedral substitutions was determined to be energetically repulsive. Similar trends were observed for montmorillonitic and beidellitic smectite mineral models with charged substitutions in the octahedral and tetrahedral sheets, respectively. In montmorillonitic models, Fe prefers to stay distant from Mg substitutions, while in beidellitic models Fe prefers to occupy octahedral positions close to the charged tetrahedral moieties.

Depending on the type of charged substitution (octahedral or tetrahedral), we determined an energy preference for cis- or trans-vacant structures of the minerals. The known preference for Fe-free minerals can be reproduced only when van der Waals corrections are accounted for. Increasing the Fe content, however, increases the preference for the trans-vacant structure. Octahedral Fe^{3+} substitutions were found to be more favorable for beidellitic than for montmorillonitic minerals.

These results together with the calculated structures, vibrational modes, and charge distributions [3] help to rationalize some of the experimentally observed correlations [1,2].

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STUDY OF MECHANOCHEMICALLY-INDUCED DEFECT SITES ON EXFOLIATED HALLOYSITE SURFACES BY ^{27}Al MAS NMR SPECTROSCOPY

János Kristóf (1)*, Erzsébet Horváth (2), Veronika Vágvölgyi (1), Balázs Zsirka (2), Dávid Fertig (2)

(1) University of Pannonia, Department of Analytical Chemistry, P.O. Box 158, H-8201 Veszprém, HUNGARY,
(2) University of Pannonia, Institute of Environmental Engineering, P.O. Box 158, H-8201Veszprém, HUNGARY
*kristof@almos.vein.hu

Although the 1:1 (or TO) type clay minerals have long been used as catalyst supports, their catalytic properties became of interest just recently. In addition to the preparation of exfoliated clay minerals and their nanohybrids, the study of the physico-chemical background leading to the understanding of the catalytic nature of these materials is now in the mainstream of research. Although the surface properties of exfoliated kaolinites are the function of their morphology, the surface concentration of defect/bonding sites is rather high due to their increased specific surface area. These systems can be considered as quasi-ideal models for the study of intended surface sites on Al/O and Si/O type bulk phases. As to the surface properties of the 1:1 or TO type exfoliated kaolinites, mostly specific surface area and porosity data are available. The qualitative and quantitative evaluation and energetic characterization of the bonding sites with instrumental techniques encounters several difficulties (e.g. high pressure drop and particle carry-over with inverse gas/liquid chromatography). Since the photochemical activity is increasing with the degree of exfoliation, it is necessary to reveal the correlation between population (and chemical character) of the defect/bonding sites and the activity of the nanomaterial.

The mechanochemical activation (dry grinding) of exfoliated halloysite minerals results in the partial dehydroxylation of the Al-OH groups. The deformation of the Al-octahedra as a function of the grinding time was followed by ^{27}Al MAS NMR spectroscopy. Both in the initial (pristine) an the deformed sample hexa-coordinated-Al (δ=3-4 ppm) and tetra-coordinated-Al (δ=55-70 ppm) centers are present. No change can be observed in the quantity of the four-coordinated Al-centers upon exfoliation. On prolonged grinding the amount of the deformed tetra-coordinated-Al centers is increased along with the appearance of five-coordinated-Al (δ=37ppm) sites. Surprisingly, bands characteristic of trigonal-Al (δ=108-112ppm) centers also appear in the NMR spectrum of the exfoliated halloysite. Their amount decreases with the increase of the grinding time. Since the trigonal-Al centers are extremely reactive, their stability could be ensured by the morphology. Based on the results of surface titrations, the chemical character of the Al-OH groups are determined by their bridging (acidic) or end-on (alkaline) positions.

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TRANSFORMATION OF THE STRUCTURE AND PROPERTIES OF MONTMORILLONITE DUE TO THE THERMOCHEMICAL INFLUENCE

Victoria Krupskaya (1,2)*, Sergey Zakusin (1,2), Ekaterina Tyupina (3,4), Olga Dorzhieva (1,5), Artem Pryadko (3), Petr Belousov (1), Boris Pokid'ko (6), Yana Bichkova (2)

(1) Institute of Geology of Ore Deposits, Petrography, Mineralogy and Geochemistry, Russian Academy of Science (IGEM RAS), Moscow, Russian Federation, (2) Lomonosov Moscow State University (MSU), Geological Faculty, Moscow, Russian Federation, (3) D. Mendeleev University of Chemical Technology of Russia (RCTU), Moscow, Russian Federation, (4) National Research Nuclear University «MEPhI», Moscow, Russian Federation, (5) Geological Institute, Russian Academy of Science (GIN RAS), Moscow, Russian Federation

Clay minerals are widely used in various industries, including radioactive waste management as the component of barrier systems for wastes disposal. Some construction concepts of waste repositories consider that bentonite barriers can be subjected to aggressive environment. For instance, it can happen in the case of the isolation of so called "historical" repositories for liquid radioactive wastes. These wastes may have a high temperature and a high content of nitric acid. Experimental study was conducted to ascertain effect of nitric acid solution at an elevated temperature (90 °C) on montmorillonites with different composition and structural features. Bentonite samples selected for this work were obtained from several Russian industrial deposits (Dashkovskoye, Zyryanovskoye, 10 Khutor), and also from near-abroad (Taganka, Dash-Salakhlinskoye) and far-abroad deposits (Trebia in Morocco). Acid treatment was carried out in nitric acid solutions on a magnetic stirrer with a heating function using reflux to keep a constant solid/liquid ratio. Solid and liquid components were separated by centrifugation. Initial and modified samples were analyzed with a series of methods: X-ray diffraction, infrared spectroscopy, scanning electron microscopy, X-ray fluorescence, inductively coupled plasma mass spectroscopy, N_2 adsorption for determination of specific surface area and pore size distribution and methylene blue adsorption for determination of cation exchange capacity.

These experiments allowed us to describe the processes of transformation of the montmorillonite structure and its adsorption properties as a result of thermochemical effect. Structural modification occurs in several overlapped stages: 1. Partial protonation of interlayer due to the substitution of interlayer cations to oxonium cations, 2. Partial protonation of OH-groups at octahedral sheets, leaching of octahedral cations and reduction of the layer charge, 3. Loss of the interlayer cations due to reduction of the layer charge, 4. Changing of interaction between octahedral and tetrahedral sheets, 5. Amorphization of tetrahedral sheets and partial deposition of amorphous silica on the particle surfaces.

Modification of bentonite properties occurs as follows: 1. The increase of the specific surface area (S_{sp}) due to the destruction of large aggregates and the development of mesoporosity. 2. The increase of the total pore volume of micropores due to the micropores appearance due to the leaching of the octahedral cations. 3. The decrease of the cation exchange capacity values (CEC) due to the reduction of the layer charge and the destruction of 2:1 layers.

The experimental results showed a decisive role of the OH groups' orientation in the octahedral sheets. Montmorillonite with a predominance of cis-vacant octahedra demonstrates the highest stability during the acid treatment (bentonites from 10 Khutor and Trebia deposits). However, Dashkovsky bentonite which is characterized by a predominance of the trans-vacant octahedra but a relatively high content of organic matter (C_{org} = 0.69% vs. 0.04% which is the average Corg content for the other investigated bentonites) shows quite high resistance to the acid treatment. With increasing isomorphous substitutions (primarily to Fe) and with the prevalence of trans-vacant octahedral, stability of montmorillonites decreases. The least stable bentonite among the studied deposits is Tagansky. The studies allow predicting the stability of bentonite to the thermochemical effect on the basis of the analysis of natural clay. The results can be used for designing the engineering bentonite barriers for highly toxic liquid chemical waste and liquid radioactive waste.

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AUTHIGENIC CLAY MINERALS IN CEMENTS OF THE LOWER TRIASSIC SANDSTONES FROM THE WARSAW -ŁÓDŹ AREA (PRELIMINARY RESULTS)

Marta Kuberska

Polish Geological Institute - National Research Institute, Rakowiecka 4, 00-975 Warsaw, Poland

The Lower Triassic deposits from the Warsaw and Lodz Troughs have been the research objects in respect to (among others) effects of diagenetic processes and their influence on the reservoir - sealing conditions.

The Lower Triassic in the research area represents the eastern part of the Central European Basin where sediments were deposited in conditions of very shallow continental - marine environments and in dry climate [5,1]. Red - brown claystone - mudstone rocks with interlayers of sandstones in complexes of diversified thickness are predominant in the Lower Triassic succession.

Arenites, less frequent, quartz and subarkosic, sporadically sublithic wackeshave been distinguished in the sandstones. Quartz is the main component of the grain fabrics, being accompanied by potassium feldspars and plagioclases. The sublithic varieties of the rocks are enriched in lithoclasts of magmatic and/or sedimentary origin. The detrital material is cemented by the matrix and by the orthochemical cement. Kaolinite, chlorite, subordinate illite are main components of the cement, besides carbonates and the authigenic quartz. Kaolinite either occurs as platy accumulation swhich fill the pore space, or it forms fillings in the detrital grains. Plates of the kaolinite are in vermicular or irregular forms. The formation of the kaolinite is often connected with processes of diagenetic alteration of feldspars and micas. A presence of dickite cannot be excluded, too, since this is a common post-kaolinite mineral in the Triassic deposits. Such a transformation occurred at temperatures between 80 and 130 °C [4]. The chloritization results may be observed in micas. The degradation of a biotite structure occurs at conditions of a weak removal of Mg^{2+}, that results in the formation of Mg-chlorites. Trace amounts of fibrous illite were found in the studied sandstones. The habit and types of the clay minerals generally influenced the petrophysical features of the sandstones [2], [3]. The diagenetic processes, e.g., the cementation and the alteration, have had a differentiated influence on the alteration intensity and the formation habit of the pore space. A creation of secondary intracrystalline porosity was extremely strongly influenced by the diagenetic alteration processes.

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MODELING X-RAY ABSORPTION SPECTRA OF Cd(II) ON CLAYS

James D. Kubicki (1)*, Heath D. Watts (1), Peggy A. O'day (2)

(1) University of Texas at El Paso, El Paso, USA, (2) University of California Merced, Merced, USA

Periodic density functional theory (DFT) calculations were performed to model the adsorption of Cd(II) onto the surfaces of gibbsite ($Al(OH)_3$) and kaolinite ($Al_2Si_2O_5(OH)_4$). Cd(II) is a critical environmental contaminant, and understanding its adsorption behaviour in soils is necessary for predicting fate and bioavailability. Obtaining information on the surface complexes formed by Cd(II) onto these common soil minerals at concentrations relevant to those found in nature is problematic due to weak spectroscopic (e.g., NMR) signals and distortion of the Cd(II) coordination shell. Consequently, a combination of experimental and theoretical XANES spectroscopy and DFT were used to explore potential surface complex structures and energetics.

A variety of monodentate, bidentate and outer-sphere complexes were constructed to interact with the (100) surfaces of gibbsite and kaolinite. Energy minimizations, followed by molecular dynamics simulations and then by energy re-minimization, were conducted with the program VASP. The relative energies of the model surface complexes were used to predict which might be the most thermodynamically stable. These periodic structures were then used as the basis for calculations using FEFF10 to predict XANES spectra and Gaussian 03 to predict Cd NMR chemical shifts. The NMR results are inconclusive as it has proven problematic to collect Cd NMR spectra on these minerals at low concentrations. The XANES calculations, however, match the energy of primary absorption features observed in XANES spectra reasonably well, although amplitudes are less well simulated. The nature of the Cd-gibbsite and Cd-kaolinite surface complexes will be discussed.

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REVOLUTIONARY METHOD TO DISPERSE REDUCED CHARGE Li$^+$-MONTMORILLONITE IN SOLVENT

Munehiro Kubota (1)*, Keiichi Kurosaka (1), Takeo Ebina (2)

(1) Iwaki Laboratory, Kunimine Industries Co., Ltd., 23-5 Kuidesaku, Jobanshimofunao-Machi, Iwaki-Shi, Fukushima 972-8312, Japan, (2) Research Institute for Chemical Process Technology, National Institute for Advanced Industrial Science and Technology (AIST), 4-2-1 Nigatake, Miyagino-ku, Sendai, Miyagi 983-8551, Japan
*m.kubota@kunimine.co.jp

A lot of studies were reported about reduced-charge smectites [1], however, there have been no reports of dispersing procedure of the reduced charge montmorillonite(RCM). Eventually, a revolutionary phenomenon in the specific recipe, where RCM could be dispersed in a solvent, was newly found.

At first, Li$^+$-exchanged montmorillonite was treated at 400 °C to prepare RCM followed by the dispersing process using solvent. The solvent includes three components; ammonia, several organic solvents with formamide group, and water. The optimal solvent composition for dispersing was confirmed evaluating the dispersibility in various solvent ratio. The dispersion was evaluated by particle size distribution and the state of particles were observed by atomic force microscopy (AFM). Next, in order to evaluate the properties of the dispersed RCM (dRCM), the dispersion was dried and grinded to obtain powder samples. Each powder; Li$^+$-exchanged montmorillonite and RCM, and dRCM, was analyzed by X-ray diffraction (XRD) and their cation exchange capacity (CEC) was measured. Particularly, the CEC value of dRCM was larger than that of RCM.

From these results, it was revealed that the CEC value was increased and these montmorillonite particles were dispersed finely in solvent.

Furthermore, since RCM could not be dispersed in water conventionally, it could not be formed a film of RCM. On the other hand, a film was successfully prepared by a casting method from the dispersion. And this film has water resistance feature.

In this paper, we will report about the new method and phenomenon with a variety of data in detail.

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PALEOCLIMATIC RECORDS FROM FLUVIAL SEDIMENTS OF CAMELI BASIN, SW TURKEY: SPECIAL REFERENCE TO CLAY MINERALOGY

Ceren Kuçukuysal*, Tural Aghayev, Merve Gulcan

Muğla Sıtkı Koçman University, Faculty of Engineering, Geological Engineering Department, Muğla, 48000, Turkey

Çameli Basin, located in the south of Denizli, is categorized as a complex tectonic graben. The basin-fill sediments are found to be of late Miocene-late Pliocene age and named as Çameli Formation which includes alluvial-fan, fluvial and lacustrine deposits [1]. The present study focuses on the mineralogical and geochemical compositions of the late Miocene-early Pliocene succession. In this project, we report a single sedimentary succession cropping out along road-cuts near the town of Akşar village, Acıpayam, southern Denizli.

The studied succession was sampled along a single outcrop and the samples were studied in terms of mineralogical, major oxide and stable isotope ratios of the bulk as well as the mineralogical composition of <2 µm size fraction. The objective is to investigate if mineralogy can provide climatic proxy data in conjunction with the other records.

Quartz, calcite, dolomite, feldspar, amphibole and clays were found in the bulk samples while smectite, chlorite, kaolinite and palygorskite were observed in the fine fraction. Higher average composition of the total clay presents reverse covariance with the calcite abundance. The same relation was captured between palygorskite and calcite. This was further confirmed with the apparent reverse variation between CaO and MgO all through the succession. In the meantime, up to the section, a gradual increase in SiO_2 suggests increasing precipitation. The authigenic presence of palygorskite was also checked with scanning electron microscope study and it was observed that the in situ formed palygorskite fibers form bridge-like morphologies which supports their authigenic precipitation. High correlation between $\delta^{13}C$ and $\delta^{18}O$ ratios of the bulk carbonate point hydrologically closed environment. The narrow range in both $\delta^{13}C$ and $\delta^{18}O$ ratios were measured as -4.93 to -2.21‰ and -5.92 to -2.97‰ VPDB, respectively. The low $\delta^{18}O$ isotope ratios suggest ^{18}O-depleted meteoric water inflow with a low diagenetic imprint. Additionally, the slightly negative $\delta^{13}C$ values may contribute to the knowledge on the old vegetation type as C3:C4 plants. All the findings suggest that the changes in the abundance of detrital minerals like quartz, feldspar with respect to calcite, dolomite and authigenic palygorskite are possible proxies for climatic reconstruction in the study area.

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OCCURRENCE OF FIBROUS CHRYSOTILE AND TREMOLITE IN THE ÇANKIRI-ANKARA REGION, CENTRAL ANATOLIA, TURKEY

Tacit Külah (1)*, Selahattin Kadir (1), Hülya Erkoyun (1), Nergis Önalgil (1), Eşref Atabey (2)

(1) Eskişehir Osmangazi University, Department of Geological Engineering, TR-26480, Eskişehir, Turkey, (2) Hacettepe University, Mesothelioma and Medical Geology Research Center, Ankara, Turkey
tacitkulah@gmail.com, skadir.euroclay@gmail.com, hlerkoyun08@gmail.com, onalgil_05290218@hotmail.com, esrefatabey@gmail.com

Occurrence of asbestos minerals such as chrysotile and tremolite are widespread in Çankırı-Ankara region, Central Anatolia, Turkey which resulted potential development of regional malign mesothelioma. Chrysotile locally associated with minor amounts of tremolite in the surfaces of fracture along the tectonic deformation zones in altered Mesozoic ophiolitic rocks. Mesozoic ophiolitic rocks composed mainly of serpentinized olivine and pyroxene associated with partially altered plagioclase and enclose opaque minerals and Fe-oxyhydroxide phases. Additionally, chlorite, talc, calcite, and dolomite are also determined. Micromorphologically, development of chrysotile and locally tremolite either as bundle or scattered or even mesh on ferromagnesian precursors and associated with talc in ophiolitic units may suggest authigenic formation of chrysotile and tremolite via dissolution and precipitation mechanism and influence of tectonic activities. Additionally, acicular structures of opal-CT and locally platy and blocky talc crystals either enclose or developed within chrysotile/tremolite fiber bundles may indicate direct precipitation from hydrothermal/meteoric waters. High concentration of MgO, Fe_2O_3, Ni, and Co with low Al_2O_3, Rb, and Ba content in chrysotile and tremolite suggest alteration of ophiolitic rocks. Structural formulae of chrysotile is $(Mg_{5.56}Fe_{0.27}Mn_{0.005})(Si_{3.91}Al_{0.15})O_{10}(OH)_8$. More depletion of Rb, Ba, Nb, Ce, Sr, Zr and Dy in primitive-mantle-normalized pattern also suggest that the serpentinization of ophiolitic rocks influence of hydrothermal fluids and high pressure conditions controlled by tectonics. This suggestion was also supported by isotope data and calculated formation of the chrysotile and tremolite at 170 - 555 °C.

Keywords: chrysotile, tremolite, genesis, mesothelioma, Çankırı, Ankara, Turkey.

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THE O-D METHOD APPLIED TO AN ODD SYSTEM: SURFACE CHARGE OF ILLITE-SMECTITE

Artur Kuligiewicz (1)*, Arkadiusz Derkowski (1), Jan Środoń (1), Vassilis Gionis (2), Georgios D. Chryssikos (2)

(1) Institute of Geological Sciences, Polish Academy of Sciences, Senacka 1, Krakow, Poland, (2) Theoretical and Physical Chemistry Institute, National Hellenic Research Foundation, 48 Vass. Constantinou Ave., Athens, Greece

In an interstratified illite-smectite (I-S) mineral the total layer charge (LC) is distributed between the illitic and smectitic interlayers (or layer surfaces), but only the smectitic surfaces are available for interactions with the environment. Therefore, the electrochemical charge exposed on the smectitic surfaces of I-S crystallites (Q_s) is the crucial parameter that controls the I-S surface properties. Moreover, the charge of smectitic surfaces is directly linked to the charge of illitic interlayers (Q_i) that must be controlled by the mechanism of I-S formation, which has been under extensive debate for decades [1].

Due to interstratification, the LC measurement techniques developed for smectites are not directly applicable for Q_s in I-S. The method based on a chemical analysis of monomineralic sample require the measurement of percent smectite layers to calculate Q_s [1]. LC determination methods based on saturation with alkylammonium cations, in turn, can cause the partial expansion of collapsed interlayers [2]. The measurement of charge developed on the smectitic surfaces of the interstratified clay mineral remains, therefore, quite challenging [1,3]. Recently, a new LC determination method was proposed: The “O-D method” is based on mid-infrared spectroscopic measurements of D_2O-saturated samples and was proven to work effectively for pure dioctahedral smectites [4]. Due to the nature of the O-D measurement, the method presents high potential to probe the external surfaces of interstratified clays. Its great advantage is the possibility of application to illite-smectite in mixtures with other minerals.

This presentation reports the application the O-D method to a series of 47 well-characterized illite-smectite samples covering the composition between 100 and 8% smectite layers [1]. Using a provisionally-calibrated O-D method, it was possible to measure LC of the expandable component of I-S. The average surface charge was 0.47 +/-0.04 e^- pfu, in good agreement with the stable value of 0.41 proposed earlier for Q_s of illite-smectite [1]. The narrow distribution of the measured layer charge Q_s within the sample-set was remarkable, confirming that the O-D method measures the charge present only in the expandable interlayers. Furthermore, no systematic changes of Q_s with smectite content were observed, in agreement with the model of polar illite fundamental particles. The O-D method is therefore applicable to interstratified structures and does not cause the expansion of the collapsed (illitic) interlayers, which may be the problem for some other methods [2].

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SYNTHESIS AND STABILIZATION OF MAGNETIC COMPOSITES OF BENTONITE

Kurmangazhy G., Sydykova A., Tazhibayeva S., Lachbayeva Zh., Musabekov K.

Al-Faraby Kazakh National University

Using Elmore's method, nanoparticles of magnetite were synthesized in the structure of bentonite of Tagan deposit (Kazakhstan). Nanoparticles of magnetite were stabilized by polyethylene glycol (PEG) and low molecular weight surfactant oxyethilenic alkylphenol (OP-7). The mass ratio of the magnetite and bentonite was 1:3, and the concentrations of PEG and OP-7 were $0.5 \cdot 10^{-3}$ and $2.5 \cdot 10^{-3}$%, respectively.

Based on the results of electron microscopic studies, the advantage of using PEG as a stabilizer in the synthesis of magnetite in interlayer space of bentonite clays over using low molecular weight surfactant OP-7, which forms a dense adsorption layer on the surface of the mineral, was substantiated.

Using light scattering method on the Zetasizer Nano instrument, dispersion analysis of magnetic clays obtained in the presence of $2.5 \cdot 10^{-5}$% PEG, was conducted. It was established that the particles of individual magnetite have size of 70 nm, bentonite - 505 nm, and the size of the magnetite-bentonite composite is 2150 nm. The presence of PEG reduces the size of the composite up to 1200 nm. Decrease of composite size is caused by the fact that the introduction of the polymer contributes to the convergence of magnetite and bentonite particles due to the formation of hydrogen bonds between its macromolecules, oxygen atoms of silicate groups of bentonite and iron oxides groups of magnetite.

X-ray analysis of magnetic clays was conducted. On the diffraction pattern of bentonite highest peaks were found at values of $2\theta=20.780°$ and $28.980°$, which correspond to silicon-oxygen and aluminum-oxygen groups of montmorillonite, contained in the bentonite. In the case of magnetite, the most intense peaks were obtained at values of 2θ of $35.240°$ and $41.572°$, which correspond to the phase Fe_3O_4 and $Fe_2O_3$of magnetite. Changes in the X-ray diffractogram of bentonite were found, which indicate the introduction of magnetite nanoparticles in the bentonite structure.

It was shown that the introduction of magnetite nanoparticles in the interlayer space of bentonite is determined by not only the physical accordance of sizes of magnetite particles and the interlayer space, but also by chemical interactions, which lead to significant changes in the bentonite structure, resulting in appearance of new phases.

Sedimentation stability of dispersions of magnetite and its composites with bentonite was studied. It was shown that the magnetite dispersions are unstable, and suspensions of magnetic composites of bentonite are much more stable. Presence of PEG and OP-7 increases the stability of the suspensions.

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DIRECT SYNTHESIS OF COLLOIDAL INTERLAYER-MODIFIED LAYERED DOUBLE HYDROXIDES USING TRIPODAL LIGANDS

Yoshiyuki Kuroda (1)*, Shiori Hayashi (2), Yuya Oka (2), Atsushi Shimojima (2), Hiroaki Wada (2), Kazuyuki Kuroda (2,3)

(1) Waseda Institute for Advanced Study, Waseda University, Tokyo, Japan, (2) Faculty of Science and Engineering, Waseda University, Tokyo, Japan, (3) Kagami Memorial Research Institute for Materials Science and Technology, Waseda University, Tokyo, Japan
*kuroda@waseda.jp

Layered double hydroxides (LDHs) are one of the most important clay-related materials because of their anion exchangeability, basicity, and environmentally benign compositions. Further functionalization of LDHs is expected, if the surface hydroxy groups of LDH layers are modified with organic groups; however, their covalent interlayer modification was hardly reported up to date. Silylation is one of versatile methods for functionalization of inorganic materials [1], though selective modification of LDH layers without self-condensation has not been shown. We have recently reported that tripodal ligands, such as tris(hydroxymethyl)amionomethane (Tris) is effective to modify surface hydroxy groups of LDHs [2]; however, the modification proceeded only on the outer surface of LDH nanoparticles (LDHNPs). If the interlayer surface of LDHNPs are modified with Tris molecules possessing NH_3^+ groups, unique interlayer nanospace with two different cationic sites can be created. Here, we report new methods for interlayer modification of various LDHNPs with Tris molecules.

Interlayer-modified Mg-Al LDHNPs were synthesized by mixing aqueous solutions of metal salts and Tris, followed by aging at 80 °C for 24 h. In our previous report [2], we used 0.50 M Tris solution, though highly concentrated solution (4.5 M) was used in this study. The product was finely dispersed in water, and aggregated by adding a Na_2CO_3 solution for characterization. The interlayer-modified LDHNP showed a basal spacing of 0.95 nm which is much larger than that of conventional CO_3^{2-}-type LDHs (0.76 nm). The basal spacing suggests that the LDH layers are modified with Tris and form an interdigitated configuration. Interlayer anions can fill the interstices of Tris molecules. The FTIR and ^{13}C CP/MAS NMR spectra of the interlayer-modified LDHNPs indicated that the Tris molecules are covalently modified with the LDH layers [2,3]. The elemental analyses show that the Tris/(Mg+Al) ratio was 0.26 and the Mg/Al was 2.1, though the Tris/(Mg+Al) ratio was only 0.05 when the LDHNPs were prepared by using a 0.50 M Tris solution. Moreover, the CO_3^{2-}/(Mg+Al) was 0.29 which significantly exceeds the value (0.16) expected from the Mg/Al ratio, suggesting that NH_2/NH_3^+ groups of the modified Tris molecules also act as anion exchange sites. Because of the expanded interlayer distance and unique interlayer environments, the interlayer-modified LDHNPs are expected to have improved anion exchangeabilities.

Interlayer-modified Co-Al and Ni-Al LDHNPs were also synthesized by using Tris. In these cases, highly concentrated Tris solutions were not required because transition metal cations form more stable alkoxy bonds with Tris than a magnesium cation [3]. Interlayer modified Co-Al and Ni-Al LDHNPs were synthesized by hydrothermal treatment of mixtures of Tris and metal salts at 190 °C. As we reported previously, the Tris molecule has an ability to suppress crystal growth of LDHNPs by surface modification. Thus, Co-Al and Ni-Al LDHNPs, forming stable bonds with Tris, tend to form very small LDHNPs that cannot be collected even by membrane filtration. They require higher temperature to promote the crystal growth. The reaction temperature should be optimized for various compositions.

Consequently, the use of tripodal ligands is very effective for the direct synthesis of highly dispersed LDHNPs whose interlayer surfaces are modified with tripodal ligands. The unique interlayer nanospaces possessing different cationic sites and high dispersibility are promising for the formation of functional nanomaterials, such as anion scavengers, catalysts, and drug carriers.

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UNFROZEN WATER FILMS IN FROZEN VOLCANIC SOILS AS THE RESULT OF WEATHERING PROCESSES

Elena Kuznetsova (1)*, Rimma Motenko (2)

(1) Norwegian University of Science and Technology, Trondheim, Norway, (2) Lomonosov Moscow State University, Moscow, Russia

Layers of volcanic ash and the Andosol soils derived from them may play an important role in preserving snow and ice as well as developing permafrost conditions. The special properties of volcanic ash that are responsible are critically reviewed, particularly in relation to recent research in Kamchatka in the Far East of Russia. Of special importance are the thermal properties and the unfrozen water contents of ash layers and the rate at which the weathering of volcanic glass takes place. Weathering of volcanic glass results in the development of amorphous clay minerals (e.g. allophane, opal, palagonite) but this takes place much slower in cold than under warmer climate conditions. Existing data demonstrates that (1) there is a strong correlation between the thermal conductivity, the water-ice content, and the mineralogy of the weathered part of the volcanic ash (2) enhanced amounts of amorphous clay minerals (allophane, palagonite) increase the proportion of unfrozen water and decrease thermal conductivity, and (3) amorphous silica does not alter to halloysite or other clay minerals even in ashes of Early Pleistocene age (Kamchatka) or in Miocene and Pliocene deposits of Antarctica due to cold temperatures.

Published data on unfrozen water content in frozen volcanic ash soils are quite infrequent. [1] and [2] mentioned volcanic ash among 17 other soils to show a relationship between dielectric constant and volumetric unfrozen water content. [3] Demonstrated by pulsed NMR the temperature dependence of the unfrozen water content in Ohya tuff in the range of the negative temperature measured. Even at -5 ^{o}C, the sample contained 7.5% unfrozen water by weight, reflecting the rough surface microstructure of pores and large specific surface area.

For volcanic ash collected in Kamchatka and Iceland, the unfrozen water varied from 0 to 27% for temperatures below -3 ^{o}C and the amount depending on the deposit's age, chemical composition, salinity, presence of amorphous clays and weathering conditions. The content of unfrozen water is found to be higher in volcanic ashes containing allophane (2-13%) than in those containing opal (0-3%). The highest proportion of unfrozen water (27%) occurred in an ash with high soil's water salinity [4]. For Icelandic samples containing palagonite, the alteration product of basaltic glass found in association with sideromelane, the unfrozen water content may reach 2-3% for temperatures below -3 ^{o}C [5]. Palagonite is a terrestrial analogue to the soil of Mars [6] and studies on its mineral behavior at negative temperatures may help in understanding weathering models of the Martian rocks by unfrozen water films.

The significance of these findings is discussed in relation to the reconstruction of past climates and the influence of volcanic ash on permafrost aggradation and degradation, snow and ice ablation, and the development of glaciers.

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AMORPHOUS CLAY MINERALS OF VOLCANIC SOILS FORMED UNDER COLD CLIMATE CONDITIONS

Elena Kuznetsova (1)*, Rimma Motenko (2)

(1) Norwegian University of Science and Technology, Trondheim, Norway, (2) Lomonosov Moscow State University, Moscow, Russia

Properties of volcanic ash and pumice, as well as volcanic soils have been widely investigated due to their unique properties. Paleoscientists and tephrochronologists use volcanic ash as a tool for linking and dating geological, paleoecological, paleoclimatic, and archaeological sequences or events. Soil scientists are concerned with the unique physical, chemical and mineralogical properties of the soils formed on the volcanic ash (or Andisols) with respect to their high permeability, organic matter, secondary minerals, high surface area as well as other aspects. In cold environments, volcanic ash is an important factor in (1) process influencing permafrost aggradation and degradation of carbon in peat accumulations, and (2) as a chronological marker in studies of rock glaciers, glacial moraines, glacier fluctuations, moraine development and glaciofluvial deposition. The influence of tephra is important to snow and ice ablation, permafrost aggradation, and the energy balance at the glacier-atmosphere interface. Terrestrial volcanoes in permafrost areas provide analogue information for volcanic permafrost models for Mars.

The glass fraction in volcanic ejecta is their most readily altered silicate component (Shoji et al., 1993; Shoji et al., 1994; Kimble et al., 2000) making it potentially a sensitive indicator of the climate as long as the environment of its alteration is realised and the time framework in which the alteration has occurred can be deduced. The rate of its weathering or its alteration in the subsurface depends not only on its chemistry but most importantly on the temperature and the availability of water. At sub zero temperatures in heavily frozen ground the decomposition rate of glass is minimal reflecting both the very slow rate of chemical reaction as well as the unavailability of water. In topographically varied terrains the situation is complicated. In areas with a mean annual temperature below -1 °C and a mean annual precipitation of less than 500 mm, clay minerals in volcanic soils are scarce, and volcanic glass is preserved mostly in the unweathered and unaltered state. With higher mean annual temperature the alteration rate of volcanic glass increases leading to the development of amorphous clays, such as allophane, imogolite and palagonite. At high elevations, higher rainfall and lower evaporation due to lower temperatures create a high-leaching environment and the colloidal fractions of these volcanic soils are dominated by amorphous clays with the absence of halloysite. In the mountains of northern Ecuador, allophane is dominant in the colloidal fraction of volcanic soils above 3200 m asl whereas it is absent below 2700 m asl, where precipitation is higher. The drier conditions in the soils below 3200 m and 2700 m asl, is associated with halloysite becoming increasingly dominant in the fine fraction (Zehetner et al., 2003).

Similar slow rates of glass weathering are associated with dry deserts whether they are cold or hot, the absence of available water for reaction is the controlling factor. Although the repeated heating and cooling of frozen and hot deserts accelerate physical weathering through fracturing of glass thereby increasing the surface area available for chemical alteration. In contrast, the alteration of volcanic glass in warm or hot humid climates is rapid. Not only are these reactions more easy to study but they are associated with soils of agricultural importance and the economic pressure for understanding them is much greater. Within the warm humid zones depending on the chemical composition of the volcanic glass the following reaction series have been suggested: volcanic glass → allophane → halloysite, volcanic glass → opal → allophane → halloysite, volcanic glass (sideromelan) → palagonite.

The most obvious academic use of understanding the factors controlling the alteration of volcanic ash is the ability to use it in the reconstruction of past-climates and weathering environments in the more recent geological past.

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LEAD AND COPPER SORPTION FROM AQUEOUS SOLUTIONS BY IRON-MAGNESIUM RICH CLAY MATERIALS

Zacharenia Kypritidou*, Ariadne Argyraki

Department of Geology and Geoenvironment, National & Kapodistrian University of Athens, Athens, 15784, Greece
zach-kyp@geol.uoa.gr

We present data on the effectiveness of threeGreek bulk clay materials, in removing lead and copper ions from concentrated aqueous solutions. The used materials, formed by the alteration of ultramafic rocks [1], included a palygorskite-rich sample (PCM), a Fe-Mg-smectite-rich sample (SCM) and a natural palygorskite/smectite mixed sample (MCM). Clay minerals contribute over 70% in the bulk composition of each sample being 70% palygorskite and 20% smectite in PCM, 6% palygorskite and 70% smectite in SCM, and 20% palygorskite and 40% smectite in MCM. Subordinatemineralogical phases in all materialsincludedserpentine, quartz, plagioclase, calcite and dolomite. FTIR and XRD analysis indicated that the Fe-Mg-smectite phasein SCM and MCM samples has both dioctahedral (nontronite) and trioctahedral (saponite) characteristics.

Sorption batch experiments were carried out at 22 ^{o}C, using Pb and Cu solutions with concentrations ranging from 0 to 800 mg/L, at a pH of 3.6, solid amount 10g/L and a reaction time of 4h. The experimental conditions were selected according to previous equilibrium studies [2]. Finally, the suspensions were centrifuged for 15 mins at ~3,000 rpm and the solution pH was measured. Lead and Cu concentrations in the supernatant solutions were measured using AAS.

Sorbed metal amount (q_s, mg/g) increasedwith increasing metal concentration in the initial solution (C_0, mg/L). The maximum sorbed Pb amount was~28 mg/g for PCM and ~50 mg/g for both SCM and MCM, whereas there spective values for Cu were~8mg/g for PCM and ~16.5 mg/g for SCM and MCM. Moreover, the pH values of the final suspensions tended to decrease inversely with q_s, ranging from 8 to 5. The Sips isotherm model fitted well to the experimental data ($R^2>0.97$ for all materials). Sips isotherm incorporates both Langmuir and Freundlich isotherms, and is used when high solute concentrations are studied [3]. The sorption process was characterized as favourable and irreversible, according to the parameter K_s (L/g) (ranging from 0.02 to 0.09), and the system was classified as heterogeneous according to the exponent n (2-2.5), regardless the sample.

Combining the mineralogical and sorption experimental data, it is evident that, among the three samples, the smectite-rich materials (MCM and SCM) show higher effectiveness in removing the studied metal ions from solution. Their affinity can be attributed to their high smectite content, and therefore, to the combination of both high specific surface area and cation-exchange capacity of the mineral phase [4]. Moreover, Pb ions are more susceptible in forming strong bonds with the mineral surface than Cu. The small hydrated radius and high hydrolysis constant of Pb probably enable the formation of inner-sphere complexes and stronger electrostatic bonds with the clay surfaces, compared to Cu.

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WASTE-BASED GEOPOLYMER ADSORBENTS FOR DYE REMOVAL FROM WASTEWATERS

Rui M. Novais*, G. Ascensão, D. Tobaldi, M.P. Seabra, J.A. Labrincha

Department of Materials and Ceramic Engineering / CICECO- Aveiro Institute of Materials, University of Aveiro, Campus Universitário de Santiago, 3810-193 Aveiro, Portugal

The presence of dyes in industrial wastewaters is a serious and long-lasting environmental problem. In fact amounts lower than 1 ppm change water colour, which is obviously undesirable. Methylene blue (MB) is commonly used in fabrics and furniture industries. MB is known to cause respiratory and abdominal problems [1] and therefore its removal from wastewaters is of the utmost importance. Adsorption is considered the most effective, simple and low cost technique for MB removal. Recently the demand for innovative and low cost adsorbents has increased, due to the high production cost of common adsorbent materials (e.g. activated carbon) which hinder their widespread use [2]. Geopolymers are a promising alternative to conventional adsorbent materials due to their low cost production and green technology. They present a negatively charged aluminosilicate network where charge-balancing cations can be exchanged with cations in the solution [3], suggesting the possibility of using them as adsorbents [4,5]

In this study the feasibility of using biomass fly ash-based geopolymer monoliths as MB adsorbents was evaluated. The influence of MB concentration in aqueous solutions, contact time and geopolymers' porosity on the MB removal efficiency by the geopolymers was investigated. Results show a very high MB uptake by the porous geopolymer monoliths which demonstrate their potential as MB adsorbents.

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INNOVATIVE GEOPOLYMER SPHERES TO BOOST BIOGAS PRODUCTION

RUI M. NOVAIS*, M.P. SEABRA, J.A. LABRINCHA

Department of Materials and Ceramic Engineering / CICECO- Aveiro Institute of Materials, University of Aveiro, Campus Universitário de Santiago, 3810-193 Aveiro, Portugal

Although the global awareness regarding the greenhouse gases emissions has risen, the energy supply still relies mainly in fossil fuels [1]. Despite this, the interest on using more-energy efficient technologies, such as biogas, has attracted increased attention. Indeed this technology can mitigate the greenhouse gasses emissions in comparison with fossil fuels [2]. The anaerobic digestion of organic material (in bioreactors) produces biogas. This complex process is highly affected by the pH of the medium, which must be strictly controlled to ensure high methane yield. The latter is especially relevant when using high organic content substrates, which suffer rapid acidification and reduce systems efficiency. One common approach to overcome this pH drop is to add commercial alkaline materials such as lime and sodium hydroxide. Nevertheless this strategy increases process complexity and cost. Geopolymers are binder materials synthesized by alkali activation of silica and alumina rich materials at relatively low temperatures. After geopolymerization free alkalis remains in the structure, and therefore is available for leaching which suggest the possibility of using them as pH buffering material [3].

In this study waste-based geopolymer spheres [4] were first developed and then evaluated as pH buffering material. Results show that the produced spheres ensure prolonged pH adjustment (over the 30 days measurements) due to hydroxyl ions leaching from their structure. The narrow pH fluctuation observed for these innovative materials demonstrates their potential as pH buffer material in several applications such as in bioreactors.

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MINERAL TRANSFORMATIONS IN ALUMINIUM-RICH CLAYS WITH FIRING AND THEIR RELATION WITH SIGNIFICANT PROPERTIES

Elisa Laita*, Blanca Bauluz

IUCA-Facultad de Ciencias, Universidad de Zaragoza, 50009 Zaragoza, Spain

Aluminium-rich clays with kaolinite and/or pyrophyllite are the most important raw material to manufacture high-quality stoneware and ceramic pavements as well as refractory ceramic. This industrial interest makes interesting to determine the mineral and textural transformations that take place during the firing process and their influence in the physical properties of the fired products.

Three Silurian shales that outcrop in the Iberian Range (NE Spain) have been selected for this study. These materials that were previously studied [1] have significant contents in pyrophyllite, organic matter, and the lack of carbonates. Mineralogical and textural transformations and changes in physical properties (color, linear contraction, density, total porosity and average pore) of three shales fired from 800 to 1300 ºC have been studied; these modifications produce significant changes in physical properties. Raw and fired samples were analyzed by X-ray diffraction, transmitted light microscopy, field emission scanning electron microscopy and transmission electron microscopy.

Initially these samples were formed by variable proportions of illite, pyrophyllite, kaolinite, orthoclase, quartz, mixed layers I/S and organic matter. Kaolinite, mixed layers I/S and the organic matter were destabilized at temperatures below 800 °C indicating that they are the least stable phases to the firing process. Illite, pyrophyllite and orthoclase remain until 1000 ºC and they show a larger stability field during the ceramic process than in natural environments. Quartz remains during all the firing process, although it is partly replaced by vitreous material. When temperature increases, hematite and mullite crystallize and the vitrification process starts from 1000 ºC. This vitreous phase that is the precursor of mullite is composed of variable amounts of Si, Al, O and minor proportions of K, Fe and Ti.

The mullite shows variable and non-stoichiometric composition. The contents in Al range from 17.55 to 35.51%, Si from 13.95 to 29.55%, Fe from 0.93 to 2.04% and Ti from 0-0.31%. Probably Fe and Ti substitute partially Al in the structure. Its composition and crystal size change with firing temperature. The (Al+Fe+Ti) /Si ratio increases from 0.87 (1000) to 1.14 (1100 ºC) and to 1.90 (1300º) being closer to the Al/Si ratio of the theoretical mullite (2.88). The crystal size (thickness) increases with temperature from 2-3 nm thick at 1000 ºC, to 20-35 nm thick at 1100 ºC and 40-70 nm thick at 1300 ºC. These changes reflect that the amount of crystalline defects in the mullite decreases.

The studied clays are less reactive to the firing process than other ceramic clays rich [2]. In carbonate and illite-rich clays the formation of vitreous phases starts at 800 ºC, and the mineral and textural changes also begin at lower temperatures those reported in this study.

Changes in colour (grey-orange-brown) with temperature are due to the loss of organic matter, the formation of hematite and its subsequent destabilization. Variations in linear contraction, density, total porosity and in average pore size are related to the destabilization of the different phases, the progress of vitrification and the crystallization of mullite.

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AMMONIUM-INDUCED DISSOLUTION OF SMECTITES. KINETICS AND SOLID CHARACTERIZATION

D. Lamarca-Irisarri (1), A. E. S. Van Driessche (2), F. J. Huertas (1)

(1) Instituto Andaluz de Ciencias de la Tierra (CSIC-University of Granada), Armilla (Granada), Spain, (2) Institute des Sciences de la Terre, CNRS, Université Grenoble-Alpes, France

The mechanisms of smectite dissolution have been extensively studied, foucusing on the effect of pH, temperature and catalysts and inhibitors of the reaction (e.g. organic ligands, phosphates, etc.) (e.g., [1], and references therein). In particular, the variation of the smectite dissolution rate with solution pH is summarized as follows: the rate increases with decreasing pH, reaches its minimum at neutral pH and increases again for basic conditions. The effect of the solution pH is related to the adsorption of protons on the hydroxyl groups of the reactive surface and the proton transfer from solution to the mineral surface occurs through the hydronium ion.

Ammonium is a weak acid in solution. Under neutral conditions where the concentration of hydroniun is very low ($<10^{-7}$ M), ammonium contributes to smectite dissolution. In order to quantify this influence, a series of flow-through dissolution experiments of K-saturated montmorillonite were carried out at temperatures of 25, 50 and 70 ºC, at five NH_4 concentrations (10^{-4}, 10^{-3}, 10^{-2}, 10^{-1} and 0.5 M) until steady state was reached.

The results show that at 25 and 50 °C the smectite dissolution rate derived from Si concentration in the output solutions increases with ammonium concentration. However, at 70 °C dissolution rate is aproximately constant, irrespecitve of ammonium concentration.

Solids were characterized after alteration by XRD, FTIR and HR-TEM. Diffraction patterns of EG solvated Ca-samples show an uncompleted swelling and the presence of a small peak at 10 Å. That was interpreted as an increased in the tetrahedral charge. Furthermore, heating at 350 ºC produces a partial collapse of the structure, with 14 Å peaks that collapse to 10 Å after heating at 550 ºC. This behavior points out to formation of some hydroxy interlayered smectites (HIS) by intercalation of Al ions favored by ammonium [2]. FTIR spectra show some bands that can be associted to exchangeable and non-exchangeable NH_4.

HR-TEM study allowed us to observe three types of fringes: 10 Å associated with non-expandable or illitic layers, 12 Å linked to a monolayer of water hydrating the smectite interlayer and 14 Å interpreted as HIS layers, with hydroxy aluminum incorporation in the interlayer. Moreover in some samples belonging to the higher temperatures series (70 ºC), some gibbisite-like phases could be identified. They were located on smectite surface, and could prevent the dissolution of the smectite, inhibiting the effect of the ammonium ion as a catalizer of the smectite dissolution by blocking the surface reactive sites.

These results allow us to establish a bridge between our kinetics observations and solid characterization, pointing to an optimum of the ammonium influence on the dissolution rate between 50 and 70 ºC.

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MINERALOGY OF SWALLOW NESTS AND THE ROLE OF CLAY MINERALS

Dimitrios Papoulis (1), George Iliopoulos (1), Olga Tzortzakaki (2), Pavlos Avramidis (1), Panagiotis Mentis (1), Paraskevi Lampropoulou (1)*

(1) Department of Geology, University of Patras, Rio 26 504, Patras, Greece, (2) Department of Biology, University of Patras, Rio 26 504, Patras, Greece

Material samples were collected from 23 swallow nests from 15 different localities in Greece and Cyprus. 11 from the sampled nests were built by the Barn Swallow (*Hirundo rustica*), 6 by the House Martin (*Delichon urbicum*) and 6 by the Red-rumped Swallow (*Cecropis daurica*). The nest of the Barn Swallow is an open cup consisting mainly of mud and plant material, placed on roof beams. The House Martin builds a closed, convex mud nest, mainly on house walls, whereas the Red-rumped Swallow builds a closed mud nest with an entrance tunnel in caves and under bridges.

The mineralogical analyses of the samples were conducted using XRD, while semi-quantitative mineralogical analyses were performed. The morphology of the mineral grains was studied using SEM. Additionally grain size analyses were performed and plasticity indexes were determined.

The differences in mineralogy, grain size distribution and plasticity indexes of Barn Swallow, House Martin and Red-rumped Swallow nests are discussed. The results show that specific clay minerals are used as cement while other clay minerals are not preferred while accessible. The amounts of clay minerals are low indicating that the studied species can identify in a pretty good accuracy the properties of the minerals that they use. As a result they use the clay minerals as an efficient cement building thus stable nests. Most of the other minerals that they use are common, easily accessible minerals like quartz, feldspars, calcite and dolomite.

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DETERMINATION OF CLAY AND SWELLING CLAY MINERALS ON AGGREGATES BY USING A COMBINATION OF THREE ANALYTICAL METHODS: METHYLENE BLUE TEST, SAND EQUIVALENT TEST AND SEMI QUANTITATIVE ANALYSIS BY XRD

Petros Petrounias (1), Panagiota P. Giannakopoulou (1), Aikaterini Rogkala (1), Paraskevi Lampropoulou (1), Eleni Koutsopoulou (1), Dimitrios Papoulis (1), Basilios Tsikouras (1,2), Konstantin Hatzipanagiotou (1)

(1) University of Patras, Department of Geology, Section of Earth Materials, 265 00, Patras, Greece, (2) University Brunei Darussalam, Faculty of Science, Physical and Geological Sciences, Jalan Tungku Link, Gadong BE1410, Bandar Seri Begawan, Brunei Darussalam

Clay minerals found in natural aggregates are associated with harmful effects in the wide range of their applications. A number of samples were tested, from different places of Greece, in order to estimate their suitability as aggregates in construction and environmental applications. An approximation of the amount of clays in the fine aggregate was performed with the sand equivalent test. The occurrence of swelling clay minerals in the aggregates was estimated with the methylene blue test, which is a rough indication for their presence in aggregates. However, sand equivalent shows poor correlation with methylene blue results, therefore no conclusive results can be drawn with regards to the influence of different clay minerals on the in-service performance of the aggregates used in constructions and specifically in road ballast. Preliminary results using X-ray diffraction and semi- quantification showed that the percentage of clay minerals in the aggregates can be a valuable asset to the determination of their suitability in a number of applications.

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A COMBINED DEFLOCCULATION AND COAGULATION PROCESS FOR DEVELOPMENT OF SELF-COMPACTING CLAY CONCRETE

Gnanli Landrou*, Coralie Brumaud, Guillaume Habert

Chair of Sustainable Construction, ETH Zürich, Switzerland

Clay minerals are widely used and are of importance to the processing in many sectors. In earthen construction sector, clay acts like binder for earth as it displays colloidal interactions and adhesion forces between particles and grains. While extensive research exists on clay dispersion [1,2] or coagulation [3,4], the purpose of this study is to understand and to control clay properties in earth material in order to propose an innovative strategy to develop a self-compacting clay concrete without use of cement. To do so, we studied the modifications of clay properties using inorganic and mineral additives.

As clay rheological behaviour is controlled by their surface charge, it is observed that an addition of dispersants such as sodium hexametaphosphate or silicate decrease clay surface charge and reduce considerably the yield stress that allows to caste earth based material. We performed extensive series of rheological and zeta potential measurement on kaolinite clay paste to identify the driven mechanism of clay dispersion and the stability during time. The results show that for sodium hexametaphosphate, it exists a linear relationship between yield stress and square zeta. We then suggested that it disperses clay particles via electrostatic repulsion forces. Furthermore, we noted that at low percent of dispersant, without reaching the maximum coverage determined with zeta measurement, kaolinite clay displays thixotropic and aging behaviour. Besides, we stress that when dispersed, at high volume fraction it is possible to observe shear thickening behaviour in clay suspension.

Although the deflocculation process allows to caste easily earth based material, it is important to accelerate the formwork removal by flocculating the clay suspension for rapid construction process. To do so, rheological measurements on dispersed clay is used to characterize the effect of magnesium ions on dispersed clay suspensions. The results show that adding magnesium cations permanently increases the yield stress during time. This process similar to internal coagulation or cement hydration [5] allow accelerating the hardening process. In this study, it is suggested that the cations annihilate the effect dispersant and interact with clay particles which enable the coagulation of clay particles. Yet SEM and DRX analysis are carried out to identify the precipitation products and the interaction with clay in order to justify and understand the hardening process.

In conclusion, we stress the dispersion mechanism of sodium hexametaphosphate and we highlight the thixotropy and shear thickening behaviour in dispersed and dense kaolinite suspension. Furthermore, we note that adding coagulants agent enable to transform permanently the rheological behaviour of clay and suppress the shear thickening and thixotropy behaviour. These findings suggest that the combined deflocculation-coagulation process and understanding of mechanism allow proposing a new sustainable route for self-compacting clay concrete.

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EXPERIMENTAL ALUMINIZATION OF VERMICULITE INTERLAYERS: AN X-RAY DIFFRACTION PERSPECTIVE ON CRYSTAL CHEMISTRY AND STRUCTURAL MECHANISMS

Bruno Lanson (1)*, Eric Ferrage (2), Fabien Hubert (2), Dimitri Prêt (2), Louis Mareschal (3,4), Marie-Pierre Turpault (3), Jacques Ranger (3)

(1) ISTerre, CNRS - Univ. Grenoble-Alpes, Grenoble, France, (2) IC2MP, Univ. Poitiers - CNRS, Poitiers, France, (3) Biogéochimie des Ecosystèmes Forestiers, INRA, Champenoux, France, (4) Eco & Sols, CIRAD, Montpellier, France
*Bruno.lanson@univ-grenoble-alpes.fr

Natural aluminization of swelling clay minerals is ubiquitous in acidic soils leading to the formation of hydroxy-interlayered (HI) minerals. This process has drawn special attention over the last 4-5 decades owing to the negative impact on soil fertility of the induced reduction of cation exchange capacity. Combination of chemical analyses and of X-ray diffraction profile modeling on a series of experimentally self-aluminized samples aimed at an improved description of HI minerals and more especially of their interlayer crystal chemistry.

Both exchangeable alkali cations and hydroxy (Al, Fe) cations coexist within HI vermiculite interlayers. The latter form discontinuous gibbsite-like interlayer sheets with ~15% completeness, despite layer-to-layer distances similar to that of chlorite. From charge compensation considerations, the isolated hydroxy (Al, Fe) cation clusters bear ~1.5 positive charges per cation.

Analysis of X-ray diffraction data indicates that aluminization of initially swelling interlayers is a layer-by-layer process leading to mixed layers composed of randomly interstratified swelling and aluminized layers, all aluminized layers likely hosting a similar number of hydroxy (Al, Fe) cations along the aluminization process.

This model contradicts the widely accepted description of HI minerals as a solid solution between expandable 2:1 clay and aluminous chlorite end-members. As a consequence, the proportion of HI layers in the mixed layer is a robust estimate of aluminization progress and both the amount of extractible (Al, Fe) and the extent of CEC decrease are positively correlated to this essential parameter.

Applicability of this model to vermiculite samples altered in forest soils will be discussed.

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DEFECTS MATTER: A VERSATILE PROGRAM FOR MODELING X-RAY DIFFRACTION PATTERNS OF DEFECTIVE LAYERED STRUCTURES

Bruno Lanson (1)*, Sylvain Grangeon (2), Alain Plançon (3), Boris A. Sakharov (4), Victor A. Drits (4)

(1) ISTerre, CNRS - Univ. Grenoble-Alpes, Grenoble, France, (2) BRGM, Orléans, France, (3) Orléans University, Orléans, France, (4) Geological Institute, Russian Academy of Sciences, Moscow, Russian Federation
*Bruno.lanson@univ-grenoble-alpes.fr

The nature, content, and possibly distribution of structure defects controls to a large extent mineral/material reactivity and properties. More especially, the high density of structure defects of layered minerals and materials is key to their reactivity. These defects range from local defects such as isomorphous substitutions, layer vacancies, or atomic displacements, to random or well defined stacking faults induced by non-periodic layer rotations, translations or twinning, and to mixed layering resulting from the coexistence within a given crystal of layers having different structure, thickness, or interlayer displacement. The occurrence of stacking faults in lamellar structures is favoured by the energetic similarity of the different stacking modes, owing to the weak interactions between adjacent layers. In addition, layered materials and minerals often exhibit minute crystal sizes that may be considered as an additional type of defect because of the induced disruption of the three-dimensional (3D) crystal periodicity.

To determine, control, or predict mineral/material reactivity a detailed structural characterization of layered structures, including structure defects, is thus essential, and X-ray diffraction (XRD) has been the preferred method of investigation for this purpose. However, as a result of their non-periodicity or their reduced periodicity, the diffraction maxima recorded from these compounds do not strictly obey Bragg's law, thus hampering the use of conventional diffraction approaches, such as the Rietveld method. Profiles and intensities of diffraction maxima are affected by the nature, content, and distribution of structure defects, however, thus allowing the determination of these parameters with diffraction techniques.

The present talk will report on a freely-available program allowing reliable interpretation of diffraction data, and thus determination of average structural information, from crystals deprived of 3D periodicity. The calculation routine, coupled to a user-friendly GUI, is based on the algorithms developed in the mid 1970's both in Orléans and Moscow, [1,2] and described in details by Drits & Tchoubar (1990) [3]. Applications to various layered structures will be reported.

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TITANIUM IN KAOLINITES. WHAT ARE ITS SOURCES?

Isaak Lapides

Institute of Chemistry, The Hebrew University of Jerusalem, E.Y.Safra Campus, Givat Ram, Jerusalem 91904, Israel
isaak8@hotmail.com

The report discusses the question of the forms of trace titanium in a layered hydroxyl-aluminosilicate kaolinite. It is known that in most natural kaolinites, titanium oxide is present in the form of anatase. There is evidence to suggest that titanium can substitute octahedral aluminum in the structure of kaolinite. This work studies SEM and X-ray Powder Diffraction (XRD) series of kaolinites, some of which have been previously analyzed by Raman and FTIR spectroscopy [1,2]. It is shown that the XRD in the area (24 ÷ 27) °2Θ allows to compare the most intense peak of anatase (*1 0 1*) with the intensity of the peak *(0 0 2)* of kaolinite, which enables semi-quantitative detection of anatase in kaolinites. In this work, we have undertaken to analyze our data as well as other published results, including previous chemical analyses, Raman and FTIR spectra, and X-ray parameters of kaolinites [3] that are derived by different genesis. The analysis appears to support the conclusion that the substitution Al^{VI} by Ti, *i.e.* the direct entry of titanium into the aluminosilicate structure, occurs only at low Ti concentrations. At high contents of TiO_2, this substitution is not realized, while the entire titanium is included exclusively in the separate crystalline anatase phase. This feature seems to be associated with two different sources of titanium in the process of kaolinite formation. One source of titanium compounds is the result of the destruction of parent rocks, which release titanium compounds which may concentrate in kaolinite in appropriate geochemical conditions. The present work examines a second possibility for the appearance of Ti, as a result of the creation *in situ* of the titanium isotope $_{22}Ti^{47}$, resulting from the hypothetical Low-Energy Nuclear Reactions (LENR) in the process of the formation of kaolinite. The process of mineral formation is considered through the model of non-equilibrium processes in open dynamic systems, where such reactions are possible, and the physics of these phenomena is fully described within the framework of quantum mechanics. The presentation analyzes the criteria of feasibility, possible reaction schemes and discusses ways of the experimental verification of the proposed hypothesis.

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CONTROLLING THE BUNDLING OF IMOGOLITE NANOTUBES BY SALT INTERCALATION

Erwan Paineau (1), Mohamed Salah Amara (1), Geoffrey Monet (1), Véronique Peyre (2), Stéphan Rouzière (1), Pascale Launois (1)*

(1) Laboratoire de Physique des Solides, CNRS, Univ. Paris Sud, Univ. Paris Saclay, 91405, Orsay, France, (2) Laboratoire PHENIX, CNRS, Sorbonne Universités, Univ. Paris 06, 75005, Paris, France

Significant developments have been proposed over the last decade on the synthesis of imogolite-like nanotubes such as $(OH)_3Al_2O_3GeOH$ (Ge-INT, where silicon in imogolite nanotubes $(OH)_3Al_2O_3SiOH$ is replaced by germanium) [1] or hydrophobic methylated $(OH)_3Al_2O_3Si_xGe_{1-x}CH_3$ nanotubes [2,3]. But while liquid phase synthesis is well controlled, it is not the case for imogolite or imogolite-like nanotube arrangement in the final solid product. In particular, nanotubes are found to self-assemble or not in bundles of various sizes, which impacts the properties of the final product.

J. P. Gustafsson [4] proposed that a weak positive charge is developed on the external surface of imogolite nanotubes, which could explain the formation of bundles thanks to bound anions. To our knowledge, such proposal has not been verified experimentally. Electrophoretic mobility measurements performed on a suspension of $(OH)_3Al_2O_3GeOH$ single walled nanotubes (Ge-SWINT) allowed us to show that Ge-SWINTs are positively charged up to pH=9.5. Then, we demonstrated that nanotubes bundling in the solid state is directly related to the amount of salts in the acidic suspension which was dried to obtain the final powder. Ge-SWINT organization in powder was studied by X-ray scattering and bundling, characterized by the number N of nanotubes in a bundle, is found to vary from $N=1\text{-}2$ to N≈60 depending on the salt amount. These experimental results show that bundling is indeed controlled by anion intercalation [5].

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INFLUENCE AND MECHANISM OF FREEZE AND THAW CYCLES ON STRUCTURAL, PHYSICAL AND MECHANICAL PROPERTIES OF CLAY SOILS

Georgy Lazorenko, Anton Kasprzhitskii*, Victor Yavna

Department of Physics, Rostov State Transport University, Narodnogo Opolcheniya sq., 344038, Rostov-on-Don, Russia
*glazorenko@yandex.ru

Intensive reclaiming of expansion areas of permafrost and seasonally-frozen soils, necessity of quality durability improvement of engineering design, construction and operation of engineering structures, railways, highways, oil- and gas pipelines installed in complex geocryological environments demand in-depth studies of processes of structural transformations in soils and changes of their physical mechanical properties under repeated freeze-and-thaw actions.

Up to now there has been accumulated plentiful experimental and theoretical material as regards mechanisms and regular patterns of development of deformations of swelling of frozen soils and thawing soil subsidence which have different composition and structure in various engineering geocryological environments [1-3]. There has been gained the data regarding forces (tensions) of swelling [4,5]. Nevertheless, some issues demand research. Among these are influence of cryogenic factors on formation of finely dispersed components of clay soils, mechanisms and regular patterns of structural transformations of clay particles of frozen soils, features of thawing soil subsidence under simultaneous development of processes of water migration and ice segregation. There isn't enough data on chemical and physical-chemical processes including transport of salts and humidity in salt soils under temperature and load changes and within time.

This research is devoted to the processes taking place in clay soils under cryogenic influence. We take into account modern considerations on synergy of water with different groups of minerals depending on temperature and ice-formation in soils. Theoretical study of ice-formation process on the surface of clay minerals has been carried out by methods of molecular simulation. Regular patterns of dispergation and degradation of clay particles under repeated freeze and thaw actions have been defined. Experimental studies of dynamics have been performed. Alongside with this regular patterns of structure transformation, content and properties of clay polymineral soils and monomineral clays under repeated freeze and thaw actions have been fetched out in accord with the data of IR-spectroscopy and X-ray structural analysis. These results are of great practical interest and have potential to be applied in engineering construction on permafrost and season-frost soils.

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HALLOYSITE BASED MATERIALS FOR CONSERVATION OF CULTURAL HERITAGES

Vanessa Bertolino, Giuseppe Cavallaro, Giuseppe Lazzara*, Stefana Milioto, Filippo Parisi

University of Palermo, Department of Physics and Chemistry, Palermo, Italy
*giuseppe.lazzara@unipa.it

The consolidation of archaeological wooden finds is an extremely complex process as the main difficulty is due to the wood high sensitivity to the environment. The waterlogged woods are found in marine or in anoxic and very humid areas; these conditions promote somewhat conservation of wooden finds because of the low temperatures and low amounts of oxygen. The maximum moisture content, the basic density and the wood substance density are parameters which also provide the preservation state of waterlogged archaeological wood. Under extreme conditions, the wood loses mechanical resistance and becomes similar to a sponge. Consequently, the drying process assumes a crucial role converting the wood into a compact material which has lost the original structure.

Similarly, paper based artefacts undergo to aging processes. In this case, a consolidation flanked by chemical protection is required.

The proposed materials used over the years for the consolidation of cellulose-based artefacts are numerous, nevertheless, many questions are still to be solved. The remarkable development in the field of nanotechnology provides new materials and approaches in principle valuable for protecting archaeological heritage. With this in mind, we prepared a consolidant based on halloysite nanotubes (HNT). Halloysite is a natural clay, abundant over the world, no-toxic and inexpensive. Halloysite nanotubes possess hollow tubes with diameters of the order of 80 nm and lengths of ca. 700 nm. The addition of halloysite nanotubes to biopolymers might cause an improvement of the mechanical and thermal properties. Another interesting aspect of using HNT as nanofiller is the ability to load active chemical agents into the lumen for a controlled release. Thermal and mechanical properties were determined for the halloysite based nanocomposites at various compositions. To the light of these insights, samples of waterlogged archaeological wood and paper were consolidated.

Thermal analysis was carried out to investigate the degradation of the materials. Mechanical experiments under controlled humidity conditions were carried out on bionanocomposites. Relative humidity (RH) is a key parameter for such a kind of biological materials.

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DYNAMICS AND REACTIVITY OF WATER IN NATURAL MONTMORILLONITES

Fourdrin Chloe (1), Aarrachi Hanane (2), Latrille Christelle (3), Bergaya Faiza (4), Righini Roberto (5), Renault Jean Philippe (2), Lima Manuela (5), Le Caër Sophie (2)*

(1) CEA/Saclay, LSI, Ecole Polytechnique, F-91128 Palaiseau Cedex, France, (2) CEA/Saclay, DSM/IRAMIS/NIMBE/LIONS UMR-3685, F-91191 Gif-sur-Yvette cedex, France, (3) CEA/Saclay, DEN/DANS/DPC/SECR, F-91191 Gif-sur-Yvette Cedex, France, (4) CRMD UMR 6619, 1b rue de la Férollerie, F-45100 Orléans, France, (5) LENS, University of Florence, Italy

The radiolytic decomposition of water has significant impact in the nuclear industry. H_2 radiolytically formed by water decomposition might lead to explosion and overpressure hazards in the waste package. In the context of high level radioactive waste management, heterogeneous materials such as clay minerals (or concrete) are possible candidates around the waste package. For instance, bentonite, which major component is montmorillonite (Mt, the most representative swelling clay mineral of the smectite group), is foreseen in France as backfilling material for its swelling and retention properties. However, the significant amount of water present in the interlayer space and between the particles might enhance the H_2 production under irradiation, and despite the environmental significance, only a few studies discuss the water radiolysis in those systems. In this context, we have decided to investigate the dynamics and the reactivity of water molecules confined in natural montmorillonites from Camp Berteau, Marocco.

Ultrafast infrared spectroscopy of the O−D stretching mode of dilute HOD in H_2O probes the local environment and the hydrogen bond network of confined water [1]. The dynamics of water molecules confined in the interlayer space of montmorillonites and in interaction with two types of cations (Li^+ and Ca^{2+}) but also with the negatively charged siloxane surface was studied. The results evidenced that the OD vibrational dynamics was significantly slowed down in confined media: it went from 1.7 ps in neat water to 2.6 ps in the case of Li^+ cations with two water pseudolayers (2.2−2.3 ps in the case of Ca^{2+} cations) and to 4.7 ps in the case of Li^+ cations with one water pseudolayer. No significant difference between the two cations was noticed. In this 2D confined geometry (the interlayer space being about 0.6 nm for two water pseudolayers), the relaxation time constants obtained were comparable to the ones measured in analogous concentrated salt solutions. Nevertheless, and in strong opposition to the observations performed in the liquid phase, anisotropy experiments evidenced the absence of rotational motions on a 5 ps time scale, proving that the hydrogen bond network in the interlayer space of the clay mineral is locked at this time scale.

Lastly, the impact of confinement on the reactivity under irradiation of confined water molecules was investigated. The radiolysis of water confined in natural montmorillonites was studied as a function of the composition of the montmorillonite, the nature of the exchangeable cation, and the relative humidity by following the H_2 production under electron irradiation [2]. It was shown that the main factor influencing this H_2 production was the water amount in the interlayer space. The effect of the exchangeable cation was linked to its hydration enthalpy. When the water amount was high enough to get a basal distance higher than 1.3 nm, then a total energy transfer from the montmorillonite sheets to the interlayer space occured, and the H_2 production measured was very similar to the one obtained in bulk water. For a basal distance smaller than 1.3 nm, the H_2 production increased with the relative humidity and thus with the water amount.

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REACTION MECHANISMS IN SWELLING CLAYS UNDER IONIZING RADIATION: IMPACT ON THE GEOLOGICAL STORAGE OF THE NUCLEAR WASTE

Laine Maxime (1), Allard Thierry (2), Balan Etienne (2), Robert Jean-Louis (2), Le Caër Sophie (1)*

(1) CEA/Saclay, DSM/IRAMIS/NIMBE/LIONS UMR-3685, F-91191 Gif-sur-Yvette cedex, France, (2) IMPMC, Sorbonne Universities, UPMC, UMR-7590, 4 Place Jussieu, F-75252 Paris cedex 05, France

The influence of ionizing radiation on clay minerals is poorly known, in spite of their use as a major component of the engineered barrier in High Level Nuclear Waste Repositories (HLNWR). In this context, the production of H_2 by clay minerals under ionizing radiation could be a real issue. It can, e.g., lead to the loss of radionuclide retention properties by creating cracks in the engineered barrier. It is thus important to determine H_2 formation reaction mechanisms and to understand the role of several parameters on this production, such as the water amount, the presence of impurities and the nature of the clay mineral.

We studied synthetic clay minerals (talc, which has no water molecules, montmorillonite and saponite which exhibit charge excess in different locations) [1-2] and also natural montmorillonites from Camp Berteau [3]. The reactivity under electron irradiation is deciphered thanks to H_2 production measurements at well-defined relative humidities together with electron spin resonance experiments that allow detecting the defects created upon irradiation. Comparing the reactivity induced in the synthetic samples enables understanding the impact of the presence of two-dimensionally confined water molecules and the influence of the charge location in the sheets of the clay mineral. Moreover, the comparison between synthetic and natural talc evidences the strong role played by impurities on the H_2 production yields [1]. We find that H_2 production is due to the presence of structural -OH groups and that the confinement of water molecules is a crucial factor. Moreover, the charge location in the sheets of the clay minerals plays only a marginal role [1-2]. All these results will be discussed and the corresponding reaction mechanisms will be presented. Lastly, the role of impurities in natural clay minerals such as Fe^{3+} that strongly decrease the H_2 production will be discussed.

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STUDY OF FLUIDS AND SOLUTES BEHAVIOR IN UNSATURATED CLAY PORE BY MOLECULAR DYNAMICS

Sébastien Le Crom (1)*, Christophe Tournassat (2), Jean-Charles Robinet (3), Virginie Marry (1)

(1) PHENIX Université Pierre et Marie Curie, Paris 75005, France, (2) BRGM, Orléans 45000, France, (3) ANDRA, Châtenay Malabry 92019, France

It has been shown that the clayey medium selected by the French Agency for the Management of Nuclear Wastes (ANDRA) as part of the Cigéo [1] Deep Storage Project is unsaturated in water after drilling. However, although many studies have focused on predicting the performances of clay minerals as barrier materials in the containment of high-level radioactive waste by evaluating the diffusion of mobile species, the systems considered are often saturated. Thus calculation codes used to study the reactive transport of species at the scale of the storage structures based on data obtained experimentally or theoretically describe rather well the saturated clay pore systems. On the other hand, available data becomes more sparse in the case of unsaturated pores. Yet, the unsaturation can deeply modify properties such as species distributions and diffusion coefficients. Thus, microscopic studies of unsaturated pores are necessary in order to implement the unsaturated case in reactive transport codes [2].

In the present work, we choose to study unsaturated pores of Na-montmorillonite, which is the main clay mineral in bentonite. The negative charge of the clay induces an overconcentration of cations at the surface as well as an exclusion of the anions described more or less well by the double layer model in the saturated case. Thereby we have investigated the impact of unsaturation and salinity on this double layer and we compared our results with theoretical models such as Poisson-Boltzmann. The impact of unsaturation on the mobility of species was also measured by calculating their diffusion coefficient. All these properties are calculated on the microscopic scale by Molecular Dynamics simulations in order to validate macroscopic laws or, if necessary, to propose new ones that could be integrated in a mesoscopic code such as calculation codes mentioned earlier. Finally, because the system presents two interfaces, a solid-liquid interface and a liquid-gas interface, we will compare the results between a reference non-polarizable force field, CLAYFF [3], and a polarizable force field that should better take into account the phenomena at the interfaces [4,5]. For the latter, we chose to use PIM [6], a new force field currently in development at PHENIX laboratory.

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CAN ORGANOCLAYS BE EFFICIENT AS GEOCHEMICAL BARRIERS FOR THE RETENTION OF PHARMACEUTICALS?

Le Forestier Lydie*, Guégan Régis

Institut des Sciences de la Terre d'Orléans (UMR 7327 CNRS-Université d'Orléans-BRGM), Orléans, 45071, France

Due to their low permeability and their high sorption properties, clay materials rich in smectite are often used as geochemical barrier in the case of waste landfill or waste water treatment. If these materials are well-known to adsorb cationic contaminants through ion exchange or by surface complexation, they appear to be less efficient to retain neutral or anionic compounds, such as pharmaceutical products (PP). Organoclays, hybrid materials based on clay materials and cationic surfactants, were proposed as realistic alternatives for the sorption of organic compounds and pharmaceuticals [1-3]. If their efficiency was highlighted in batch experiment conditions, no study stressed out the sealing performance of organoclays during percolation experiments, where the solution is constantly renewed.

Thus, the aim of this work was first to characterize, through percolation experiments by using an œdometric cell coupled with an injection system under controlled pressure [4], the hydromechanical properties (swelling and hydraulic conductivity) of different organoclays prepared with various cationic surfactants. The hydromechanical properties determined by using pure water as injected solution and compared to the sodium exchanged smectite from Wyoming (Na-SWy2) appeared to be closely related to the nature of surfactant and its organization. The incorporation of surfactants within the interlayer space of the layered materials increases the hydraulic conductivity of about 100 times to that of the Na-SWy2 ($k = 10^{-12}$ m.s^{-1}). This significant increase of permeability will unfortunately lead to a lower interaction duration between organoclays and contaminants in solution, a disadvantage for sorption mechanism which was more particularly studied in the case of the amoxicillin, one of the most useful antibiotic for the treatment of several bacterial infections.

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INVESTIGATION OF TEMPERATURE EFFECTS ON THE FORMATION AND PHYSICOCHEMICAL PROPERTIES OF STRUVITE

Seon Yong Lee, Young Jae Lee*

Department of Earth and Environmental Sciences, Korea University, Seoul, 02841, Republic of Korea
*youngjlee@korea.ac.kr

Struvite ($MgNH_4PO_4 \cdot 6H_2O$) is an important mineral in environmental, material, medical sciences and industries [1-5]. Precipitation of this mineral is commonly used for a treatment of wastewater contaminated by phosphate and a recycling of precipitates as a fertilizer [1,2]. In addition, struvite is of great interest in medical science because it is often found in kidney stones related to urinary systems [5]. The structure of struvite is very sensitive to temperature changes, which may result in its drastic thermal decomposition [4-6]. Struvite also has a temperature-sensitive equilibrium in solution, which can lead to significant changes in the formation of struvite particles with different physical properties [7,8]. Therefore, studies on temperature-dependent struvite have focused on developing fertilizers and controlling the removal of P in wastewater treatment, as well as on the thermal stability of struvite for medical purposes improving its applicability in various fields.

Struvite and other magnesium minerals were synthesized by a wet precipitation under different temperature ($T_{(S)}$), 15-60 °C, and dried 45 and 60 °C, respectively. All samples were characterized by XRD, TGA, ATR FT-IR, and FE-SEM. Struvite was only formed at $T_{(S)} \leq 30$ °C and had an inverse relationship between its crystallinity and $T_{(S)}$. The crystallinity of struvite decreased with increasing drying temperature ($T_{(D)}$) due to the escape of water and ammonium from the structure of strivite, indicative of critical thermal decomposition temperature point between 45 to 60 °C. Interestingly, struvite formed at lower $T_{(S)}$ showing higher crystallinity was more resistant to the thermal decomposition. Crystal morphologies for the samples are also related to temperature. Penniform-like crystals formed at $T_{(S)}$, 15-20 °C were dominant more than prismatic shape crystals formed at $T_{(S)}$, 25-30 °C. Our results demonstrate that the formation and physical properties of struvite can be controlled by temperature seriously.

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USE OF CLAYS FOR PHARMACEUTICAL, COSMETIC AND FOOD APPLICATIONS IN KOREA

Sung-Rock Lee (1)*, Il-Mo Kang (2), Kimin Roh (2), Sung Man Suh (2)

(1) International School for Geoscience Resources, Korea Institute of Geoscience and Mineral Resources(KIGAM), 34132, Daejeon, Republic of Korea, (2) Advanced Geo-Materials Research Department, Korea Institute of Geoscience and Mineral Resources(KIGAM), Pohang, Republic of Korea
*srlee@kigam.re.kr

Korea Institute and Mineral Resources (KIGAM) has implemented a project for the application and utilization technology development using clays minerals in pharmaceutical, food and cosmetics usages since 2014. The primary target in the initial stage of development aims to evaluate the applicability of bentonites for the pharmaceutical and food usages. The geological mapping and the drilled core specimens show promising bentonites resources from the volcanic complex at south-eastern area of the Korean peninsula, and the bentonites mineralization is closely related to the geological structure like faulting system.

One of the critical issues for the use of clays in the pharmaceutical industry is the content of toxic heavy elements and microbial contaminants which defined in US and European pharmacopoeias. The particle size control using continuous centrifuging was done, and the spray drying was applied to the microbial limit test evaluation. The bentonites samples were separated using a sedimentation method, subsequently fractional yield, analysing mineral assemblage, montmorillonite content, and cation exchange capacity fir the purification of the bentonites. However, opaline phase was remained after the simple sedimentation method. A novel method, using by combining ultrasonic dispersion and ultra-fine particle separation, was applied to separate opaline phase from the bentonites. KIGAM is collecting more than 500 representative clay specimens from the country for the standardization for the food and pharmaceutical quality of domestic clay minerals. And KIGAM is building the clean manufacturing pilot facility to fulfil the Bulk Good Manufacturing Practise (BGMP) regulation.

For the application of microbials in the bentonites to the food industry, it is revealed microorganisms in the phylum and proteobacteria and firmicutes were identified to be dominant members. The isolated Bacillus and Lactic acid bacteria are applied to the fermented food affecting the enzymatic reactions of industrial enzymes including cellulose, protease, and lipase. It suggests that clay mineral can be used as fermentation modifier for Korean fermented foods.

In the presentation, we will introduce a case study using organic-rich mud for cosmetic application. In the local beach area, there is a well-known mud festival which attracts tourists to enjoy the effectiveness of mud painting and mud cosmetic products.

We will further be activating the multidisciplinary researches relating with medical, pharmaceutical, and applied clay sciences. And the domestic production of purified and quality-assured bentonites will safely and effectively widen our research development into the use of clay minerals as drug delivery systems, diagnostic media, or a material in various formulations of drug products.

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DEHYDROXYLATION *VS* DEHYDROGENATION IN THERMAL DECOMPOSITION OF Fe-CHLORITE

Małgorzata Lempart (1)*, Arkadiusz Derkowski (1), Artur Błachowski (2)

(1) Institute of Geological Sciences, Polish Academy of Sciences, Senacka 1, 31 002 Krakow, Poland, (2) Institute of Physics, Pedagogical University, Podchorazych 2, 30 084 Krakow, Poland

Besides dehydroxylation that a common reaction for all heated phyllosilicates, thermal transformation of phyllosilicates containing ferrous iron involves dehydrogenation related to oxidation of Fe^{2+} [1,2,3]. If dehydrogenation occurs, it removes hydrogen that is a crucial element in the dehydroxylation reaction. Therefore, if no dehydrogenation prior to dehydroxylation occurs, mass loss corresponding to dehydroxylation should match the mass loss calculated from the mineral formula.

In this study isothermal thermogravimetric experiments were carried out to determine the mechanism and order of these overlapping reactions in ferrous chlorite. An iron-rich chlorite $(Fe^{2+}{}_{3.4}Mg_{0.9}Mn_{0.1}Fe^{3+}{}_{0.2}Al_{1.3})(Si_{2.65}Al_{1.35})O_{10}(OH)_8$, chamosite IIb (Gendarme, Mont Blanc) was investigated under isothermal conditions in pure nitrogen flow by heating for a period from 1 hour to 48 hours at different temperatures in the range of 350-475 °C, followed by a ramp heating to 1000 °C with a 10 °C/min rate. Mössbauer spectroscopy was used to determine the extent of Fe^{2+} oxidation after isothermal heating and subsequent ramp heating.

In the studied chlorite a thermal treatment involving only the fast-rate ramp heating resulted in the total mass loss closely corresponding to the theoretical mass loss. Such a fast and complete dehydroxylation at 1000 °C led to the insignificant increase of iron Fe^{3+} from 5% to 8% of total iron. These results imply no or little oxidation, thus no dehydrogenation, during progressing dehydroxylation. However, when isothermal heating was involved prior to the ramp heating, the total mass loss was lower. The greatest difference between the theoretical and experimental total mass loss was obtained by heating the chlorite for 48 hours at 390, 400 or 410 °C, and the Fe^{3+} fraction of the isothermally-heated sample reached almost 80%. Any lower or higher isothermal temperatures resulted in greater mass loss and lower degree of Fe oxidation. The reason behind this variation is the decrease of the quantity of OH groups available for dehydroxylation due to dehydrogenation of OH groups coordinated to Fe^{2+} releasing hydrogen. At isothermal temperatures below 390-410 °C dehydrogenation is minimal while at greater temperatures dehydroxylation precedes dehydrogenation. The Mossbauer spectroscopy returns the change of relative amount of oxidized iron, which directly correlates to the extent of dehydrogenation thus the lower mass loss upon dehydroxylation. After isothermal heating small structural changes take place. Newly oxidized Fe^{3+} tends to form of the OH coordination in R^{2+} R^{2+} Fe^{3+} and R^{2+} Fe^{3+} Fe^{3+} associations, which gives minor infrared absorption bands [1,2]. Mossbauer and infrared spectroscopy indicate that not all OH groups initially coordinated with Fe^{2+} are lost during the oxidation process stimulated by dehydrogenation.

Although the processes of dehydrogenation linked to Fe^{2+} oxidation and dehydroxylation occur simultaneously during isothermal heating, in a particular range of temperature and isothermal time one of these reactions is more favourable. When the minimum temperature for the particular reaction is attained the dehydroxylation occurs faster while dehydrogenation requires more time. A fast ramp heating highly enhances dehydroxylation over dehydrogenation.

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NON-IDEAL LAYER STACKING CONTRIBUTIONS TO X-RAY POWDER DIFFRACTION PROFILES OF KAOLINITE SAMPLES

Alberto Leonardi*, David L. Bish

Department of Geological Sciences, Indiana University, Bloomington, Indiana 47405, U.S.A.
*alby_leo@yahoo.it

Layer stacking disorder contributions to X-ray powder diffraction (XRPD) line profiles of KGa1, KGa2, API9 and Keokuk kaolinite samples were investigated exploiting a variety of reference patterns simulated via the Debye scattering equation (DSE) [1]. XRPD patterns of a large collection of numerical models of different kaolinite microstructures were simulated to evaluate the effects of crystallite size distribution and various types of stacking disorder. In particular, the line profile features corresponding to variable in-plane shift of stacked layers were investigated. Not only were the *hkl* peaks affected, but the *00l* peaks also shifted and broadened depending on the spacing and degree of overlap of the stacked layers. High resolution XRPD patterns for the kaolinite samples and their comprising particle-size fractions were characterized based on the relative intensity sequence of the *hkl* peaks, accounting for the different crystallite size distributions and several sources of stacking disorder. As all measurements were made using capillary geometry while the sample was spinning at high frequency, no aberrations due to preferential orientation of crystallites were considered, in agreement with assumptions in the DSE. Although roughly confirming previous estimates of the disorder in layer stacking, a non-negligible relative shift of stacked layers was observed to significantly affect the estimation of stacking fault probability. In addition, disorder in layer stacking was characterized as a function of the particle size, separating the different types of line broadening contributions (i.e., stacking fault, layer-shape shift, misorientation and crystallite size).

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SMALL INORGANIC ANIONIC ADDITIVES FOR PROBING THE INTERPARTICLE FORCES IN BENTONITE SLURRIES

Mingyong Du, Yee-Kwong Leong, Jishan Liu

School of Mechanical and Chemical Engineering, The University of Western Australia, Perth, Australia 6009

Bentonite (Na montmorillonite) is an important commercial clay mineral with many uses such as drilling mud, binder of iron ore pellets, latex paint additive, facial mask, purification additive of edible oils, nuclear waste storage barrier and impermeable slurry wall for isolating contaminated water in construction sites. Aqueous bentonite slurry displayed many intriguing properties such as particle swelling, time-dependent mechanical properties and a very high yield stress at a low concentration of 5-10 wt% solids. When this mineral is found in significant quantity in mine tailings it poses a huge waste disposal problem. Such tailings are very low density and difficult to consolidate requiring a massive area for its disposal. The strength and nature of the interparticle force, the particle concentration and shape, heterogeneity and location of surface charges, and the microstructure all contribute to this low density, time dependent, yield stress behaviour. Surface chemistry-rheology correlations such as that between yield stress, a measure of strength of interparticle attractive force in the particle network, and zeta potential, a measure of the interparticle repulsive force, appeared not to hold for this slurry [1]. The zeta potential was shown repeatedly to be quite insensitive to pH [1-2]. Phase state analysis of experimental microstructural data assigned a "flocculated" state to this slurry at an unusually high ionic strength of >0.2 M of a 1:1 electrolyte [3] corresponding to the collapse of the gel [4]. In this study, phosphate-based additives, 3-charge phosphate, 4-charge pyrophosphate and 5-charge triphosphate, were used to probe the strength of the interparticle force in 7 wt% bentonite slurries. The positive charge residing on the edge of the alumina sheet (being sandwiched between two silica sheets) is postulated to interact with these anions. The thickness of this alumina sheet may affect the interaction with these additives of different size and charge.

The yield stress showed a sharp decrease with additive concentration for all three phosphate-based additives in the low concentration region. The reduction in the yield stress is an indication of a weakening attractive interaction between particles in the gel. At the high additive concentration region, the decrease is more gradual for $P_2O_7^{4-}$ and $P_3O_{10}^{5-}$. The (normalised) yield stress decrease behaviour for $P_2O_7^{4-}$ and $P_3O_{10}^{5-}$ was almost identical across the whole concentration range. However, with the PO_4^{3-} additive, the decrease stopped at a certain concentration and began to rise again but in a gradual manner. Complete dispersion of the slurry was not observed even at $P_2O_7^{4-}$ and $P_3O_{10}^{5-}$ concentration as high as 2 dwb% (g $P_2O_7^{4-}$ or $P_3O_{10}^{5-}$ per 100g bentonite) as indicated by the presence of a finite yield stress. There is currently no plausible model that can explain this behaviour.

1. The gel with 2.0 dwb% PO_4^{3-} displayed time-dependent behaviour where its yield stress increased with ageing time. In contrast the gel with the same concentration of $P_2O_7^{4-}$ did not show such time-dependent behaviour. A possible explanation is a much stronger adsorption bond being formed by $P_2O_7^{4-}$ on the alumina edge. The size of this anion must be just right to sit ideally on the alumina surface with minimal repulsive interaction of the negatively charged sites on the silica edge.
2. Drilling mud is composed of many ingredients [5]. One of these phosphate additives is an important ingredient added to drilling muds as a wetting and dispersing agent. The knowledge gained from this study will help the drilling mud formulator to achieve the desired mud rheology and stability with the correct selection of the phosphate additive and concentration to use.

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FAST AND ACCURATE DIFFRACTION PATTERN CALCULATION FROM DISORDERED CLAYS: OLD *VERSUS* NEW APPROACHES

Matteo Leoni (1)*, Alberto Leonardi (2)

(1) DICAM University of Trento, Trento, Italy, (2) FAU Erlangen, Erlangen, Germany

The quantitative analysis of the powder diffraction pattern of disordered clays has been the subject of extensive publications since the fifties. The stacking disorder, in fact, modifies the symmetry of the material locally: as a consequence the small unit cell that we can clearly identify as repeating unit in the plane, is no longer sufficient to describe the material in its entirety. The feature is common to a multitude of materials of undoubted scientific and technological importance.

Recently, the interest in the topic has been revived and a few approaches have been proposed/reprised, such as e.g. the use of the Debye scattering equation [1], the matrix method [2,3], a Fourier/matrix structure/microstructure formalism based on the recursive approach [4] and a Rietveld-compatible supercell method [5,6].

A framing of those methods in the context of the existing literature (e.g. [7-12]) is proposed, to show advantages and limits in terms of accuracy and speed. Several apparently different methods are just a different parameterisation of the same formalism. A recently proposed form of the matrix/recursive method is presented for a fast reconstruction of the powder pattern of clays and of materials with faults on possible multiple orthogonal axes, properly taking the microstructure (thus e.g. size distribution) into account [13]. The current computing speed opens the possibility of real time computing and refining - thus not just simulating - the structure/microstructure of layered materials, and to accurately quantify them in mixtures.

Theory, benchmarking and applications are shown and discussed.

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RAW MATERIALS OF BELARUS FOR SAFE STORAGE AND DISPOSAL OF RADIOACTIVE WASTE

Tatyana Leontieva*, Daria Korob, Eugeni Prokopieu, Vladislav Gatsko

Joint Institute for Power and Nuclear Research - Sosny, NAS of Belarus, Minsk, P.O. Box 119, 220109, Belarus
*t.leontieva@tut.by

Due to the intensive nuclear power development worldwide there is an emerging problem of safe management of radioactive waste (RW), long-term storage and disposal of radioactive waste, as well as radioecological safety and elimination of the radiation accidents consequences at nuclear power plants (NPP). The search of low cost materials with high sorption properties which can selectively sorb radionuclides is a major task nowadays. Chemically stable alumosilicates (bentonite, illite, kaolinite, natural and synthetic zeolites, feldspars, pollucite, nepheline, etc.) which have a layered structure, characterized by a large sorption capacity and selectivity for several radionuclides are promising materials for conditioning radioactive waste (creating curing matrix). Such alumosilicate systems based on low-cost natural and synthetic materials are also used to create isolation barriers for near-surface storages of radioactive wastes.

In Belarus, promising sorption materials for use as backfills in the construction of engineered barriers for radioactive waste disposal are the bentonite from “Ostrozhanskoye” deposit (Gomel region) and clay-salt slimes (CSS) - chemical industry wastes produced by reprocessing sylvinite ore at the JSC “Belaruskali” (Soligorsk region, Belarus).

The calcium bentonite of Belarus has low montmorillonite content. However, processing results to significant increase in the montmorillonite content and increased sorption capacity for ^{137}Cs. Thus, the distribution coefficient (K_d) and the Radiocaesium Interception Potential (RIP(K)), describing the ability of a material to selectively adsorb ^{137}Cs in the presence of potassium cations, for bentonite samples fraction size less than 0.63 mm are $1.2 \cdot 10^3$ l/kg and 1123 mmol/kg respectively. Processed bentonite samples with particle size less than 45 microns have increased K_d and RIP(K) values, $1.4 \cdot 10^4$ l/kg and 7167 mmol/kg respectively. Study of the kinetics of ^{137}Cs sorption-desorption on the bentonite samples revealed that after equilibration time $t = 10$ min the sorption ratio ^{137}Cs (F_s) reached almost 99%. An increase in the radiocaesium distribution coefficients was observed in the bentonite-solution system with time. After $t = 30$ days the $K_d(^{137}\text{Cs})$ value increased more than twice the original value. The processed bentonite samples of “Ostrozhanskoye” deposit can be effective materials for use as anti-migration barrier and buffer fillings in radioactive wastes safe disposal.

Along with bentonite, one of the most promising sorption materials is CSS, with reserves exceeding 110.5 mt on (data 01.01.2016). The CSS are weighted clay sediments in a saturated solution of salts (KCl and NaCl), which have a fine structure and are composed of minerals such as montmorillonite, and illite. Water treatment of CSS can significantly reduce the water-soluble salts content, and the modification (dissolution of calcite and dolomite) allows increasing the content of the sorption-active components. Due to the modification and therefore the significant reduction of the $CaCO_3$ content, is possible to use the CSS as anti-migration barriers and buffer materials. The study of sorption properties of the processed CSS samples allowed determination of the efficiency for sorption of ^{137}Cs and other radionuclides (^{85}Sr, Eu, Am). The degree of ^{137}Cs sorption on modified CSS samples reached 99.3% after 24 h of contact with the radioactive solution, the ^{137}CsCl, K_d value was $1.3 \cdot 10^4$ l/kg and the RIP(K) was 6724 mmol/kg. The study of the kinetics of ^{137}Cs sorption-desorption processes on the CSS samples revealed that sorption is a very fast process: after 1 min $F_s(^{137}\text{Cs})$ reached 98.2% and after 30 days $F_s(^{137}\text{Cs})$ was 99.6%. The equilibration time was about 20 min, wherein $K_d(^{137}\text{Cs})$ was 10^4 l/kg; beyond that time $K_d(^{137}\text{Cs})$ increased by 2.3 times. The modification of CSS significantly increased the abundance of sorption-active minerals.

This work has shown that according to the physiochemical and sorption properties, the CSS is not inferior to known world analogues (bentonite). This suggests the possibility of their application, along with the bentonite “Ostrozhanskoye” deposit as anti-migration barriers and buffer fillings for shallow land burial which are planned to be constructed in the Republic of Belarus.

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MINERALOGICAL AND GEOCHEMICAL APPROACHES FOR ANALYSIS OF AEGEAN MARINE SEDIMENTS: PROVENANCE AND PALAEOCLIMATIC IMPLICATIONS

G. Leontopoulou (1), G.E. Christidis (1)*, G. Papatheodorou (2), M. Geraga (2), E. Koutsopoulou (2)

(1) Technical University of Crete, Department of Mineral Resources Engineering, 73100 Chania, Greece, (2) University of Patras, Department of Geology, 26500 Rio, Patras, Greece
*christid@mred.tuc.gr

The distribution of clay minerals, major and trace elements, organic carbon and particle size were examined in two deep-sea bottom cores from the Myrtoon basin in the SW Aegean Sea (core C40) and Eastern Cretan Sea (core TI13). The study included quantitative mineralogical and geochemical analysis of the bulk sediments in order to further assess paleoclimatic and paleoenvironmental changes in notherneastern Mediterranean, based on the combined investigation of clay minerals and geochemical indicators. The sediments are dominated by calcite, Mg-calcite, quartz, feldspars and clay minerals (illite, chlorite, kaolinite, smectite and palygorskite). Accessory serpentine, talc and hornblende attest to contribution from ultrabasic sources in the surrounding areas. The abundance of palygorskite was used to quantify the aeolian input. Comparison of the clay mineral abundances in the bulk samples, determined by Autoquan® software with Rietveld refinement and profile fitting using ZnO internal standard, and the clay fractions determined according to Biscaye (1964) [1], showed that the bulk sediment is enriched in kaolinite and chlorite and depleted in smectite relative to the clay fraction, whereas illite is more evenly distributed in the bulk sample and the clay fraction. Moreover no particular relationship was observed between the abundance of illite and smectite, suggesting different mode of enrichment of the two clay minerals.

A sharp decrease was observed in the Mg-calcite content and the Mg/Ca ratios of the carbonate fraction in organic-rich sapropelic sediments, followed by an increase in the sand and silt fractions, which is reflected in the increase of the average grain size. A well expressed negative relationship between illite and smectite was observed in the clay fraction in full accordance with previous studies. However this trend is absent from the bulk sediments, because smectite is significantly overestimated in the oriented clay fractions due to particle size effects. Therefore the paleoclimatic and paleoenvironmental interpretations based on the ratios of clay minerals in the clay fractions should be examined cautiously, at least in recent sediments of closed basins such as the Aegean. Also, interpretations based on computer modelling of XRD traces of oriented clay fractions, although considerably more accurate than semiquantitative approaches, they are affected by overestimation of smectite.

Heating of the clay fractions at 400 and 530 °C and subsequent ethylene glycol solvation (EG) according to Christidis & Koutsopoulou (2013) [2], showed different sources of smectite in the sediments. The smectites in the Myrtoon basin are mainly *trans*-vacant, whereas their counterparts in Eastern Cretan Sea are mainly *cis*-vacant. The predominance of *cis*-vacant smectites in TI13 is compatible with contribution of volcanogenic smectites from the nearby volcanic islands of Santorini and Milos, in agreement with the existing water circulation patterns in the Cretan Sea. The *trans*-vacant smectites are considered pedogenic derived from the soils in the nearby landmasses of the Balkan Peninsula and Western Anatolia. The mineralogical results suggest that the composition of the recent Aegean sediments is controlled by supply from the nearby continental and island landmasses via small rivers, whereas significant input from SE Mediterranean waters is less likely. In addition, the distribution of the main clay minerals is affected mainly by shorting, with the sapropelic sediments displaying also climatic influence. Thus, the distribution of chlorite and illite especially in the S1 sapropel horizon of core C40 indicates climatic control, which is associated with the inflow of large masses of fresh water from rivers, due to the melting of ice sheets in Eurasia in the last post-glacial period at the beginning of the Holocene. The major supply of riverine sediments suggests that geochemical indicators such as the Al/Ti ratio, often used to identify aeolian input should also be used carefully in the Aegean sediments, because the aeolian Al/Ti signal is diluted by the riverine sediments derived from Turkey and the Balkan Peninsula.

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INSIGHT INTO THE STRUCTURE OF KAOLINITE AND LAYERED ZIRCONIUM PHOSPHATE INTERCALATED WITH PHOTOACTIVE MOLECULES

Anna Łepko, Izabela Biskup, Anna Koteja, Jakub Matusik*

AGH University of Science And Technology, Faculty of Geology, Geophysics And Environmental Protection, Department of Mineralogy, Petrography And Geochemistry, al. Mickiewicza 30, Krakow, 30 059, Poland
*jmatusik@agh.edu.pl

Layered structures, both of natural and synthetic origin, may serve as supports for the intercalation of several organic molecules. Thus prepared hybrid nanomaterials possess functionalities which depend on the type of inorganic host as well as chemical properties of the inserted molecules. The new materials may serve as e.g. adsorbents or catalysts. The intercalation of photoresponsive molecules enables to design layered materials showing photoactive behavior when exposed to UV-Vis radiation [1]. The isomerization of intercalated species triggered by UV light may lead to changes of interlayer distance of the host. Thus the structure of such intercalation compounds can be remotely controlled at an atomic level giving rise to new materials. Several layered minerals and synthetic phases were reported as hosts in such application. These include smectite minerals, synthetic micas and layered double hydroxides [2]. The goal of presented research was to intercalate photoactive molecules into the structure of natural kaolinite and synthetic layered zirconium phosphate. For the experiments a highly ordered kaolinite from Polish Maria III deposit was selected. The α-zirconium phosphate (ZrP) was synthesized by refluxing 10 g of zirconyl chloride ($ZrOCl_2 \times 8H_2O$) with 9 M aqueous solution of phosphoric acid at about 100 ºC for 24 h [3]. Azobenzene (Az) and 4-aminoazobenzene (pAz) were used as photoactive molecules. Prior to their intercalation the layered hosts were pre-intercalated. The kaolinite was intercalated with benzyldimethylhexadecylammonium chloride (BC_{16}) using methoxy-kaolinite as a precursor [4]. In the case of ZrP, hexylamine (C_6) and dodecylamine (C_{12}) were intercalated. Az was co-intercalated in a vapour form at ~120 ºC using a closed teflon vessel. In turn, the co-intercalation of pAz was conducted by dry grinding technique. Prior to UV-Vis radiation exposure the obtained materials were characterized using X-ray diffraction (XRD) and infrared spectroscopy (FTIR). The intercalation of BC_{16} into methoxy-kaolinite resulted in an increase of 8.7 Å peak up to ~42.0 Å. The large d_{001} value suggested that the BC_{16} molecules formed an arrangement nearly perpendicular with respect to the kaolinite layers. Their presence was confirmed by FTIR bands attributed to C-H stretching and bending vibrations found in the 3000-2800 cm^{-1} and 1500-1300 cm^{-1} regions, respectively. The co-intercalation of Az caused a further increase of the basal spacing to ~50.0 Å. The broad basal spacing peak and corresponding second and third order reflections as well as methoxy-kaolinite peak of high intensity (8.7 Å) and 7.2 Å kaolinite peak suggested mixed-layered character of the derivative structure. In the FTIR spectra, the co-intercalated Az led to an appearance of bands at: 3060-3030 cm^{-1} (C-H ring stretching) and 780, 690 cm^{-1} (C-H ring bending). The CHN analyses showed that Az/BC_{16} molar ratio was equal to ~1.6. The alternate exposure to UV (365 nm, 5 mW/cm^2, 2 h) and Vis light (sunlight, 2 h) showed that the d spacing reversibly changed by about 2 Å. The XRD patterns of ZrP intercalated with C_6 and C_{12} revealed series of integral reflections with basal spacing equal to: 22.9 Å and 36.0 Å, respectively. The acid-base interaction between NH_2 group and hydroxyls of ZrP was confirmed by changes of the OH stretching bands in the FTIR spectra. The intercalation of pAz was only successful for the C_{12} pre-intercalate where an increase of basal spacing up to ~40.0 Å was noticed. Also the use of this pre-intercalate for the intercalation of Az resulted in most significant changes of the basal spacing. This value decreased to 34.5 Å and the basal spacing peak has become broader. Additionally, higher order reflections formed an integral series. The bands connected with Az or pAz were visible in the FTIR spectra. The exposure to UV light lowered to only a small extent the basal spacing values for the intercalates with Az. This suggested that the arrangement of Az was mostly parallel to ZrP layers.

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CLAY MINERALS FROM THREE DIFFERENT GEOLOGICAL PERIODS IN LATVIA

Oskars Lescinskis*, Ruta Svinka, Visvaldis Svinka

Riga Technical University, Latvia, LV1048
*oskars.lescinskis@inbox.lv

Latvia iswith clays rich country and there are a lots of clay deposits containing various kinds of clays with various mineral and chemical compositions. Clays are used mainly as a raw material for producing of pottery, building materials, fillers for dyes etc. Clays, especially their nanosize fraction, have become a raw material for nontraditional and more delicate purposes - they are being used in medicine, pharmacy etc. In the present work it is a must to know the structures and properties of these minerals in order to obtain high quality composites. Some clay may be more appropriate for specific goals than others due to its properties; therefore it is very important to carry out investigations to find the most appropriate ones.

Description and characterization of 3 different nanosized clay minerals from 3 different geological periods (Liepa clay from Devonian period, Saltiski clay from Triassic period and Apriki from Quaternary period) are summarized. The main minerals in these clays are illite and kaolinite. Nanosized clay mineral particles were obtained using sedimentation method. Comparison of mineralogical composition, BET nitrogen adsorption, Zeta potential, DTA analysis and FTIR spectra is given. XRD phase analysis results are very close to each other and shows that mineral of illite is more than that of kaolinite. BET nitrogen adsorbtion data shows that Apriki clay has the highest specific surface area (81 m^2/g), whereas Saltiski clay has the lowest (43 m^2/g) specific surface area. Zeta potential values for Apriki, Liepa and Saltiski clay are -40,9 mV, -49,6 mV and -43,0 mV, respectively. DTA analysis and FTIR spectra show similar tendencies for all 3 clay minerals.

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TRANSFORMATION OF MAFIC AND ULTRAMAFIC ROCKS INTO SOIL CLAYEY MATERIALS IN THE CRITICAL ZONE OF COLD ENVIRONMENTS

Sofia N. Lessovaia (1)*, Michael Plötze (2), Yury Polekhovsky (1)

(1) St. Petersburg State University, St. Petersburg, Russia, (2) ETH Zurich, Institute for Geotechnical Engineering, Zurich, Switzerland

Studies of creating fine earth materials from hard rocks and following transformation into clayey material in soil environments are very important to understand the processes that are active in the critical zone of high latitudes and polar zones. These zones are widely thought to be areas of physical weathering only. The aim of the present research was to study (i) the conversion of highly weathering mafic and particularly ultramafic rocks into clayey materials and (ii) the characteristics in clay mineralogy including clay minerals distribution in the soils profiles in the cold environments. The study plots were located on the Polar Urals and the Central Siberian Plateau (Russia). The objects were mature profiles of Haplic Cryosol (Reductaquic) and Entic Podzol derived from and underlain by ultramafic and mafic rocks, correspondently. Haplic Cryosol (Reductaquic) was located on mountainous tundra of the Rai-Iz massif, the Polar Urals, which are the part of the Ural Mountains in the area of the Arctic Circle. Entic Podzol was located in the central part of the flood basalt complex, or traps (traprocks) of the Central Siberian Plateau. The traprocks, which are mafic rocks, were represented by dolerite in the study plot. Mineral association in rock fragments sampled from lithic contact of soil profiles were studied in thin sections using optical microscopy. Quantitative mineralogical compositions of rocks and soils (the fine size <1 μm fractions) were determined on randomly oriented powder specimens using XRD followed by Rietveld analysis. Despite the fact that the investigated soils have been forming from the different types of rocks, high proportions of smectite were identified in the bottom horizons. Smectite was not identified in the ultramafic rock itself, which are dominated by olivine, serpentine, talc, chlorite, and sometimes amphiboles. Appearance of smectite in the soil from ultramafic rock was due to chemical weathering in the fine earth formation from hard rock. In contrast, both di- and trioctahedral smectites were found in mafic rock previously subjected to chemical weathering. An inherited nature of smectite in the soil on mafic rock was revealed. Based on XRD patterns of oriented samples, smectite was predominant in the bottom horizons of the soils. The amorphous content significantly increased in the fine size fractions particularly in the middle and upper soil horizons of both soil types in comparison with that in the rocks, which was additionally indicated by the increase of proportions of extractable Fe, Al, and Si. These observations would illustrate intensive chemical weathering during pedogenesis. A smectite transformation into an amorphous phase could be concluded due to (i) acidification in the soil on mafic rock and (ii) acidification only in the rhizosphere in soil on ultramafic rock characterized by neutral to alkaline pH-values. However, the quantitative analysis of the XRD patterns from the randomly oriented powder of these specimens revealed that the smectite was still present and proportions of amorphous materials did not significantly increase in the upper horizons. In the soil profile on ultramafic rock the proportions of predominant dioctahedral smectite and trioctahedral smectite were approximately the same in the upper and bottom horizons, whereas in the soil profile on mafic rock the proportion changes from the bottom to the upper horizons with a decrease of trioctahedral and an increase of dioctahedral smectite. Thus, this study revealed that smectite is a more stable mineral in the critical zone of cold environments than previously thought [1], correlating data [2] of predominance of non-crystalline or poorly ordered materials in the weathering crust and soils of cold climates.

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POLYMER-CLAY COMPOSITE SORBENTS FOR THE REMOVAL OF GEMFIBROZIL FROM TREATED WASTE WATER

Lior Levy*, Yael Mishael

Department of Soil and Water Science, The Robert H. Smith Faculty of Agriculture, Food and Environment, Hebrew University of Jerusalem, Rehovot 76100, Israel
*lior.levy4@mail.huji.ac.il

Gemfibrozil is one of the highly detected pharmaceuticals found in treated wastewater effluent (EfOM) due to its environmental persistency [1]. Polymer-clay composite shave been widely developed, tested and employed as sorbents for organic pollutants [2,3]. For the removal of gemfibrozil a novel composite was designed by adsorbing, a newly synthesized polymer, to montmorillonite (MMT). The polymer is based on completely and partially substituting poly-4-vinylpyridine (PVP) with bromo-ethanol, obtaining OH(100)PVP and OH(50)PVP, respectively. The structures of the composites were characterized by zeta potential, FTIR, X-ray diffraction, and thermal gravimetric analyses [4]. These measurements suggest that the OH(50)PVP composite has a larger faction of polymer extending into solution in comparison to the OH(100)PVP composites (at the same loading (0.15 g/g)). Indeed, gemfibrozil affinity (K) and capacity (Q_{max}) towards the OH(50)PVP composite (K=100 l/mmol, Q_{max}=0.06 mmol/g) was higher than to the OH(100)PVP composite (K=23 l/mmol, Q_{max}=0.045 mmol/g). Our hypothesis was that, the composite has a higher affinity towards gemfibrozil than granular activated carbon (GAC), even in the presence of EfOM components, due to specific pollutant-polymer interactions. Removal of gemfibrozil from tap water was more efficient by OH(50)PVP-MMT than by OH(100)PVP-MMT and GAC, 1.5 and 30 fold higher, respectively. Its removal from secondary EfOM was two orders of magnitude higher by OH(50)PVP-MMTin comparison to its removal by OH(100)PVP-MMT and GAC. The kinetics of gemfibrozil removal from distilled water and from EfOM was faster by the OH(50)PVP composite than by GAC[5]. The kinetic adsorption of gemfibrozil removal from EfOM by OH(50)PVP composite and by GAC reached 10 and 90 min, respectively. These results support our hypothesis that gemfibrozil forms specific interaction with OH(50)PVP-MMT, due to its configuration, resulting in high and fast removal of gemfibrozil by the composite even in the presence of competing components.

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THERMAL ACTIVATION OF LAYERED AND FIBROUS CLAYS AND THEIR APLICATION IN THE REMOVAL OF CADMIUM (II) FROM AQUEOUS SOLUTION

Erika Padilla-Ortega, Roberto Leyva-Ramos*, Jesus Ivan Martínez Costa

Centro de Investigación y Estudios de Posgrado, Facultad de Ciencias Químicas, Universidad Autónoma de San Luis Potosi,
Av. Dr. M. Nava 6, San Luis Potosi, SLP 78210, México
*rlr@uaslp.mx

In this work, we studied the effect of thermal activation on the physico-chemical properties of bentonite, sepiolite and vermiculite, as well as on their adsorption capacity towards Cd(II) from aqueous solution. Clay samples were thermally activated in the temperature range of 300-900 ºC. The physico-chemical characterization demonstrated that the elimination of superficial, interlaminar and crystalline water resulted in materials with smaller specificsurface area and greater negative surface charge.

Cation exchange capacity of the clays varied with the thermal activation depending on their crystalline structures. The adsorption capacity of bentonite towards Cd(II) was reduced from 32 to 55% when the activation temperature was raised from 300 to 900 ºC. The capacity of sepiolite for adsorbing metal cations was enhanced by around 40% withincreasing activation temperature from 300 to 800 °C. Natural vermiculite presented a greater capacity for adsorbing Cd(II) than the thermally activated vermiculite; e.g., the capacity of vermiculite for adsorbing Cd(II) was 50% greater than that of a thermally activated vermiculite.

The adsorption capacity of the thermally activated clays towards Cd(II) was affected by the chemical and textural properties of the activated clays. Furthermore, it was demonstrated that the adsorption capacity of the thermally activated clays was strongly dependent on the magnitude of negative surface charge and their cation exchange capacity. Thus, the predominant adsorption mechanisms were the electrostatic attractionbetween the negatively charged surface of clays and Cd^{2+} in aqueous solution, and cation exchange between Cd^{2+} in the solution and either the interlaminar cations or the hydroxyl groups of the clays.

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SORPTION OF DICLOFENAC AND CADMIUM (II) ONTO ORGANOBENTONITE FROM AQUEOUS SOLUTION. DICLOFENAC-CADMIUM (II) COMPLEX INTERACTIONS AND SORPTION MECHANISM

Jesus Iván Martínez-Costa, Roberto Leyva-Ramos*, Erika Padilla-Ortega

Centro de Investigación y Estudios de Posgrado, Facultad de Ciencias Químicas, Universidad Autónoma de San Luis Potosí,
Av. Dr. M. Nava No.6, San Luis Potosí, SLP 78210, México
*rlr@uaslp.mx

Organoclays are engineered adsorbents prepared by adsorbing a cationic surfactant on the negatively charged external surface of clays and, in some cases, in the interlayer spacing of the clays. Diclofenac (DFC) is a non-steroidal anti-inflammatory drug and is one of the most commonly detected pharmaceuticals in the effluents of water treatment plants. Various works have reported that some pharmaceuticals in water reservoirs, even at low concentrations, can have adverse effects on human life, flora and fauna [1]. Heavy metals are also found in aqueous effluents such as cadmium, which is a very toxic metal with unknown biological functions. The excess of Cd(II) released into the environment in industrial wastewater can cause high ecological risks to groundwater, and poses a serious risk to human health, [2]. DFC can form complexes with some heavy metals that are also found in aqueous effluents such as cadmium. The sorption on organoclays has been applied for the removal of several toxic compounds presents in an aqueous solution such as organic micropollutants, pesticides, insecticides and nonionic organic compounds [3-6].

An organobentonite was prepared by adsorbing HDTMA (OBHDTMA), and the sorption capacity of the organobentonite towards DFC was investigated in detail. Additionally, the sorption isotherms of DFC on the OBHDTMA were obtained under various experimental conditions of temperature and pH, and the sorption mechanism of this emergent pollutant on OBHDTMA was elucidated. It was shown that the maximum sorption capacity of the OBHDTMA to remove DFC was 500.5 mg/g at pH = 7 and T = 25 ºC. The maximum desorption was 30.83% at pH = 10, and it was obtained by modifying the pH of the aqueous solution. Additionally, the adsorption capacity decreased as the ionic strength of the solution increased. The sorption process was endothermic, and the isosteric heat of adsorption was 11.46 KJ/mol.

Interactions between the OBHDTMA, DFC and Cd(II) were also studied in this work. DFC sorption onto OBHDTMA was characterized by elemental analysis, N_2 physisorption, zeta potential, XRD, TGA, Raman and IR spectroscopy. The characterization provided relevant information to propose that the DFC sorption mechanism included both electrostatic interactions and van der Waals partition. Besides, the sorption capacity of OBHDTMA towards Cd(II) was enhanced by raising the DFC loading on OBHDTMA.

The competitive sorption of DFC and Cd(II) onto OBHDTA was also investigated. FTIR and Raman analytical techniques showed that a complex between DFC and cadmium (II) was created on the surface of the OBHDTMA. The Raman and FTIR analysis corroborated that the complex was formed between the carboxylate group of DFC and cadmium, and the complexation involved electrostatic attractions and π-cation interactions.

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EXPLORATORY STUDY OF MODIFIED-ZEOLITES AS SORBENTS FOR POLY- AND PERFLUOROALKYL SUBSTANCES AND POLYCYCLIC AROMATIC HYDROCARBONS IN STORMWATER RUNOFF

Loretta Y. Li (1)*, Monireh S. Hedayati (1), Chris Johnston (2)

(1) Department of Civil Engineering, University of British Columbia, Vancouver, Canada V6T 1Z4, (2) Kerr-Wood-Leidal Consulting Engineers, 4185 Still Creek Dr #200A, Burnaby, BC, Canada V5C 6G9

Pollutants of concern in stormwater include nutrients (P, N), metals (copper, lead and zinc), and organic compounds (e.g., polycyclic aromatic hydrocarbons, PAHs) originating from landscaping, transportation, construction and other human activities. The removal of heavy metals from stormwater has been studied extensively in the past three decades [1-3]. Polycyclic aromatic hydrocarbons (PAHs) released to stormwater through wear of asphalt and tires, as well as deposition of vehicle exhaust, are of great concern as they occur frequently in stormwater at concentrations exceeding environmental quality standards. Emerging contaminants such as poly- and perflurooalkyl substances (PFASs, persistent organic pollutants) have been detected in stormwater [4,5]. These pollutants show acute toxic, carcinogenic and estrogenic effects on aquatic organisms [6,7]. Stormwater contaminated with organic substances poses a threat to receiving waters. These organic pollutants are now of major global concern. Sorption is an emerging technology with high efficiency and low cost [8]. Surfactant modified zeolites have been found to be able to adsorb certain organic pollutants [9,10].

The major objective of this study is to evaluate various zeolite modifications and their effectiveness in removing these organic pollutants from stormwater. These zeolites could be used as sorbents in stormwater infiltration technologies such as rain gardens. Batch adsorption tests will be used to study the adsorption of PAHs onto selected sorbents. The effects of contacting time (i.e. sorption kinetic), sorbent dosage (solid:liquid ratio), and temperature will be investigated. GC-MS and HPLC-MS will be used to analyze the concentration before and after treatment. At the end of life, organic-pollutant-loaded sorbents will need to be discarded, either on landfill or by incineration. Batch desorption tests will be carried out to determine the leachability of these pollutant-loaded sorbents. Preliminary 24-h batch test results indicate promising adsorption of these persistent organic pollutants. This is an on-going study; we will present updated results at the conference.

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INNOVATIVE AND SUSTAINABLE TREATMENT OF METALS FROM MINE DRAINAGE USING CLINOPTILOLITE

Loretta Y. Li (1)*, Wanjing Xu (1), John R. Grace (2)

(1) Department of Civil Engineering, University of British Columbia, Vancouver,, Canada V6T 1Z4, (2) Department of Chemical and Biological Engineering, University of British Columbia, Vancouver, Canada V6T 1Z3

An innovative chemical process has been developed in which a natural soil mineral (clinoptilolite) removes metals from acid rock drainage (ARD) in a slurry bubble column. The metals are cyclically adsorbed from spiked ARD by the clinoptilolite and then desorbed to regenerate the sorbent. Experimental results indicate that clinoptilolite is a good sorbent for Zn and Cu from ARD. XRD, SEM and TEM showed that the original sorbent structure was retained over 27 adsorption/desorption cycles at pH ≥ 2.5. The slurry bubble column was superior to fixed beds and rotating columns for zinc removal, indicating that enhanced external mass transfer can significantly accelerate sorption. Recent work will be presented on optimization of the operating conditions. The results indicate that clinoptilolite is an effective sorbent for removing Zn from ARD in slurry bubble column, with the Zn concentration decreasing from 100 ppm to as low as 0.8 ppm after eight adsorption stages. Satisfactory regeneration could also be achieved in the slurry bubble column, indicating that loaded clinoptilolite can be successfully regenerated for treatment of ARD. However, the slurry bubble column with clinoptilolite cannot alone achieve satisfactory results efficiently for in site remediation. Instead it should be used in conjunction with other water treatment measures to meet discharge requirements in an efficient manner. It is generally more effective when used to treat ARD with high initial Zn concentration.

Previous studies have neglected dealumination of clinoptilolite and its impact during remediation. The effect of dealumination of clinoptilolite and its impact on capture of zinc from ARD will also be assessed in this paper. In order to model and optimize the performance of slurry bubble column with clinoptilolite, further tests are needed to explore more parameters such as particle surface properties.

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INTERACTIONS OF RHODAMINE 6G WITH PALYGORSKITE

Zhaohui Li*, Nicholas Potter, Brian Sockness, Ian Nebendahl, Joseph Rasmussen

Geosciences Department, University of Wisconsin - Parkside, Kenosha, WI, USA

Clay minerals have large specific surface area and high cation exchange capacity (CEC), and thus are commonly studied for the uptake and removal of heavy metals from water. In addition to the adsorptive removal of inorganic cations, numerous studies were also conducted for the removal of organic contaminants, either cationic or hydrophobic in nature, from water. Cationic dyes have strong affinity for clay minerals. Rhodamine is a family of related chemical compounds with fluorine as the backbone. It is extensively used in biotechnology applications, due to its high photostability. It is highly chemical stable against degradation [1]. Sorptive removal of rhodamine using red mud, palygorskite, and sepiolite we conducted in recent years. However, significant discrepancies were found in the literature regarding to the adsorption of rhodamine 6G (R6G) on clay minerals. For example, in one study the adsorption of rhodamine B (RhB) increased from 55% to about 95% as the solution pH increased from 2 to 10 [2]. In a different study, the RhB adsorption decreased from 19 to 6 mg/g as the solution pH increased from 2 to 12 with the highest RhB adsorption of 24 mg/g in pH 4 solutions [3]. Adsorption of R6G on palygorskite increased from 70 to 90% as the solution pH increased from 2 to 12, however, the isotherm of R6G adsorption on palygorskite was incomplete and the data were mis-fitted to different models [4]. Thus, there is a need to further expand the study.

In this study, the interaction between R6G, a cationic and, and palygorskite, a type of fibrous clay mineral was investigated under different physic-chemical conditions. Uptake of R6G on palygorskite was fast and equilibrium could be reached in 1 h. The uptake of R6G on palygorskite followed the Langmuir sorption isotherm with a sorption capacity of 130 mmol/kg, close to the CEC of 175 mmol/kg [5]. The sum of the desorption of exchangeable cations K^+, Na^+, Ca^{2+}, and $Mg^{2+}$from the kinetic study and isotherm study matched quite well with the amounts of R6G sorption, confirming that cation exchange is the dominant mechanism for R6G uptake on palygorskite. Equilibrium solution pH and ionic strength had minimal influence on R6G uptake in the pH range of 3-11. Studies of R6G uptake by kaolinite are currently underway. As the rhodamine WT was commonly used as a tracer for water flow monitoring, the presence of significant clays in water after a storm could put strong deviation of flow velocity monitoring as the clays would have strong affinity for rhodamine. Meanwhile, the strong affinity of R6G for clay minerals suggested that using clay minerals as sorbents in wastewater treatment could not only remove inorganic cations, but also cationic organic dyes and pharmaceuticals.

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INFRARED SPECTROSCOPIC STUDY OF WATER CONFINEMENT IN STANDARD AND HYBRID IMOGOLITES

Yuan Yuan Liao (1),* Pierre Picot (1), Jean-Blaise Brubach (2), Pascale Roy (2), Antoine Thill (1), Sophie Le Caër (1)

(1) CEA/Saclay, DRF/IRAMIS/NIMBE/LIONS UMR 3685, Bat.546, F-91191, Gif-sur-Yvette Cedex, France,
(2) Synchrotron SOLEIL AILES Beamline, L'Orme des Merisier, Saint-Aubin, BP 48, F-91192, Gif-sur-Yvette Cedex, France

Imogolite is a family of aluminium silicate clay minerals, originally found in volcanic soils. Their nanotubular structure makes them good candidates for the study of water confined in restricted geometries. The behaviour of water confined in imogolite self-sustaining thin films, whose porosity was estimated, was studied by means of infrared (IR) spectroscopy. Two types of synthetic imogolites were studied: a hydrophilic imogolite (IMO-OH) with a hydrophilic inner surface fully covered with Si-OH groups and a hybrid imogolite (IMO-CH_3) with a hydrophobic inner surface fully covered with Si-CH_3 groups. The infrared spectra were recorded in the 50 - 4000 cm^{-1} range as a function of the relative humidity (0 - 100% RH) and temperature (295 K to 50 K). The evolutions of the O-H stretching band, and the bending, libration and connectivity bands of water were studied. The special features of the H-bond network revealed in both the mid- and far- IR range during the water adsorption and desorption processes will be detailed, evidencing that the water confinement in imogolites is significantly affected by the geometry of the nanotube, the packing of the tubes, and also by the hydrophobic vs. hydrophilic character. Insights into the relationship between (1) the large specific surface area, (2) restricted geometries, (3) the tunable hydrophilic/hydrophobic character, can serve the scientific community interested in deploying these materials as membranes, catalyst supports, adsorbents and other similar applications [1,2].

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MULTISCALE ANALYSES OF POLYACRYLAMIDE ENHANCED SMECTITE FOR USE IN CLAY LINERS

Wolfgang Lieske*, Tom Schanz

FacultyofCiviland Environmental Engineering, Ruhr-University Bochum, Germany

One of the most extensively used soil materials in Geotechnics is bentonite. Favourable properties, e.g. swelling, low hydraulic permeabilityand anion exclusion make it suitable for the construction of sealings, diaphragm walls and for the use as buffer materialin nuclear waste disposal. The before mentioned properties are caused by the negative charged surface of the three-layer silicate montmorillonite which is the main component of bentonite.

However, subjected to aggressive leachate, e.g. water containing dissolved salt, the barrier performance is drastically decimated up to an entire loss sealing capacity. Reasons for the decline regarding the hydro-mechanical behaviour are dedicated to an increase in ion concentration and the presence of divalent ions in the bulk phase, which in turn affects the interacting forces between the particular clay particles. Another difficulty of clay as sealing material is causedby desiccation induced cracks, inducing flow paths of unrestricted flow for leachate. These shortcomings limit the scope of application for bentonite as a barrier material, and doubted the reliability of previous applications.

Recently, new capabilities to maintain sealing capacity of clay subjected to aggressive leachate and to improve desiccation resistance were find in polymer-modification. Polymers are long-chained macromolecules, which can be categorized regarding charge (positive, negative, neutral, polar/non-polar), structure (branched/ non-branched), and length of polymer chains. The functional groups of polymers are interacting with the charged clay surfaces and the bulk fluid. Polymer sections can be classified regarding their arrangement relative to the clay surface. Trains are parts of the polymer, which lie flat on the clay surface while polymer segments that loom away from the surface arrange in loops or free tails, respectively. Although, the efficacy of this new technology has been demonstrated successfullyin various laboratory studies, there is still a lack of understanding regardingthe multiscaled behaviour of polymer-enhanced clay.

The objective of the present research is the systematic and multiscale study of polymer-modified bentonites. Investigations are conducted on the microstructural level and on the level of laboratory testing in order to attribute modifications on the level of clay matrix to geotechnical properties.

Laboratorytests were conducted on natural bentonite (MX80) and bentonite modified by wet-intercalation using different Polyacrylamide (Charged, Non-Charged), respectively. Investigations of fabricby environmental scanning microscopydepict the unique microstructure of the clay-polymer composite and provide fundamental information about spectate-polymer interaction.

On the macro scale, swelling and permeability test were carried out in an isochoric fixed-volumecell using a multi-step test procedure. The material wasrehydrated by deionized water and afterwards subjected to different CaCl2-Solutions of increasing molarity. Evolution of swelling pressure and permeability-properties were monitored and analysed with respect to ion concentration in the pore fluid. The outcome of the current study allows for an improved understanding of polymer-modified materials to be used in geo-environmental applications.

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WEATHERING CRUSTS OF THE EAST EUROPEAN CRATON: PALEOCLIMATIC INTERPRETATION AND GEOCHEMICAL EVIDENCE OF LIFE ON THE EDIACARAN LAND

Sirle Liivamägi (1)*, Jan Środoń (1), Maciej Bojanowski (2), Jan J. Stanek (3)

(1) Institute of Geological Sciences, Polish Academy of Sciences, Krakow, Poland, (2) Institute of Geological Sciences, Polish Academy of Sciences, Warsaw, Poland, (3) Jagiellonian University, Krakow, Poland
*ndsirle@cyf-kr.edu.pl

Paleosols are fossil soils, remains of ancient soils, which unlike marine sediments are formed on land, in direct contact with climatic and environmental conditions. Paleosols potentially hold important information of past continental environments and those that were formed at the transition from Proterozoic to Paleozoic could reflect the evolution of atmospheric oxygenation; help us understand environmental and ecological conditions during weathering, when soil formation took place under absence of higher plants, and can provide evidence of life on land. Precambrian paleosols are found all over the world. Until recently these old soils were often overlooked because they lack well-defined soil horizons and biological features; their age is difficult to determine and their usefulness as indicators of paleoclimate is questioned as they tend to be diagenetically altered or metamorphosed to a different level and they are hard to distinguish from alteration zones caused by hydrothermal activity. Several recent studies however proved that with new quantitative methods of geochemistry including isotopes Precambrian paleosols are just as suitable for paleoclimatic studies as are their younger analogues.

Paleosols were found on top of the Ediacaran basalt trap, 140 thousand km^2 and up to 500 m of lavas and volcanoclastics, which covers the western margin of the East European Craton (W Belarus, NW Ukraine and E Poland). These weathering crust profiles are unique among other Precambrian paleosols because their age is well constrained (ca. 550 Ma) and most of them are unaffected by post-burial diagenesis. Studied paleosol profiles were accessed from drillcores located in NW Ukraine (7 profiles) and E Poland (1 profile). They are on average ca. 10 (up to 30) meters thick, reddish colored and most of them are characterized by a well-developed and well-defined alteration sequence with a lateritic uppermost horizon indicated by Chemical Index of Alteration - CIA [1] values reaching 95.

Mineralogical composition of all weathering sequences follows a transition from pure smectite to smectite-kaolinite to kaolinite along with increase of hematite and decrease of feldspar minerals and trioctahedral clays. Kaolinite content in the uppermost horizons can reach over 60 wt%. Smectite is replaced with illite/mixed layer illite-smectite in one profile affected by burial diagenesis. Carbonates (calcite and dolomite) are found in lower parts of several profiles. Weathering profiles containing micas and microcline were considered contaminated and left out from further research.

Several meters thick kaolinite and hematite-rich paleosol profiles are usually interpreted to represent intense weathering in warm and humid (tropical) climate. Fe^{2+}/Fe^{3+} ratio decrease to 0 (Mössbauer data on the bulk rock) confirms that weathering took place under oxidative conditions and geochemical mass-balance analysis shows that element enrichment-depletion trends are similar to modern deeply weathered tropical soil profiles. For those reasons these Ediacaran paleosols can be interpreted to represent typical lateritic (or Oxisolic) deep-weathering profiles, indicative of hot and humid climate.

Geochemical evidence of life on the Ediacaran land, gathered in the course of this study, involves the presence of organic carbon, negative values of $\delta^{13}C$ ranging from -17.6 to -8.8 ‰ and negative Fe isotopic anomaly ($\delta^{56}Fe$ and $\delta^{57/54}Fe$) in the bottom parts of profiles. They imply microbial action during weathering.

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PROVENANCE AND CLAY MINERAL ORIGIN OF MIDDLE TRIASSIC SANDSTONE IN THE NORTHEASTERN MARGIN ORDOS BASIN, CHINA: IMPLICATIONS FOR THE EROSION VULNERABILITY OF PI SANDSTONE

Li Liu*, Hanggai Bai, Xiaoran Ming, Na Liu, Chunyan Hu

College of Earth Sciences, Jilin University, Changchun 130061, China
*Liuli0892@vip.sina.com

The Pi sandstone refers to a type of terrigenous clastic rock assemblage composed mainly of sandstone, siltstone and mudstone with red and white color, which is characterized by exposing or being covered with sand or loess, vulnerable to weathering and erosion, distributed in the contiguous area of Shaanxi province, Inner Mongolia autonomous region and Shanxi province in China, and formed during Late Paleozoic - Mesozoic [1]. “Pi” comes from the folk name (pishuang) of arsenic in Chinese, the appellation of “Pi sandstone” means that it is harmful to soil and water conservation. In recent years, Great progress has been made in soil erosion control in Pi sandstone distribution area, however, the cause of the erosion vulnerability of the Pi sandstone has not been fully understood. Fourteen Pi sandstone samples from the Middle Triassic Ermaying Formation in the eastern margin of the ordos basin, China, have been investigated to determine its provenance and clay mineral origin which is blamed for the erosion vulnerability of the Pi sandstone using Petrography, X-ray diffraction (XRD), and X-ray fluorescence (XRF). Field observations confirmed that the samples were collected from the ephemeral fluvial facies. Mineralogically, the Pi sandstone is composed of quartz (av.39.4%), clay minerals (av.35.1%) and feldspar (av.20.9%) as well as calcite (0-13.3%) and dolomite (0-3.1%). X-ray diffraction (XRD) analysis of < 2 m portion shows that smectite (av.72.1%) is a dominant clay mineral followed by kaolinite (av.20.1%) and illite (0-15.0%). Geochemically, the Middle Triassic Pi sandstone are classified as wacke, arkose, and litharenite. Detrital components in Pi sandstones are most probably derived from the igneous and sedimentary provenance based on the discriminant functions, La/Yb-∑REE diagram and δ Eu. A low chemical index of alteration (CIA) (av. 62.3) and the Al_2O_3-CaO^* + Na_2O-K_2O (A-CN-K) diagram reflect a low chemical weathering degree in the source area, which suggests that a semi-arid to arid climate prevailed during the Middle Triassic. In clay minerals, smectite is considered responsible for the erosion vulnerability of the Pi sandstone. Smectite can be weathering or authigenic or detrital in origin. Some workers believed that smectite derived from weathering of the Pi sandstone in situ [2]. This is in contradiction with the facts that smectite also is a dominant clay mineral in its subsurface counterparts (Zifang Formation) collected from depths ranging from 958 to 1310 meters below the surface. The authigenic variety is mainly produced by digenetic processes. In spite of the paleoclimate condition of arid to semi-arid that is favor of smectite precipitation we have not found any typical authigenic smectite under SEM. Most of Clay minerals (smectite as well as illite), which occur in the Middle Triassic Pi sandstone as platelets that are tangentially arranged around the detrital grain surfaces, are typically formed by mechanical infiltration of detrital clay minerals. All those facts above show that smectite occurs in the Middle Triassic Pi sandstone is detrital in origin.

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A NOVEL MINERAL-DYE COMPOSITE WITH IMPROVED FLUORESCENT PROPERTIES FOR ITS APPLICATION IN PHENOL DETECTION

Guocheng Lv (1), Meng Liu (1), Libing Liao (1)*, Hao Liu (2)

(1) Beijing Key Laboratory of Materials Utilization of Nonmetallic Minerals and Solid Wastes, National Laboratory of Mineral Materials, School of Materials Science and Technology, China University of Geosciences, Beijing 100083, China,
(2) School of Science, China University of Geosciences, Beijing, 100083, China
*lbliao@cugb.edu.cn; guochenglv@cugb.edu.cn

Although fluorescence detection is a sensitive method in the field of pollutant analysis [1-2], its application is restricted due to the quenching of organic molecule after aggregation [3]. Herein, we report fabrication of a novel inorganic/organic composite prepared by intercalating a photo-active molecule (lucigenin, guest) into the interlayer space of montmorillonite (host), which can significantly inhibit quenching [4]. Phenol in aqueous solution can be detected by naked eyes at the mM level and by instruments in the range of 0.01 to 100 mM with a detection limit of 0.01 μM. For gas phase phenol, the detection limit was as low as 0.3 ppb and a linear response was found at concentrations of 0 - 2 ppb. A full fluorescence quenching occurred at liquid and gas phase concentrations of 50 mM and 177 ppm, respectively. Such a low detection for gas phase phenol is superior to other current available analytical methods. In addition, the method is fast in comparison to current available methods for gas phase detection, eliminating large volume of sample collection and enrichment. The novelty of this study lies on both the development of a new type of mineral-dye composite material, as well as its practical applications for fast, yet supersensitive phenol detection and quantification in liquid and gas phases.

Keywords: Phenol; Mineral/dye composite; Fluorescence detection; Fluorescence quenching.

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SELF-ASSEMBLY OF HALLOYSITE NANOTUBES INTO REGULAR PATTERNS

Mingxian Liu*, Tengfei Liu, Rui He, Changren Zhou

Department of Materials Science and Engineering, Jinan University, Guangzhou, China

HNTs are ideal candidate for the self-assembly studies because of their tubular morphology with high aspect ratio, high dispersion ability in water without chemical modification, and low cost. HNTs can be assembled into highly ordered strips pattern surface in a glass capillary tube or concentric ring pattern via drying the HNTs aqueous suspension. The pattern structure depends both HNTs dispersion concentration and the drying condition. An ordered alignment of HNTs in the ring strips especially with high HNTs suspension concentration. The self-assembly of such nanotubes offering a large variety of applications, for example, in high performance composite, cell isolation interface, and electrochemical devices. The patterned surface can be used as model for preparing PDMS molding with regular micro/nano structure. Also, the HNTs rough surfaces can provide much higher tumor cell capture efficiency compared to blank glass surfaces. The HNTs rings can guide the growth and orientation of C2C12 myoblasts cells perpendicular to the rings.

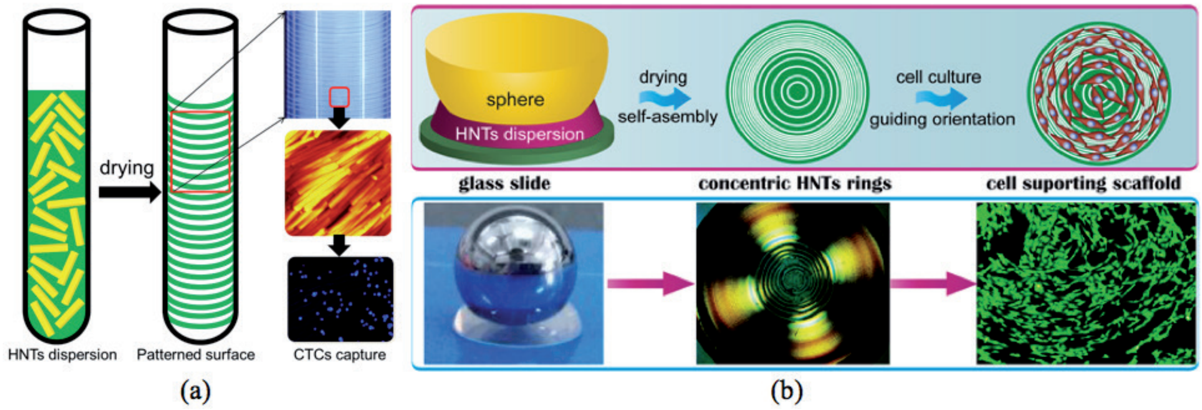

Fig. 1 Schematics illustrating the assembly behaviour of HNTs into highly ordered strips pattern surface in a glass capillary tube (a) or concentric ring pattern in a sphere-on-flat geometry (b).

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INTERLAYER SPACE RESTRUCTURING OF THE KAOLINITE UPON THE TYPES OF GUEST SPECIES

Qinfu Liu (1)*, Xiaoguang Li (1,2), Ding Wang (1)

(1) School of Geoscience and Surveying Engineering, China University of Mining & Technology, Beijing, 100083, China,
(2) Department of Ecosystem Science and Management and Materials Research Institute, Materials Research Laboratory, The Pennsylvania State University, University Park, 16802, USA
*lqf@cumtb.edu.cn

Differ from the interparticle space and interaggregate space that are derived from the different arrangement of kaolinite particles, interlayer space is formed between the tetrahedral oxygen and the octahedral OH ions. Interlayer space could be restructured upon the types of the intercalated molecules. New space and lumens could be obtained by delamination and exfoliation of kaolinite particles.

Displacement intercalate served as an ideal way for kaolinite delamination. Kaolinite-anionic surfactants intercalation compounds can be synthesized via displacement method using organic grafted derivative of kaolinite as a precursor. The basal spacing of the compounds is determined by the molecular length, PH of the suspension and surfactant concentration. The X-ray diffraction data showed that the basal spacing increased to 2.0~4.5 nm from 0.86~1.1 nm of the pre-modified kaolinite. The volume of the interlayer space increased 2~6 times upon the structure of the guest species. The expanded interlayer spacing of intercalation compound is an ideal space for further nano-interaction. For kaolinite-stearic acid intercalation compound, a 4.1 nm basal spacing was obtained when methoxy-grafted kaolinite used as the precursor. The intercalated molecules occupied the kaolinite interlayer space with the 1:1 sheets regularly linked in stacks, and can be further displaced or removed by a specific method.

Exfoliation of kaolinite can be achieved via intercalation of cationic surfactants. For example, simultaneously by the formation of kaolinite-cetyltrimethyl ammonium bromide compound, the single layer of the platy kaolinite get curled up into one-dimensional nanoscrolls automatically. The morphology of kaolinite nanoscrolls is dramatically different from the anionic surfactants intercalation compounds. The lumen generated by the scroll of kaolinite layer is larger than that of halloysite nanotube. Moreover, a smaller number of layers and wall thickness were observed for the wall of kaolinite than halloysite. BJH pore size distribution data showed that the average lumen diameter of the nanoscrolls is ca.18 nm. Unlike the platy intercalation compounds, the interwall space of the kaolinite nanoscrolls is constructed by the octahedral sheet and the tetrahedral sheet of the same layer. The van der Waals' force and the hydrogen bond between the adjacent walls are newly formed because the component atoms of one side of the spiral interwall space are all changed. It was proposed that the interaction forces between the two atomic planes of the interwall space are weakened. It is easier for the prepared nanoscrolls to accommodate guest molecules than the original kaolinite.

Not only the newly formed lumen space of the nanoscrolls but also the restructured interlayer spaces of the nanoscrolls and the prepared kaolinite compounds made them qualification for the creation of novel utility areas such as adsorbent, catalyst, and the matrix of hybrids.

Keywords: kaolinite, intercalation compound, interlayer space, delamination, exfoliation.

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KEROLITE-PIMELITE: THE HYDRATED TALC SERIES REVISITED

Cristina Villanova-de-Benavent (1)*, Francisco Longo (2), Esperança Tauler (1), Josep Roqué-Rosell (1), Joaquín A. Proenza (1), Salvador Galí (1), Fernando Nieto (3)

(1) Dept. Mineralogia, Petrologia i Geologia Aplicada, Universitat de Barcelona, Barcelona, Spain, (2) Faculty of Engineering, Universidad Católica Tecnológica del Cibao, La Vega, Dominican Republic, (3) Dept. Mineralogía y Petrología and IACT-CSIC, Univesidad de Granada, Granada, Spain

Kerolite and its Ni analogue pimelite are 2:1 layer trioctahedral phyllosilicates without interlayer positions [1], with the ideal structural formula $(Mg, Ni)_3Si_4O_{10}(OH)_2 \cdot nH_2O$ (n = 0.75-1.25) [2]. They can be described as minerals with talc affinity and extra water in the structure, however, they have been historically classified either as members of the smectite group [3] or of the talc group [2]. Despite both kerolite and pimelite are discredited mineral species by the IMA Commission on New Minerals, Nomenclature and Classification (CNMNC), they are included in the recommendations for the nomenclature of phyllosilicates by the Association Internationale Pour l'Étude des Argiles (AIPEA) [1] and these names are still used nowadays [4,5,6]. In the Falcondo Ni-laterite mining district (Dominican Republic), kerolite-pimelite occurs as millimetre to centimetre sized coatings superimposed over other Ni-Mg phyllosilicates and over rocky fragments, or as millimetre sized, rounded, non-spherical granules embedded in a greenish white, microcrystalline quartz matrix. The X-ray diffractogram shows a broad diffraction peak at 9.58-10.02 Å suggesting that it consists uniquely of a poorly crystalline, talc-like phase. This is coherent with the transmission electron microscopy (TEM) high resolution imaging, which revealed thin lamellae composed of two to six layers with basal spacings of 9.5-9.8 Å. The small particle size, together with the wide and diffuse rings observed in the electron diffraction patterns (typical of a random polycrystalline pattern), confirms the low crystallinity. The thermogravimetric study shows a remarkable mass loss at low temperatures, indicating that the mineral contains more water than talc (which has a single mass loss of about 6% above 800 ºC, corresponding to OH^-). Under the optical microscope, kerolite-pimelite consists of yellow to brown, banded, botryoidal aggregates. It is commonly intergrown with, superimposed and/or crosscut by quartz veinlets. These features suggest that kerolite-pimelite and microcrystalline quartz precipitated from a colloidal silica gel. Its anhydrous chemical composition is similar to that of ideal talc-willemseite, but the electron microprobe analyses show low oxide-totals. The average structural formula is $(Ni_{1.67}Mg_{1.33})Si_{3.80}O_{9.53}(OH)_{2.19} \cdot nH_2O$ (153 analyses). Kerolite-pimelite displays a wide range of Ni concentrations (0.47-2.58 apfu, 7.77-40.52 wt.% NiO). According to synchrotron measurements on kerolite-pimelite, the best fit of Ni K-edge µEXAFS suggested a model of clustered Ni, only surrounded by a defective shell of Ni [7], which is coherent with its disordered nature. These results are comparable with those obtained in minerals of the kerolite-pimelite series described in New Caledonia [4,6]. As a conclusion, the terms kerolite and pimelite, despite invalid, should be considered to describe this mineral series as a different mineral entity than talc and willemseite.

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MODULATING THE LUMINISCENT PROPERTIES OF PYRONIN DYE/ SMECTITES HYBRID FILMS

Nerea Epelde-Elezcano, Virginia Martínez-Martínez, Eduardo Duque-Redondo, Hegoi Manzano, Iñigo López-Arbeloa*

Department of Physical Chemistry, University of the Basque Country (UPV-EHU), Bilbao, Spain
*inigo.lopezarbeloa@ehu.eus

The encapsulation of photoactive molecules into different inorganic matrices could provide functional hybrid materials with interesting photo and optoelectronic applications such as photocatalysts, optical sensors and solid-state microlasers. In this sense, well-organized 2D-multilayer clay minerals are one of the most used laminar systems as an inorganic host because of their high adsorption capacity by cationic exchange mechanism.

Two trioctahedral Smectite-type clays, Laponite (Lap) and Saponite (Sap), were used to elaborate macroscopically ordered films. These clays are chosen due to their excellent properties, such as high interlayer space swellability, purity and transparency, requirements for optical applications. Furthermore, cationic Pyronin Y (PY) dye was used as guest to be intercalated into interlayer mineral space of the clays by ion exchange mechanism. PY dye is a xanthene dye characterized for its bright pink colour and high fluorescence quantum yield, but usually has a high tendency to aggregate either in solution or adsorbed in solid state [1], affecting drastically its photophysical properties.

In this work, on the one hand, the aggregation type of PY dye intercalated into Lap and Sap thin films, at different PY loadings is analyzed by the evolution of PY/clay films absorption spectra. Thus, different aggregates types are favoured in both clays, i.e., H-dimers (sandwich like disposition) for Lap and J-aggragates (head to tail geometry) for Sap, which is attributed to different strengths between the dye and the layered silicate. On the other hand, the photoluminescence of the PY/clay films is also studied by steady state fluorescence spectroscopy. With the aim of optimizing the PY/clay films fluorescence efficiency, the PY molecular aggregation was reduced by the co-intercalation of dodecyltrimethylammonium bromide (DDTAB) [2]. Finally, the orientation of PY molecules respect to the normal to the clay surface is determined by the anisotropic response of the hybrid films to the linear polarized light [3]. This order is not disrupted by the previous intercalation of the surfactant molecules in the interlayer space.

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INDUSTRIAL MICROWAVE PROCESS FOR POZZOLANIC POP METAKAOLIN AND CALCINED CLAYS

ANGEL M. LÓPEZ-BUENDÍA (1), JOAQUÍN BASTIDA (2), M. MAR URQUIOLA (1), BEATRIZ GARCÍA BAÑOS (3), JOSÉ M. CATALÁ-CIVERA (3)

(1) CEINNMAT (INNCEINNMAT SL). PCUV, Paterna, Valencia, Spain, (2) Dept. Geología. Universidad de Valencia, Burjasot, Valencia, Spain, (3) ITACA Institute, Universitat Politècnica de València, Valencia, Spain

Calcined clays are widely used in cement industry, where they are produced to replace parts of the clinker content as supplementary cementitious materials (SCM) and hydraulic lime because they exhibit pozzolan activity.

Kaolinite ($2SiO_2 \cdot Al_2O_3 \cdot 4OH$) is, after dehydroxylation by heating to amorphous phase metakaolinite ($2SiO_2 \cdot Al_2O_3$), a very active and well know manufactured SCM. However, other calcined clays (e.g. illite, montmorillonite) also exhibit pozzolanic acitivity, particularly after partial transformation and low temperature ceramic phases.

Microwave process show a good alternative as a new industrial process for calcination with an energy-efficient process for pozzolan manufacturing. Under the electrical microwave field, the volumetric heat conversion is produced by the clay mineral at grain, crystal and molecular level, and can be expressed according with the well-known following expression:

$Q_{gen}=2\pi f\ \varepsilon_0\ \varepsilon''|\ E_{eff}|^2$

where Q_{gen} is referred to the volumetric heat generated by microwave energy(W/m^3); *f* is the working frequency (Hz); E_{eff}, is the effective electric field intensity (V/m); ε_0 is de permittivity of the vacuum, and ε” is the loss factor of the dielectric material (or materials to be heated).

Microwave activated clays show high performance pozzolan at high-energy efficiency and cost-effective process. Microwave energy is mainly consumed during main endothermal changes of dehydroxylation, decomposition, transformation and sintering process. Improved performance can be obtained for *pop metakaolin* obtained with microwave with high disordering at lower temperature after the excitation of the hydroxyl groups (OH) in kaolinite up to sudden sublimation.

To evaluate the changes during heating, a new method of Dielectric Thermal Analysis under Microwave heating (MW-DETA) was made. The complex permittivity was measured identifying the mineral changes during heating. Samples of clays rich in kaolinite and smectite were selected and their dielectric properties during microwave heating were determined. Mineralogical analysis of clay minerals and associated minerals were made using X-ray powder diffraction at several temperature of treatment. Dielectric constant (ε’) and loss factor (ε”) during heating was correlated with the mineralogical changes.

An industrial microwave kiln in continuous flow was fabricated for clay calcination adapted to dielectric changes during heating.

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LAYERED DOUBLE HYDROXIDES: A NOVEL USE AS MICRONUTRIENT FERTILIZER

Sandra Lopez-Rayo (1,2)*, Jan K. Schjoerring (1), Hans Chr. Bruun Hansen (1), Jakob Magid (1)

(1) Department of Plant and Environmental Sciences, Faculty of Science, University of Copenhagen, Frederiksberg C, Denmark, (2) Department of Agricultural and Food Chemistry, Faculty of Science, University Autonoma of Madrid, Madrid, Spain
*rayo@plen.ku.dk, sandra.lopez@uam.es

Layered Double Hydroxides (LDH), also known as anionic clays, consist of alternating layers of positively charged metal hydroxides and interlayers of charge-compensating anions. The metal hydroxide layers typically include both a divalent and a trivalent metal cation, e.g. Mg^{2+} and Fe^{3+}/Al^{3+} but others, e.g. essential micronutrients such as Cu^{2+}, Zn^{2+}, Mn^{2+}, B^{3+}, can also be incorporated [1]. In addition, many different interlayer anions can be accommodated into the interlayer [2]. The LDHs are stable at pH higher than 7 to 8. However, when pH decreases, the LDHs partially dissolve. They have been proposed as nitrogen fertilizers, since nitrate anions can be released from the interlayer. The intercalation with organic anions has also been explored, e.g. for controlled release of herbicides [3]. We have recently demonstrated that Zn doped Mg-Fe(III) LDHs can be used as an “on-demand” Zn fertilizer [4]. This is interesting from an agronomic point of view, since Zn and other metal micronutrients essential for plant growth (i.e. Cu and Mn) can be dissolved from the LDHs in the rhizosphere due to the acidification accompanying root nutrient acquisition. We have therefore further investigated the metal release pattern of different LDH compounds.

LDHs were synthetized by co-precipitation at constant pH under inert atmosphere. Six LDHs were studied: with variations of the doped metal cation (Zn, Cu or Mn) and the anion in the interlayer (nitrate or carbonate). Zinc and Cu LDHs consists in Zn or Cu-doped type Mg(II)-Fe(III) LDH interlayered with nitrate or carbonate. Similarly, the Mn(III)-LDH consist in a Mn doped type Mg(II)-Fe(III) LDH interlayered with carbonate, while Mn(II)-LDH corresponds to a nitrate-containing Mn(II)/Al(III). Nutrient release was studied in incubation experiments in buffered solutions of different pH values (5.2 (MES), 5.5 (MES), 6.0 (MES), 7.1 (HEPES), 8.1 (HEPES)) for 28 days.

According to the nutrient release experiments, the maximum release of Zn from the two anionic forms of Zn-LDHs was approximately 20% of the total Zn content and was reached at pH 5.2, the lowest pH value studied. The Cu-LDHs showed similar patterns. The release rate can be described by first-order kinetics. The Mn(II)-Al containing LDH, released a quantity of Mn close to the total Mn content in the LDH. After that, a post-release oxidation and precipitation took place in the solution. A different release pattern was observed for the Mn(III)-LDH, which released Mn at slower rate and in smaller proportion of the total content due to Mn(III) disproportionation. For all the LDHs, the release increased under acidic conditions. This work demonstrates that micronutrients can be released from the LDHs in a pH dependent manner and that the LDHs respond to pH changes in the interval normally encountered in the rhizosphere of plants (4.5 - 6.5). In order to achieve the full advantage of release-on-demand LDH-based fertilizers it is important to take into consideration both the rate of nutrient release and the maximum quantity that can be released. Further experiments are in progress to investigate the uptake by plants of micronutrients from LDHs and how their efficiencies are affected by LDH composition.

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CLAY MINERAL TRANSFORMATION AND FLUID SOURCES AT MUD VOLCANOES IN THE ALBORAN BASIN (WESTERN MEDITERRANEAN)

Carmina López-Rodríguez (1,2)*, Francisca Martínez-Ruiz (1), Menchu Comas (1), Fernando Nieto (1,3), Gert J. De Lange (4)

(1) Andalusia Institute of Earth Sciences (IACT)-CSIC-UGR, Armilla, Granada, Spain, (2) Centre of Advanced Studies in Earth Sciences (CEACTierra), University of Jaen, Jaen, Spain, (3) Department of Mineralogy and Petrology, University of Granada, Granada, Spain, (4) Department of Geosciences - Geochemistry, Utrecht University, Utrecht, the Netherlands

In the West Alboran Basin (WAB), mud diapir structures and associated mud volcanoes (MVs)are fed by over pressured sediments and mega breccias/olistostromes, which occur in the deepest unitsoverlaying the metamorphic basement [1,2,3]. For this basin, MVs arerelated tothe existenceof overpressure and the upward migrationof solid and fluid phases containing hydrocarbons driven by tectonic processes [4]. Extruded materials ascending through layers of diverse ages assimilate further elements from the feeder channels, and this complex mixture is transported upward to the seafloor. The extruded MV deposits, namely mud breccias, usuallycontaina clay or silty-clay matrix enriched in expandable clay minerals and containabundantrock-clasts of heterogeneous ages, lithology, and size. Mineralogicalcompositionofthis complex mixture of clastsand mud provides relevant information on MV processes. In particular, the occurrence of illite/smectite mixed layer indicates mineral dehydration, which can be of major significance regarding diagenetic processes associated with fluid flow at depth and also provide insights into source rocks and thermal maturity. Our analyses were performed in gravity and piston cores taken at two MVs from the WAB. A total of three cores containing mud breccias, drapes and intercalated hemipelagic sediments have been studied. Two are from the Carmen MV, one recovered at the flank (MS385G) and one at the summit (GP05PC), and another one (MS280G) from the craterof the Kalinin MV. Results from bulk and clay mineralanalyses performed by X-ray diffraction (XRD) on drapes and hemipelagic intercalations associated with mud breccias reveal amineral composition that is comparable to those from regular marine sediments described off the MV provinces in the Alboran Sea. The bulk and clay mineral composition of mud-breccia matrix from all these cores show similar composition between the two studied structures, evidencingthat a common source contributes to nourish the extruded material. The clay mineral assemblages of the mud-breccia matrix are characterized by dominance of smectite and mica, and also mixed-layers of illlite/smectite (I/S) are recognized. An ample range of ordering from randomly interstratified (R0) illite-smectite minerals (I/S) to more illitic (up to95% I) and ordered ones (R1-R3) was observed. Our results indicate that smectite to illite transformations occurred atvariable but significant depth. Stable isotope composition of porewaters ($\delta^{18}O_{pw}$ = 5.7‰ VSMOW and δD_{pw}= -10 ‰ VSMOW) from mud breccias of piston GP05PC are in line with these mineralogical data, indicating theoccurrence of smectite dehydrationand fluid generation [4]. This finding, together with water-formation temperatures calculated with empirical geo-thermometers (K-Na, K-Mg and K-Ca) and geothermal gradient (25-27 ºC/km), allowsto constrain the diagenetic conditions for deep-fluid generation within this basin occurring at temperatures of up to 150 ºC [4]. In this regards, our results evidence that smectite dehydration constitutes an essential mechanism for fresh-water fluid releaseat depth, thus contributing to theoverpressure in the volcano's source area, and resultingdeep fluid migration and subsequent MV activity.

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CRYSTALLITE TERMINATION, IRON AND VACANCIES DISTRIBUTION IN THE 2:1 AND INTERLAYER SHEETS OF THE Mg-Fe CHLORITES

Katarzyna Luberda-Durnaś, Małgorzata Lempart, Marek Szczerba, Arkadiusz Derkowski

Institute of Geological Sciences PAS, Research Centre in Krakow, Krakow, Poland

Seven monomineralic chlorite samples representing the Mg-Fe chlorites series were carefully selected for structural studies using powder X-ray diffractometry (PXRD). All samples were prepared as oriented specimens and measured in the Bragg-Brentano geometry. Capillary measurements of randomly oriented powder were also performed. However, even using capillaries and the Debay-Scherrer geometry, preferred orientation was observed. The orientation increased gradually with increasing iron content in the samples.

The diffraction profiles of all samples (background, zero shift, unit cell, and profile parameters, including asymmetry) were fitted using La Bail method implemented in the program package Jana 2006 [1] which allows to obtain cell parameter for all chlorites. All analyzed samples were classified as nearly pure trioctahedral chlorites, polytype IIb (some of them possess little impurities, total below 3%). In all samples the semi-random stacking in c* direction was observed, which manifests in the slowly decreasing intensity bands in the region between 22 to 26 2θ (CoKα); in this region the hkl band with $k \neq 3$ are present. The observed phenomenon practically precluded the differentiation between IIb-2 and IIb-4 (monoclinic and triclinic crystal system). The structure models, in all seven chlorites, were established in triclinic C-1 space group based on [2] suggesting that all chlorites with semi-random stacking would have triclinic symmetry as the result of averaging of two triclinic and one monoclinic possible layer symmetries.

The main goal of the study was to obtain the structure refinement regarding the distribution of iron and octahedral vacancies in the 2:1 and interlayer sheets. New calculation approach was implemented in Sybilla program package developed by Chevron™ [3]. Following the significant influence of the outer surface layers of clay crystallites on the distribution of basal reflection intensities [4], the two additional crystal models of termination, with 2:1 layers or octahedral hydroxide layers were added. In all cases, the information about total content of iron and vacancies (found with microprobe analysis and Mossbauer spectroscopy) in the cell was used as a constrain during the refinement. The results show that, depending on established model, the distribution of iron between 2:1 and interlayer sheets can differ. For all models in Mg-chamosites, however, total content of iron in 2:1 layer reached 55-60%. In turn, the calculations for samples with low iron content suggest that more than 70% of total iron is located in the 2:1 layer.

The PXRD measurements were also performed on an iron-rich chlorite after thermal treatment. Upon isothermal heating at temperatures up to 450 °C for 24 hours, providing mixed dehydroxylation and dehydrogenation [5], 14 Å chlorite is still present and no new phases occur. Together with increasing temperature of isothermal heating, the peaks became broader and additional chlorite fraction with smaller d_{001} seems to appear.

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MINERALOGY, DEPOSITIONAL MECHANISMS AND FACTORS CONTROLLING THE CLAY DEPOSITS IN BAY DELTAS FROM MESOTIDAL COASTAL ENVIRONMENTS (CADIZ BAY, SW SPAIN)

Antonio Luna del Barco (1)*, José Manuel Gutiérrez Mas (1), Oscar Álvarez (2), Ángel Sánchez Bellón (1)

(1) Department of Earth Sciences, Faculty of Marine and Environmental Sciences, University of Cadiz, Spain,
(2) Department of Applied Physics, Faculty of Marine and Environmental Sciences, University of Cadiz, Spain

In opposition to classical model of ebb-tidal deltas in mesotidal coastal environments, located seaward of littoral sand bars and linked to tidal inlet mouths [1], bay deltas are located lagoonward at the mouth of tidal creeks irrigating salt marshes, without connection with open sea through the littoral sand bars. In absence of large significant waves, tidal currents and tidal range are the main factors responsible for the shape and extension of these deltas, as well as transport and deposition of suspended matter. Consequently, fine-grained sediments (mainly clay minerals) dominate the deposits.

This work presents a wide research about the inner bay deltas developed in lagoon area from the Cadiz Bay (SW Spain). The aims of this study are to establish the mineralogy and sediment nature, and the depositional mechanisms and control factors involved in the evolution of these depositional environments. The research is focused on the innermost area of the bay, a lagoon zone characterized by shallow sea waters and the presence on its edges of an extensive muddy salt marsh zone. The marshes are fringed by a twisty net of tidal creeks and old salt pans, being this the zone where the clayey bay deltas are developed. The lagoon communicates through the Strait of Puntales with the outer bay, an open sea area that reaches depths up to 20 m. Here the sand is the predominant sediment in both, bottom and coast [2]. Tides are dominantly semidiurnal co-oscillating with amplitudes of ~1 m for the M_2 constituent and ~0.4 m for the S_2 constituent [3].

Clay Mineralogy of the suspended matter and sea bottom sediments was determined by XRD techniques, while grain size distribution was established by *Coulter Counter* particle analyser. The extension and shape of the bay deltas was determined by ortophotography analysis. The temporal and spatial variability of the suspended matter concentration (SMC) was established from the analysis of *Landsat TM* image series, correlating water reflectance, measured by remote sensor, with SMC data from surface water sampled simultaneously to satellite overpass. Finally, the dynamic and depositional results were compared to the data obtained from the application of a two dimensional and nonlinear finite-difference, hydrodynamic model, which simulates the spatial distributions of the tidal elevation, specially applied to the Cadiz Bay [3].

The results indicate that Smectite (47%) and Illite (40%) are the dominant clay minerals in the suspended matter. Smectite is more abundant than Illite in samples closer to input sources and from inner embayment, but the ratio is quickly inverted in outer sector, suggesting a preferential deposit of Smectite in inner zones. That is consistent with the higher Smectite contents and lower Illite contents in the bay delta deposits [2]. In regard to the suspended matter, the results show a high temporal and spatial variability of SMC in surface water, with values from 1 to 25 mg/l, depending on the tide situation and the location from input sources. Nevertheless, there is also a marked seasonal variability. The hydrodynamic model has allowed us to delimit the zones of effective sedimentation, while the numerical results show small non-linear tidal asymmetries, which suggest the state of general morphodynamic equilibrium, despite the observed local changes.

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INVESTIGATION OF THE MECHANISM FOR THE UPTAKE OF PHOSPHATE BY DIFFERENT LDHS

Laura Lundehøj (1)*, Belayneh Bekele (2,3), Ulla Gro Nielsen (1), Claude Forano (2,3), Vanessa Prevot (2,3)

(1) Department of Physics, Chemistry, and Pharmacy, University of Southern Denmark, 5230 Odense M, Denmark, (2) Institut de Chimie de Clermont-Ferrand, Université Clermont Auvergne, Université Blaise Pascal, Clermont-Ferrand, France, (3) CNRS, Aubiere, France
*lundehoj@sdu.dk

Phosphorous in the form of phosphate is a necessary fertilizer in the agriculture. It is obtained from mines which eventually will be depleted [1]. Hence, it would be an advantage if phosphate from wastewater could be recovered and recycled. Layered double hydroxides (LDHs) have a high affinity for the sorption of phosphate and therefore have high potential in the recovery of phosphate from wastewater [2-4]. Layered double hydroxides have the general formula $[M_{1-x}{}^{2+}M_x{}^{3+}(OH)_2]^{x+}(A^{n-})_{x/n} \cdot mH_2O$, where M is metals and A is anions. A variety of cations and anions can be incorporated and intercalated into the structure [2]. Both the anions and the cations have been reported to influence the phosphate sorption [3,4].

In order to develop an LDH ideal for phosphate sequestration from wastewater, the mechanism and the factors influencing must be fully understood. Therefore adsorption studies with a range of phosphate concentrations and a detailed characterization of the solid product by powder x-ray diffraction (PXRD) and solid state NMR (SSNMR) was performed on MgAl and CaAl-LDHs. The combination of PXRD, Raman spectroscopy and SSNMR provided new insight into the mechanism. PXRD was used for characterization of the crystalline phases present including monitoring of formed calcium phosphate and confirmed the incorporation of phosphate, which was observed as a splitting of the (003) reflection. SSNMR was used for identification and characterization of both crystalline and amorphous phases. Raman spectroscopy clearly differentiate the structural changes of the local environment of P in MgAl and CaAl host structures. ^{31}P MAS SSNMR allowed identification and quantification of the different phosphate species. ^{27}Al SSNMR monitored the LDH content and the concentration of amorphous aluminium hydroxide which also previously have been observed in LDHs [5,6]. The analysis showed that the CaAl-LDH was dissolved to form calcium phosphate whereas the MgAl-LDH showed a much complex mechanism with multiple P-binding sites formed.

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THM ANALYSIS A CLAY BARRIER USING ADVANCED FLOW MODELS

Xi Luo (1), Marcelo Sanchez (2), Antonio Gens (3), Maria Victoria Villar (4)

(1) Research assistant, Zachry Department of Civil Engineering, Texas A&M University, College Station, TX, U.S.A., (2) Associated Professor, Zachry Department of Civil Engineering, Texas A&M University, College Station, TX, U.S.A., (3) Professor Departamento de Ingenieria del Terreno Universitat Politecnica de Catalunya Barcelona, Spain, (4) CIEMAT, Centro de Investigaciones Energéticas, Medioambientales y Tecnológicas, Madrid, Spain

Clay barriers are basic components in the conceptual design of repositories for high level nuclear waste. They are generally made of unsaturated bentonite (or a mixture involving expansive clays) compacted at a relatively high dry density. This engineered barriers are envisaged as a buffer around the canisters (containing the very pollutant waste) in either horizontal drifts or vertical large diameter boreholes excavated at great depths in an appropriate geological media. This clay-based isolation system has the multiple purposes of providing mechanical stability to the metallic canister (by absorbing stresses and deformations); serving as a buffer around it; sealing discontinuities in the emplacement boreholes and drifts; and delaying the water flow from the host rock.. The behavior of the clay barrier is highly complex, since it involves coupled thermo-hydro-mechanical (THM) phenomena that take place due to the simultaneous heating, generated by the waste radioactive decay and hydration of the barrier, because of the water inflow from the surrounding rock. The understanding of the main THM processes and their couplings requires the contribution of experimental and fundamental studies. This paper presents the modeling of two infiltration cells using different model approaches. The tests were conducted at the CIEMAT facilities in Spain in cylindrical cells 40 cm long and 7 cm diameter. They were made of Teflon© to minimize lateral heat conduction, and were externally covered with steel semi-cylindrical pieces to prevent the deformation of the cell by bentonite swelling. In one of the tests (i.e., GT40) the clay was heated through the bottom surface at a constant temperature of 100 ºC. The other test (i.e., IT40) was carried out at isothermal conditions. The cells were instrumented with relative humidity and temperature sensors placed inside the clay at three different levels. The relative humidity and temperature evolution at different levels inside the clay were recorded. The FEBEX clay was compacted with its hygroscopic water content (around 14%) at an initial nominal dry density of 1.67 Mg/m^3. The tests were modeled using different approaches, considering single and double porosity assumptions and incorporating advanced flow models as well.

Keywords: unsaturated soil, expansive clay, constitutive modeling, THM coupled problem, FEM.

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SYNTHESES OF NZVI/MMT AND ITS PROPERTIES OF MICROWAVE ABSORPTION

Hao Liu (2), Danyu Wang (1), Libing Liao (1)*, Guocheng Lv (1)

(1) Beijing Key Laboratory of Materials Utilization of Nonmetallic Minerals and Solid Wastes, National Laboratory of Mineral Materials, School of Materials Science and Technology, China University of Geosciences, Beijing 100083, China,
(2) School of Science, China University of Geosciences, Beijing, 100083, China
*lbliao@cugb.edu.cn

Nano zero-valentiron (nZVI), due to its large specific surface area, light weightand magnetism, can be used as a novel absorbing material. Nevertheless, the aggregation and passivation of nZVI particles prohibit its wide use. The nZVI intercalated into montmorillonite (MMT) can be evenly distributed in montmorillonite interlayer space and not easy to form a conductive network [1]. The research prepared a new flexible absorbing material and studied adsorption performance of the composite material. The conductive polymers are important absorbing agents, while polypyrrole is one of widely used conductive polymers due to its low density and easy synthesis [2]. Combining conductive polymer and the inorganic magnetic material could improve the absorption performance of the composite, due to electric loss and magnetic loss of it [3]. The researchshowedthat the composites with different nZVI/MMT contents have different absorption performances. Flexible absorbing material with a thickness of 3 mm has thebest absorption performance; when the mass proportion of nZVI/MMT is 35%, the composite has a reflection loss of 38.5 dB at 6.32 GHz. However, as the content of nZVI/MMT increased, the conductive magnetic particles can finally form a conductive network, showing a shielding reflection on the electromagnetic wave and inhibiting the absorption performance.

Keywords**:** montmorillonite, nano zero-valentiron, polypyrrole, functional materials.

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RHEOLOGICAL PROPERTIES OF BENTONITE SUSPENSIONS AFTER DYNAMIC AGING AT HIGH TEMPERATURES

S. Lytra, G.E. Christidis*, D. Marinakis

Technical University of Crete, Department of Mineral Resources Engineering, 73100 Chania, Greece
*christid@mred.tuc.gr

Recent advances in the drilling industry have led to the design of the drilling wells at greater depths and demanding environments. In this sense, the exposure of drilling fluids at high temperatures and pressures requires a better understanding of their rheological parameters. Clays and especially bentonites, are commonly used in the formulation of drilling fluids because they form stable and viscous suspensions. However, the rheological properties of the bentonite fluids are affected by temperature. This study examines the influence of temperature on the rheological behavior of bentonite samples. For this purpose, 4 Wyoming type bentonites and one hectorite, were utilized. The quantitative bulk mineralogy of the samples was determined by X-Ray Diffraction (XRD) on random mounts using the Rietveld approach (Autoquan® software). Oriented mounts of the clay fractions were rendered homoionic with K and Li. K-saturation followed by ethylene glycol solvation was used to determine the layer charge of the smectites present (Christidis & Eberl, 2003) [1]. Li-saturation followed by heating at 300 °C for 24 h was used to estimate the beidellitic content of the smectites (Green-Kelly test). DTG-TG analysis was used to determine the dehydroxylation temperature of the smectites. The chemical composition of the samples, was determined by X-Ray Fluorescence spectroscopy (XRF). The cation exchange capacity (CEC) which is also related to the layer charge of smectite, was determined by the Kjeldahl method after saturation with ammonium acetate. In order to identify the influence of temperature on the rheological properties of the bentonites, the dynamic aging method was applied (A.P.I. 13A, 2010) [2]. Hence, 5% suspensions were prepared and subjected to temperatures 25 - 176 °C under continuous rolling for 16 h. After cooling at room temperature, the rheological properties of the bentonite suspensions (apparent viscosity, plastic viscosity and yield point) were determined with a Grace-M3500 and a Fann 35S viscometer. The filtrate properties of the suspensions after dynamic aging were determined with an API standard filter press at room temperature. The rheograms obtained after aging at the different temperatures were modelled with a MATLAB code, which has been designed to determine rheological behaviors varying among Bingham Plastic, Power Law and Herschel-Bulkley rheological models.

The Wyoming bentonites contain 68-79% montmorillonite, whereas the hectorite-rich sample contains 89% smectite. The smectite present is montmorillonite with up to 7% beidellitic layers. All 5 samples are dominated by smectites with layer charge of 0.41 ± 0.02 e/huc, i.e. by low charge smectites. Also, the thermal properties of the Wyoming bentonites are comparable and the main dehydroxylation event is focused at 620-680 °C (*cis*-vacant smectites). Hectorite dehydroxylated at 800 °C. Therefore the temperatures encountered in the drilling well will not cause dehydroxylation of smectites. The rheological properties of the different bentonites varied between broad limits. In addition, temperature significantly affected the rheological and filtrate properties of the bentonite suspensions. At 25 °C 3 of the Wyoming bentonites displayed Bingham Plastic behavior whereas the remaining bentonite and the hectorite displayed Power Law behavior. With increasing temperature, the rheological model changed; nearly all suspensions displayed a pseudoplastic behavior and were fitted to Herschel Bulkley or Power Law models. The apparent and plastic viscosity varied between broad limits and gradually increased with increasing temperature up to 149 °C. At higher temperatures two of the Wyoming bentonites and the hectorite displayed lower viscosity, whereas in the remaining Wyoming bentonites viscosity continued to increase. In addition, the yield point and the filtrate loss also varied between broad limits and increased with increasing temperature.

The observed differences cannot be explained by differences in smectite crystal chemical properties, because all smectites have a comparable layer charge and a low tetrahedral charge being characterized as typical montmorillonites with less than 10% beidellitic layers and hectorite without tetrahedral charge. The differences in the rheological properties is attributed to the variable degree of hydration of the smectite forming quasicrystals of different thickness, which cannot break up to smaller particles even at high rates of shear. The rheological properties might be improved by using suitable additives (e.g. causticised lignite) or by appropriate processing.

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COMPARATIVE ANALYSIS OF FIFTEEN SOUTH AMERICAN BENTONITE SAMPLES AIMING TO ESTABLISH CORRELATIONS BETWEEN GEOLOGICAL TRACK AND INDUSTRIAL APPLICATIONS

Gabriel G. Machado*, Henrique Kahn, Francisco Valenzuela Diaz

University of São Paulo, Escola Politécnica. São Paulo- 05508-030, Brazil
*machagg@gmail.com

It is widely recognized that diagenetic features and subsequent geological events such as hydrothermal/deuteric alteration, weathering and burial history, would set the fingerprint on bentonite occurrences that determines potential industrial uses, this regional characteristics may also have local deviations when it comes to smectite rich deposits. However, not always this birthmarks rule the way deposits are being exploited, neither have they ruled market destinations, particularly in small-scale mining operations. We approach this issue in order to challenge some of these establishments aiming contribute to a more adequate mining technique and optimization in market targeting.

Four years ago at the 15th International Clay Conference, a work regarding spatial distribution of layer charge upon a single Bentonite deposit located in Uruguay was presented, It would set the frame in which we now count with 15 samples coming from 12 different deposits and 6 different mineralized regions located in Brazil (10), Argentina (3) and Uruguay (2). They have all been characterized under the same conditions and tried several typical industry-processing techniques such as acid activation, Clay polymer nanocomposites, organophilization without previous Na activation. Only the latest will be used for the propose of this abstract, given the fact that it will allow to build a link between the geological context and application performance.

From X-Ray diffraction (XRD) of randomly oriented powder and X-Ray fluorescence (XRF) chemical analysis on bulk samples, we approach the issue of grade and mineral phase semiquantitative annalisys using Rietveld refinement on Topas software. The presence of accessory minerals that would have implications in organophilization at the <1 µm size fractions where observed at this stage; finding Kaolinite, Pyrophillite, Cristobalite, Hematite and I/S mixed layers as penalty accessory phases. Scanning electron microscopy (SEM/EDX), Thermogravimetric analysis (TGA), Size distribution analysis by Malvern and Fourier transform infrared spectrometry (FTIR), were also used as complementary methods when the error bar at the molar sum from XRF vs XRD was not acceptable. Cation exchange capacity was calculated using the ammonium acetate method finding values that range from 52.7 meq/100 g to 90,2 meq/100 g. The structural formula, was estimated from the <1 µm size fractions XRF chemical analysis on fused beads, in order to gather information regarding isomorphic substitutions in terms of location and magnitude of layer charge. Although, we found a clearer trend and easier to access, between layer charge as a function organo-sorption behaviour; by simply evaluating the 001 peak positions on oriented slides after first K saturation and ethylene glycol solvation, against Organoclays Oriented slides XRD traces, being inversely proportional.

Over the <1 µm size fraction and using a 16 carbon chain ammonium salt, we evaluate the organic sorption for all samples having as a result, a broad variety Organophilic XRD patterns showed distinctive expandability behaviour in terms of their 001 ($C_{16}H_{33}CH_3$)-Montmorillonite d-spacing peak position, ranging from 15,2 Å To 21,68 Å. As a function of sorbed Organoclay according size of the alkyl chain used, and the known sorption isotherm, basically all patterns of organo-compound sorption where observed, going from Lateral Monolayer to Paraffin type bilayer

Finally, we explore the Cluster analysis by means of the PolySnap tool now integrated to a XRD interpretation software. We used several multiset combinations from XRD patterns and XRF chemical data on both: whole rock and clay size fraction. Finding dramatic clustering when Organoclays oriented slide XRD patters are contrasted to the <1 µm size fraction XRF, finding almost a perfect correlations between clusters and the six mineralized geological regions object of this study.

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THE EFFECT OF HEAD-GROUP STRUCTURE ON THE CONFORMATION OF ALKYLAMMONIUM CATIONS IN MONTMORILLONITE INTERLAYERS

Jana Madejová (1)*, Michal Slaný (1), Luboš Jankovič (1), Viktor Hronský (2)

(1) Institute of Inorganic Chemistry, SAS, 845 36 Bratislava, Slovakia, (2) Department of Physics, Faculty of Electrical Engineering and Informatics, TUKE, 04200 Košice, Slovakia
*jana.madejova@savba.sk

Clay-surfactant hybrids are employed in a variety of industrial and environmental applications. Their behaviour and properties depends largely on the structure and arrangement of the organic cations (surfactants) within clay mineral interlayers. Detailed information on the conformation of surfactants have provided IR and NMR spectroscopies showing the coexistence of disordered *gauche* and ordered all-*trans* conformations for the alkyl chains depending on the surfactant size and loading level. Less often, however, the relationship between head-group structure and chains conformation is reported. In this paper the near-IR (NIR) and ^{13}C MAS NMR spectroscopies are used to study the effect of head-group structure on the ordering of surfactants with different alkyl-chain length treated at different temperature. The samples were prepared from Na-montmorillonite Jelšový Potok (JP, Slovakia) and trimethylalkylammonium (C_N-TMA) and alkylammonium (C_N-NH_3) cations with increasing number of carbons (N = 6, 8, 10, 12, 14, 16 and 18) in alkyl chain. The NIR spectra of organo-montmorillonites showed the complex band in the 6100-5600 cm^{-1} region related to the first overtone (2νCH) of the stretching vibrations of the CH_3 and CH_2 groups. The position of the $2\nu_{as}CH_2$ component, observed in the 5820-5780 cm^{-1} interval, reflected an abundance of *gauche* - *trans* conformers. With increasing alkyl chain length the band was shifted from 5811 cm^{-1} (C_6-TMA-JP) to 5782 cm^{-1} (C_{18}-TMA-JP) indicating decreasing number of disordered in favour of ordered conformers. Even more pronounced shift, *i.e.* from 5826 cm^{-1} (C_6-NH_3-JP) to 5787 cm^{-1} (C_{18}-NH_3-JP), was detected for samples containing NH_3 head-group. Moreover, for the same alkyl chain length the wavenumber of the $2\nu_{as}CH_2$ band was always higher for C_N-NH_3-JP than for C_N-TMA-JP sample. It is evident that smaller size of the C_N-NH_3^+ cations as well as H-bonds between hydrogens from the NH_3 group and basal oxygens of montmorillonite contribute to the higher disorder of the C_N-NH_3 surfactants. To probe the effect of temperature on the alkyl chains ordering the C_{18}-NH_3-JP and C_{18}-TMA-JP samples were chosen. A special diffuse reflectance cell allowing the *in-situ* measurement in the 25 - 180 °C range was used to obtain NIR spectra. Heating of the C_{18}-TMA-JP up to 100 °C evoked the upward shift of the $2\nu_{as}CH_2$ band position by 2 cm^{-1} (to 5784 cm^{-1}) further increase of the temperature to 180 °C moved the band to 5787 cm^{-1}. The NIR spectra of C_{18}-NH_3-JP revealed only a small shift of the band to 5789 cm^{-1} upon heating at 100 °C but no additional change was detected even for the sample heated to 180 °C. The NIR spectra of both samples confirmed that with increasing temperature the conformational transition of the chains takes place leading to an increase of the amount of disordered conformers. The insight into the arrangement of alkyl chains as a function of head-group structure, alkyl chain length and temperature provides also ^{13}C MAS NMR spectroscopy. The main signal (30-33 ppm), assigned to internal methylenes of the alkyl chain, was examined and the ratio of *trans* (~33 ppm) and *gauche* (~30 ppm) conformers ($Y = I_t/I_g$) was determined from the signals intensities obtained by deconvolutions of the NMR spectra in 20-40 ppm interval. The number of *trans* conformers (with respect to *gauche*) increases with the length of alkyl chain in both C_N-TMA-JP and C_N-NH_3-JP series. The highest number of *trans* conformers (at 30 °C) was detected for the C_{18}-TMA-JP (Y=1.57) and C_{18}-NH_3-JP (Y=1.49), the lowest for C_6-TMA-JP (Y=0.43) and C_6-NH_3-JP (Y=0.28). For the samples with the same chain lengths more ordered structures were confirmed for those with TMA head-group. The *trans/gauche* ratio decreased markedly with temperature for both, C_{18}-TMA-JP and C_{18}-NH_3-JP. The Y decrease to 0.70 and 0.44 for C_{18}-TMA-JP heated at 70 and 100 °C, respectively. Similar values were obtained also for C_{18}-NH_3-JP for which the calculated ratio was 0.77 and 0.54 for samples heated at 70 and 100 °C, respectively. The agreement of NMR results with those obtained by NIR spectroscopy supports the utilization of the NIR spectroscopy, simple and relatively cheap technique, for probing the conformation of alkyl chains.

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FAST AND CLEAN SYNTHESIS OF NYLON-6 / SYNTHETIC SAPONITE NANOCOMPOSITES

Alejandro Madrid-Acevedo, Raquel Trujillano*, Elena Pérez-Bernal, Beatriz González, Vicente Rives

GIR-QUESCAT, Departamento de Química Inorgánica, Universidad de Salamanca, Salamanca 37008, Spain

In situ intercalation-polymerisation was the first method used for the preparation of polymer/clay nanocomposites by Toyota researchers to obtain nylon-6 nanocomposites from the Ɛ-caprolactam monomer [1-3] and previously organophilizated natural montmorillonite. In this method the clay is swollen in a solution of the monomer, this diffuses into the interlayer space of the clay and then the polymerisation is carried out by application of heat or radiation [4].

The aim of this work is the synthesis and characterisation of nanocomposites prepared through a fast, efficient, low cost, and environmentally friendly method. To this end, delaminated saponites have been directly synthesized to be used as a filler of a polymer matrix formed by nylon-6, by *in situ* intercalation-polymerisation of the Ɛ-caprolactam monomer without using surfactants or other organic reagents to organophilize the clay, thus avoiding contamination drawbacks. The efficiency of the preparation method has been increased and significant savings have been achieved in energy and reaction time by using microwave radiation as an energy source during the synthesis of the nanocomposites.

Delaminated saponite was synthetized following the method described by Trujillano et al. [5] and preparation of the precursor clay/monomer mixture (5% on saponite) was based on the method reported by Fukushima and Inagaki [6]. *In situ* polymerisation was achieved by calcining the precursor at 250 ºC. Full characterisation of the samples was performed by Element Chemical Analysis, PXRD, FT-IR spectroscopy, TG and DTA analysis, etc.

The chemical analysis and PXRD results revealed the formation of delaminated synthetic saponites (SSA) and intercalation of Ɛ-caprolactam without the use of any other organic modifier to organophilize the surface of the sheets. The production of the nylon-6/saponite nanocomposite (5% w/w) was achieved by *in situ* polymerisation of Ɛ-caprolactam in a conventional muffle furnace or in a microwave oven. The polymerisation is catalysed by the hydroxyl groups of the sheet surface, together with the water retained in the interlayer space of the saponite. The optimum time for obtaining the nanocomposite in the conventional muffle was 24 h. The use of MW radiation greatly decreases the synthesis time to only 8 h. The powder X-ray diffractograms of the nanocomposites revealed that the reflection due to the (001) planes is shifted to lower 2θ values indicating a swelling of the interlayer space, i. e., nylon-6 has been formed in the interlayer space of the clay, obtaining nanocomposites of intercalated type.

When comparing the thermogravimetric curve of the MW-prepared sample solid with that for pure nylon synthesized in the laboratory, the differences observed allow to conclude that the presence of dispersed sheets within the polymer matrix increases its thermal stability.

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IMPACT OF CLAY MINERALS IN SANDSTONE RESERVOIRS ON FORMATION DAMAGE DURING ENHANCED OIL RECOVERY AND STIMULATION OPERATIONS

Mohamed Mahmoud, Muhammad Shahzad Kamal, Ibnelwaleed Hussein

(1) Petroleum Engineering department, College of Petroleum & Geosciences, King Fahd University of Petroleum & Minerals, Dhahran 31261, Saudi Arabia, (2)Center for Integrated Petroleum Research, College of Petroleum & Geosciences, King Fahd University of Petroleum & Minerals, Dhahran 31261, Saudi Arabia, (3) Gas Processing Center, College of Engineering, Qatar University, PO Box 2713, Doha, Qatar
*mmahmoud@kfupm.edu.sa

Sandstone oil reservoirs consist of different clay minerals such as kaolinite, illite, and chlorite. These clay minerals highly affect the formation damage during enhanced oil recovery (EOR) and well stimulation operations in these reservoirs. No attention was paid to investigate the effect of these clay minerals on the formation damage during different reservoir processes. In addition, no solution was introduced to mitigate the effect of clay minerals on the formation damage in sandstone reservoirs. In this study, and for the first time, the effect of clay mineral content and type on the formation damage during sandstone acidizing and sandstone enhanced oil recovery applications are studied in detail. Sandstone rocks with various clay mineral content, representing actual and outcrop sandstone reservoir rocks, were studied. XRD was used to characterize the sandstone rocks to determine the clay type and content in each rock. SEM was carried out before and after the acidizing and enhanced oil recovery operations for the tested rocks to locate the change in the clay distribution inside the rocks. Different fluids were used in the acid and enhanced oil recovery treatments. In sandstone acidizing fluids, such as mud acid (13.5 wt% HCl/1.5 wt% HF), low and high pH chelating agents (pH 4 and 11) such as EDTA, GLDA, and HEDTA were used in the experiments. In EOR experiments, fluids such as seawater with high and low salinity, surfactant flooding, and high pH chelating agents flooding were used. In the coreflooding experiments, fluids were injected in the cores at 100 °C and 1500 psi. The ICP (Inductively Coupled Plasma) was used for EOR effluent fluid analysis. In addition, NMR was used to locate the damage inside the rock due to the migration of clay minerals. The results of this study showed that the used sandstone rocks in this study consists of illite, kaolinite, and chlorite clay minerals. The illite content ranges from 1 to 14 wt%, kaolinite from 3 to 7 wt% and chlorite from 1 to 4 wt%. Based on the coreflooding, SEM, and ICP effluent analysis, the illite clay mineral was the most damaging clay because it broke down and migrated in the cores during the experiments of acidizing using mud acid and during low salinity water injection in EOR experiments. Kaolinite has little effect on formation damage compared to illite. Chlorite clay mineral has iron and this affected the EOR when seawater, low salinity water, and surfactant flooding were used. Chelating agents eliminated completely the formation damage effect of all clay minerals during sandstone acidizing and sandstone enhanced oil recovery. In sandstone acidizing, chlorite clay mineral caused iron hydroxide precipitation inside the cores during treatment with mud acid. Chelating agents, used in this study, were compatible with all sandstone rocks with different clay content and did not cause formation damage. NMR showed that clay minerals plugged the pore throats of the rocks and reduced the rock permeability during the injection of low salinity water.

Keywords: Clay minerals; acidizing; sandstone; enhanced oil recovery; coreflooding.

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MINERALOGICAL AND CRISTALLOGRAPHIC EVOLUTIONS OF CLAY MINERALS IN FAULTS OF THE HIKURANGI PRISM (NEW-ZEALAND)

Tatiana Maison (1)*, Sébastien Potel (1), Pierre Malié (1), Frank Chanier (2), Julien Bailleul (1)

(1) Basins-Reservoirs-Resources (B2R), UniLaSalle, Geosciences department, F-60026 Beauvais, France, (2) UMR 8187 - LOG, Laboratoire d'Océanologie et de Géosciences, Université de Lille/ULCO/CNRS, 59650 Villeneuve d'Ascq, France

Clay minerals could fill fault zones, where they can act either as drains or as barriers for fluid circulation. Their mineralogical nature and their crystallographic evolution can be driven by several parameters such as their origin (creation by metasomatism from fluid circulations, in situ evolution by diagenesis, mechanical and/or diagenetic neoformation), the evolution of fault zones or the associated fluid behaviour.

In this study, we present a clay mineral analysis of three major fault zones that developed in an active margin setting, the Hikurangi Margin, eastern North Island, New Zealand. This active margin developed in association with the westward subduction of the Pacific Plate beneath northern New Zealand since 25 Ma [1]. The onset of subduction was accompanied by the development of large seaward directed thrust sheets responsible for the growth of an accretionary wedge [1]. This first accretionary wedge was then dissected by extensional deformation during a period, between c. 12 and c. 6.5 Ma, dominated by normal faulting [2]. More recently, from c. 6.5 Ma to present day, the active margin was again submitted to dominant compressional deformation responsible for the inversion of some of the former normal faults. We document the clay composition of some fault gouges in three fault zones that have recorded this complex tectonic history and that are now exposed within the Coastal Ranges, in the emerged part of the Hikurangi active margin.

Two of the faults analysed in this study, the NE-SW directed Tinui and Whakataki faults, correspond to the soles of large imbricated thrust sheets formed just after the onset of subduction. The third one, N-S in direction, is the Breakdown Fault that is a younger large deformation zone cross-cutting the main thrust sheets. The Breakdown fault zone had a complex evolution from extensional at its origin to positive tectonic inversion during further compressional deformation [3].

Clay minerals are studied from a petrological and crystallographic point of view. The mineralogical composition inside and outside the fault zone shows, in variable amounts, the occurrence of quartz, feldspars, calcite, glauconite and clay minerals as illite/muscovite, kaolinite and interstratified species. Each fault zone shows a homogeneous chemical composition, where only the mineral paragenesis changes, probably due to the P-T condition evolution. Inside the fault zones, the texture is fine-grained without detrital grains. This should indicate that the clay minerals are neoformed. Indeed, in the surrounded rocks, the texture is coarser-grained, with recrystallized minerals, suggesting a detrital inheritance. The evolution of crystallographic parameters is addressed with the determination of the Kübler Index (KI) [4] that reflects the illite "crystallinity". KI values indicate high diagenetic metamorphic conditions. A difference of crystallinity is observed between the three faults. The Whakataki and Tinui faults present KI values around $0.5\Delta°2\theta$. The Breakdown fault presents KI values around $0.7\Delta°2\theta$. This shows that metamorphic conditions were higher in the Whakataki and Tinui faults than those in the Breakdown fault. This may reflects the difference in age and in motion between basal Miocene thrusts related to the onset of subduction and older poly-phased faults related to the deformation of the Coastal Ranges. In this context, fluid circulations and P-T conditions would have been different and played a role in the mineralogical behaviour of clay minerals.

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THERMAL ACTIVATION OF A LOW KAOLINITIC CLAY AND ITS USE IN A LIMESTONE-CALCINED CLAY CEMENT

Palaskumar Haldar (1), Soumen Maity (1)*, Santanu Mithia (1), Shashank Bishnoi (2)

(1) Technology and Action For Rural Advancement, New Delhi 110016, India, (2) Department of Civil Engineering, Indian Institute of Technology Delhi, New Delhi 110-016, India

Concrete is one of the most abundantly used material in the world after water. This is due to the abundance and easy availability of raw materials, low cost of production and versatility of use in any shape, size, quality and application [1]. One of the most important constituent of concrete is cement. The major raw material used in the preparation of cement is limestone. Apart from all the modern techniques and processes being adopted, the manufacture of cement still emits quite a large amount of CO_2, mainly from the dissociation of raw limestone and burning of fuel. Apart from CO_2 emissions, in recent years quite a lot of attention is being focussed on the availability of natural raw materials for the production of cement. The present study addresses the twin issues of environmental emission and resource use by lowering the clinker factor and utilizing mining wastes for the production of a general purpose cement.

It has been well understood that reactivity of calcined china clay depends on the geology of formation of clay, chemical and mineralogical compositions, temperature and duration of heating, soaking at the peak temperature etc [2-4]. A previous study by Bishnoi et. al. [5] showed the benefits of production of a new type of ternary blend cement, containing 50% clinker, 30% calcined clay, 15% crushed limestoneand 5% gypsum (LC^3), carried out in India. The raw materials required to produce the cement were found tobe easily available in the quality required for the production. Calcination of clays was carried out in static kilns used to fire potteries. Grinding and blending of the cements was carried out at a cement grinding unit. The blends produced were tested in the laboratory and building materials were produced using the cement. Good results were obtained from the blends despite the sub-optimal conditions of production of the cement, demonstrating the viability and robustness of the technology.

The present investigation deals with the effect of calcination temperatures on the pozzolanicity of a low grade china clay and its effect on the properties of a pozzolanic cement. The china clay used in the study was from Katni, Madhya Pradesh, Central India which has abundant supply of low grade china clay not suitable for use in ceramic or other refractory purposes. This is due to their low kaolinitic and high iron content. TGA studies of the clay showed a kaolinite content as low as 30% with a majority of silica. The clay was heated at various temperatures between 700 °C to 900 °C and characterized for degree of dehydroxilation and the formation of any unreactive crystalline phases e.g. mullite. The pozzolanic reactivity of the calcined clays was also measured by isothermal calorimetry and correlated with the dehydroxilation extent. Structural properties of the calcined clays were investigated by ^{27}Al NMR and ^{29}Si NMR technique to understand the reactivity mechanism.

It was found from TGA analysis that maximum weight loss of the clay occurred at 900 °C. However reactivity was maximum at 800 °C and decreased at higher temperatures. No detectable formation of crystalline mullite was found at higher temperatures. Thus the decrease in pozzolanicity at higher temperatures was inferred to be due to the formation of spinel phases and initiation of crystallinity of the amorphous phases. Application of the calcined clays in a ternary blend of clinker, calcined clay, limestone and gypsum revealed a similar behaviour. The performance of the cement was as expected with the maximum strength coming from the highest reactivity clay calcined at 800 °C. Thus it was concluded that low kaolin content clays can be thermally activated at lower temperatures and can be used to produce a high performance cement containing rejected mine wastes of around 45%. These type of cements will also be environment friendly and resource efficient due to the reduction in clinker factor to 0.50.

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INFLUENCE OF SMECTITE LAYER CHARGE ON THE GEOTHECHNICAL PROPERTIES OF BENTONITES FROM MILOS ISLAND, GREECE

P. Makri*, G.E. Christidis, E. Steiakakis

Technical University of Crete, School of Mineral Resources Engineering Chania, 73100, Greece
*pmakri@mred.tuc.gr

Two profiles from the Aggeria and Agia Irini bentonite deposits in Eastern Milos were studied, in order to determine the influence of layer charge and charge distribution of smectites in the cation exchange capacity (CEC), free swelling, liquid limit (LL) and hydraulic conductivity (k). The evaluation of bentonite profiles was performed by determination of the grade (smectite content) and their quality (performace in industrial applications because of their physicochemical properties). Grade was determined through measurement of the CEC and quality via activation with sodium carbonate (Na_2CO_3) and determination of the free swelling volume and the Liquid Limit (LL) with the Casagnande and the Cone penetrometer methods [1]. Layer charge and charge distribution of the smectites present in bentonites was determined according to [2], which is based on the comparison of XRD patterns of K-saturated, ethylene-glycol solvated smectites with calculated XRD-patterns for three-component interlayering (fully expandable 17.1 Å layers, partially expandable, 13.5 Å layers and non-expandable 9.98 Å layers). Measurement of layer charge and charge distribution is possible by means of the LayerCharge program. The Green - Kelly (Green-Kelly, 1953) test was used to differentiate montmorillonite from beidellite. The CEC was determined by saturation with 1M CH_3COONa and back saturation with 1M CH_3COONH_4 and measurement of exchangeable Na^+ with flame photometry. The free swelling test was performed with addition of 1-6% sodium carbonate to 2 g of bentonite samples and measurement of the swelling volume after 24 h. Both CEC and swelling were affected by the layer charge and charge heterogeneity and charge localization (tetrahedral or octahedral). As it was expected the CEC increased with increasing layer charge. Furthermore, the smectite samples with abundant fully expandable 17.1 Å layers (low layer charge), have low CEC. Also, the presence of high percentage of abundant non-expandable 9.98 Å layers (high layer charge), increased the CEC. The smectite content significantly affected the swelling volume. The swelling index of the high charge smectites is low (e.g. 19-24 ml/2g clay) while low-intermediate charge smectites have the capacity to develop much expansion of up to 35 ml/2g clay. The LL varied with the localization of the layer charge, both in beidellitic and montmorillonic layers. In low to intermediate layer charge smectites LL decreases with increasing layer charge, while a decrease of LL is observed in smecites with high Layer Charge (both two methods). In addition, the LL increased with increasing smectite content in the bentonite samples.

The hydraulic conductivity of bentonites containing smectites with different layer charge and charge heterogeneity was determined using the falling head method. The samples were activated with optimum amount of Na_2CO_3, determined from the swelling tests, in order to avoid possible sample failure during the experimental procedure. The specimens were prepared at optimum water content and consolidated under pressure equal to 10-12 kPa. The hydraulic conductivity of the bentonites varied by varying the layer charge of the smectites, and tended to decrease with increasing smectite content. However bentonites containing smectites with high layer charge located in the tetrahedral sheet (i.e. beidellites) did not follow the overall trend. In general the hydraulic conductivity of the bentonites tended to increase with decreasing content of fully expandable smectite layers and increased with increasing content of the non-expandable smectite layers. However, scattering was observed due to the heterogeneity of the bentonite samples. In addition, bentonites containing smectites with greater octahedral charge have lower hydraulic conductivity. As a general trend the hydraulic conductivity increased with increasing layer charge of smectites for layer charge up to -0,45 e/huc.

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APPLICATION OF ORGANIC MATTER AND CLAY STUDIES TO THE MIO-PLIOCENE TECTONIC HISTORY OF THE HIKURANGI PRISM (NORTH ISLAND, NEW ZEALAND)

Pierre Malie (1)*, Sébastien Potel (1), Rafael Ferreiro Mählmann (2), Julien Bailleul (1), Frank Chanier (3), Tatiana Maison (1), Renaud Toullec (1), Geoffroy Mahieux (4), Brad Field (5)

(1) Basins-Reservoirs-Resources (B2R), UniLaSalle, Geos dept., F-60026 Beauvais, France, (2) Technische Universität Darmstadt, Institut für Angewandte Geowissenschaften, Schnittspahnstraße 9, D-64287 Darmstadt, Germany, (3) UMR 8187 - LOG, Université de Lille/ULCO/CNRS, 59650 Villeneuve d'Ascq, France, (4) Basins-Reservoirs-Resources (B2R), University of Picardie Jules-Verne, 80000 Amiens, France, (5) GNS Science, PO Box 30368, Lower Hutt, New Zealand

On the emerged accretionary prism of the Hikurangi Margin (North Island, New Zealand), Early Miocene to Pliocene burial history and successive tectonic events are accompanied by fluids migration. In the study area (Wairarapa Region, eastern North Island), the outer wedge of the accretionary prism is extending offshore eastward whereas the inner wedge is widely exposed within the Coastal Ranges. Since the onset of subduction about 25 Ma ago, the Coastal Ranges have undergone several deformation episodes leading to complex stratigraphic and structural patterns. Three major deformation episodes were identified during the Neogene: i) An Early Miocene to early Middle Miocene compressional episode, beginning with seaward emplacement of thrust-sheets and followed by E-W contraction that is responsible for the development of confined trench-slope basins bounded by structural highs [1]; ii) A Middle-Late Miocene period of widespread subsidence accompanied by dominantly normal faulting that is attributed to tectonic collapse [1 and 2]; iii) Tectonic inversion of normal faults during a new compressional period that started at about 6.5 Ma and lasted until present-day [1]. The onland exposure of Neogene trench slope basins together with their Cretaceous to Oligocene basement permits high resolution sampling grids of the whole lithological units. It provides the spatial study of nature and depositional distribution of the sedimentary organic matter and clay minerals. This study, which is preferentially based on onshore sampling, is also extended locally offshore through the analysis of cuttings from two prospecting oil wells: Titihaoa-1 and Tawatawa-1. We performed a multi-proxy approach, including the analysis of organic matter (Rock-Eval pyrolysis, organic petrography, vitrinite (VR) and solid bitumen reflectance (BR) %) and the analysis of clay minerals (illite Kübler-Index (KI) and clay mineral reactions). The combination of clay mineral indices and organic matter reflectance [3] and VR versus BR [4] allows the recognition of heat flow changes during sedimentary and tectonic burial. Vitrinite reflectance (%) and Rock-Eval pyrolysis results show no significant maturity evolution in the thick Neogene sedimentary cover. These measurements reflect a very low geothermal gradient through the Early Miocene to Late Miocene within the Coastal Ranges. Distribution of illite/smectite interstratified phases in the Cretaceous up to the Miocene strata, and their occurrence even in the deepest stratigraphic levels, is consistent with the low burial temperatures deduced from our Rock-Eval and vitrinite reflectance results. KI determination from Late Miocene rocks from offshore wells (Titihaoa-1 and Tawatawa-1) and from onshore outcrops, indicates a clear influence of detritus (comparison of KI from the <2 µm and <10 µm fractions). We observe that illite from Lower to Middle Miocene series are less crystallized than in the Late Miocene. KI determination from Lower to Middle Miocene series reflect low grade diagenesis while the Late Miocene series indicate an anchizonal grade. The input of such detrital material can be associated with a Late Miocene erosional phase that affected the main structural highs separating the Neogene slope basins or other contemporaneous reliefs further west. These results allow us to constrain an evolution scenario for the trench slope basins and associated structural highs as also for the exhumation of the Axial Ranges in Central North Island.

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MAJOLICA PRODUCTION IN SASSARI (NORTH-WESTERN SARDINIA, ITALY). INSIGHTS ON THE PROVENANCE OF CLAYS

Paola Mameli (1)*, Chiara Giuseppina Pasteriga (1), Giacomo Oggiano (1), Daniela Rovina (2)

(1) Dipartimento di Scienze della Natura e del Territorio, Università degli Studi, Sassari, 07100, Italy; (2) Soprintendenza ai Beni Archeologici, Sassari, 07100, Italy

Archaeological excavations in the city centre of Sassari (Sardinia, Italy) in 2009-2010 have brought to light the remains of a castle and a significant amount of ceramic findings. These are mainly waste materials including spacers, incomplete ceramic products and polychrome majolica, whose abundances suggest the presence of a production centre in the town. The possible local pottery was stratigraphically associated with monochrome and polychrome Ligurian, Tuscan (Montelupo), Latium and Spanish pottery, dating from the sixteenth and seventeenth century [1].

Mameli et al. [2] [3] hypothesized the provenance of the clayey raw material from local marls of Langhian age on the base of petrographical analyses. This work, through the textural, mineralogical and chemical comparison between archaeological ceramic sherds and pastes artificially obtained, provides information about the quarries and gets some data on the manufacture.

Ninety-five samples, containing 11 spacers, 8 painted open shapes, 1 uncoated open form and 75 pastes artificially obtained from eleven different clays (CP1-CP11) collected in some outcrops in the district of Sassari, have been selected for the study of fine pottery.

The ceramic samples have been analysed using different methods; the observations of thin sections by optical microscopy (OM) have been carried out in order to characterize the microstructure and the morphology of the pastes and microfossil relics, while the compositional data have been performed through X-ray diffraction (XRD) and inductively coupled plasma mass spectrometry (ICP-MS).

The samples of fine ceramics show small variations in composition and texture. They are characterized by a very fine and isotropic, or mildly anisotropic, marly groundmass. The inclusions are essentially single minerals with prevailing quartz, K-feldspars, plagioclase, muscovite and rare augite and opaques. Fossils, mainly are globigerinae and orbulianae. XRPD analyses of the archaeological sherds revealed the presence of gehlenite, diopside, analcime and sometimes traces of larnite as secondary phases. The artificial paste were prepared from marly levels, of the so-called “Borutta Formation”, sampled in 6 different sites close to the city and fired at temperatures varying between 600 °C and 1100 °C. Among the experimental briquettes those that best fit the majolica sherds are those fired at temperatures higher than 900 °C. In thin section these revealed a quasi-isotropic groundmass with inclusion (smaller than that of the majolica sherds) represented by single minerals with prevailing quartz, sporadic muscovite and few feldspars. XRPD analyses revealed the presence of gehlenite, diopside, analcime, wollastonite, spurrite and larnite as secondary phases.

On the basis of chemical analyses it may be inferred that all the spacers and some sherds of majolica have been made using a single clay, or clays from very similar outcrops, compatible with the considered marly formation clays. On the other hand these analyses reveal higher contents of SiO_2 and Al_2O_3 in the archaeological pottery than in sampled marly clays, probably due to previous settling of raw materials with a consequent enrichment in clay minerals.

The temperature of firing approached 850 °C for the bricks as testified by the occurrence gehlenite, and was possibly higher than 900 °C in the faience kilns for the occurrence in some samples of new-formed diopside. Whether the presence of analcime is due to high firing temperature (greater than 900 °C) and/or to secondary alteration after burying of the sherds is to be established. In fact, in a wet landfill, some elements such as potassium could have been leached, and analcime could have formed, due to sodium scavenging by the environment.

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INFLUENCE OF THE PRETREATMENT IN THE CATION EXCHANGE CAPACITY AND SURFACE PROPERTIES OF ABSORBENT CLAYS

Eva Manchado (1), Emilia García-Romero (2,3), Mercedes Suárez (1)*

(1) Department of Geology, University of Salamanca, Salamanca, 37008, Spain, (2) Department of Crystallography and Mineralogy, Complutense University of Madrid, Madrid, 28040, Spain, (3) IGEO, UCM-CSIC, 28040, Madrid, Spain
*msuarez@usal.es

Sepiolite, palygorskite, and smectites are special clays bellonging to the group of adsorbent minerals, and their industrial applications in this field are related to the physical-chemical properties, mainly to the surface properties and the cation exchange capacity. These properties vary among samples from different deposits, similar to most industrial minerals, and their description and comparison is a common topic in studies of these special clays. For instance, the specific surface area of sepiolite may vary from 77 m^2g^{-1} to 399 m^2g^{-1}, as shown in a comparative study of sepiolites from 22 localities around the world [1]. The presence of impurities, the variation in the crystal-chemistry, and the texture may influence greatly these properties; however, there are also differences for samples from a same deposit because the conditions of study, mainly the pre-treatment of the sample, may be very different.

In this study we compare the results obtained from a) sample with its original texture, in grains of ~4 mm, b) ground sample in manual agate mortar, c) ground sample by mechanical grinding, and d) re-sedimented sample. The studied samples are i) two smectites, a trioctahedral smectite from the Tajo Basin (Spain) and a dioctahedral Na-smectite from Wyoming (U.S.A.), ii) two sepiolites, from Tajo Basin (Spain) and from Polattli area (Turkey), and iii) a palygorskite from Attapulgus (U.S.A.). The mineralogical composition from X-Ray diffraction, textural features from scanning electron microscopy, the surface properties from the adsorption of N_2 isotherms and the cations exchange capacity (CEC) and exchangeable cations were studied.

The X-Ray diffraction patterns of samples b and c show that mechanical grinding produces a loss of crystallinity with partial amorphization of the sample as can be deduced by the diminution off the diffraction peaks of the clay mineral and the small elevation of the background in the central zone of the pattern. The results obtained show a variation in all properties for each sample that may be very large; for instance Wyoming smectite displays a four-fold increase of the specific surface area (BET) after mechanical grinding. The variations are different for the different minerals, and the highest values of BET and total volume of pores was obtained either for natural, powdered or re-sedimented samples. However, there is a general increase of microporosity accessible to N_2 in all samples when they are ground mechanically, with the exception of the sepiolite from Polattli in which the textural microporosity of natural sample is probably high. When only the manual and mechanical grinding were compared, all samples displayed higher microporous area and micropore volume after mechanical grinding. The cation exchange capacity is also higher for samples ground by the mechanical procedure with the exception, of the Wyoming smectite in which the CEC is higher for the sample ground in the agate mortar. The X-Ray patterns show that this sample has higher crystal order than its counterpart ground mechanically. The increase of of CEC and the amount exchangeable Mg^{2+} obtained after grinding might be related with partial dissolution of the octahedral Mg.

The change of the natural texture by grinding or suspension and sedimentation affects to the surface properties in different ways depending on the meso and macroporosity. In general, more extensive grinding causes an increase of the microporosity and the CEC.

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CHARACTERISATION OF CLAYS FROM THE KINSHASA REGION (D. R. CONGO) USED FOR MANUFACTURE OF RAW EARTH PRODUCTS

Mango Itulamya Lavie Arsene (1)*, Frederic Colin (2), Fabienne Courtejoie (3), Fagel Nathalie (1)

(1) Argiles, Géochimie et Environnement sédimentaires (AGEs), Quartier Agora, University of Liège, 4000 Liège, Belgium, (2) Géotechnique, Quartier Polytech, University of Liège, 4000 Liège, Belgium, (3) Architecture, Boulevard de la Constitution, University of Liège, 4020 Liège, Belgium
*lmango@doct.ulg.ac.be

The region of Kinshasa contains abundant raw clay materials. These clays are either residual formed by in situ alteration of the Inkisi Neoproterozoic sandstones, or alluvial deposits from the Congo or Ndjili rivers. They are already highly valued in terracotta construction. This work aims at valorising these natural clay resources in another sector of construction which is the raw earth, and by this, defining them as a sustainable and energy-saving alternative.

Three sites marked by important clay resources were sampled in the low Congo River Basin (Kasangulu, Lutendele and Ndjili Cecomaf). The materials of the different localities were characterized in terms of their suitability for raw earth constructions according to current techniques and standards.

The samples were studied with respect to their mineralogical (X-ray diffraction), physical (density, natural water content, grain size, plasticity index) and geotechnical properties (compressive and bending strength). Sampled clays from the three localities are characterized by the following properties.

(1) Kasangulu material are characterized by a 28-day compressive strength (Rc28) ranging from 2.33 to 2.58 MPa and a low 28-day bending strength (Rf28) from 0.56 to 0.59 Mpa, a high density (1800 to 2605 kg/m^3), a low natural water (<15%) and clay content (<6% of particles lower than 2 microns) and a plasticity index between 10 and 16.

(2) Lutendele material is marked by low Rc28 (1.69 MPa) and Rf28 (1.33) values but a high natural water (>15%) and clay (>20%) content. The measured plasticity index is lower than 10.

(3) Ndjili Cecomaf material is characterized by the highest Rc28 value (3.81 Mpa) and intermediate Rf28 (1.01) and density (1677 kg/m^3) values. Like Lutendele, the Ndjili Cecomaf raw clays contain a high percentage of natural water (>15%) and clay (17%) but the plasticity index is slightly higher of 12.

Those parameters allow to propose two different applications for the raw clays from the three sampled localities. The Kasangulu material can be classified as more favorable in compressed earth constructions (i.e., rammed earth and compressed earth block). The Lutendele and Ndjili Cecomaf materials can rather be classified as more suitable for molded earth constructions (adobe, mortar, cob).

In the rest of the study, characterized clays will be valorised for the production of blocks of raw earth stabilized by the addition of vegetable waste coming from households, markets or the agriculture sector. In the region of Kinshasa, clay mining for construction is generally artisanal. It produces small quantities of materials which are not accessible to all and whose price remains high for a large part of the population. In order to limit the energy cost of production and produce a resistant building material, the use of vegetable waste seems to be a solution. These wastes are widely available at low cost and their use in construction constitutes new outlets for these materials. The recycling of those waste also reduces environmental impacts.

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MOLECULAR SIMULATION OF CLAY-DYE HYBRID MATERIALS

Eduardo Duque-Redondo (1), Hegoi Manzano (2)*, Virginia Martinez-Martinez (1), Nerea Epelde-Elazcao (1), Iñigo Lopez-Arbeloa (1)

(1) Departamento de Química Física UPV/EHU, Leioa, Spain, (2) Departamento de Física de la Materia Condensada UPV/EHU, Leioa, Spain

Clay-dye hybrid materials are a great example of a beneficial host-guest interaction. The confinement of the organic dye into the 2D interlaminar space of the clay provides thermal and chemical stability, allows dispersion in water, increases the rigidity of the molecule, and can help to control the spatial ordering and aggregation of the dyes. Using different host-guest pairs, and even combination of various guest molecules in a host, gives rise to a very versatile range of materials [1]. Our group prepares and characterizes this kind of dye/clay hybrid materials for applications as sensors, electronic devices, and nanocarriers [2-4].

In many cases, the properties of the hybrid materials are difficult to elucidate based solely on experimental results. In those situations, we add molecular simulation as a complementary technique that can help us to understand the underlying mechanisms. Using molecular dynamics simulations [5,6] we try to cover all the aspects of the hybrid material lifetime, from the preparation to the stability, including of course the host-guest interactions that influence the desired photophysical properties of the material.

In this presentation we will cover the following aspects of the dye/clay materials:

- Preparation: Diffusion of dyes in the clay's interlaminar space

- Photophysical properties: Effect of confinement, solvation and aggregation of dyes [3,4]

- Stability: Shear strength of dye-modified clays [7]

from the point of view of classical molecular dynamics, and with special emphasis in the correlation between experiments and simulations. We will show how molecular simulations can help in the understanding of the photophysical properties, and briefly discuss some of the limitations.

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PERFORMANCE EVALUATION OF ITY MINE SITE RECLAMATION (IVORY COAST) USING PHYSICAL MODELS BASED ON CLAY MATERIALS

Abdelkabir Maqsoud, Sékou Diaby, Mamert Mbonimpa

Institut de Recherche-Mine et Environnement, Université du Québec en Abitibi-Témiscamingue, Rouyn-Noranda, Québec, Canada

Mining industry generates large amounts of solid and liquid wastes. These wastes have the potential to adversely impact the environment if not properly managed. Special attention is required when the wastes contain sulfide minerals. The oxidation of sulfides minerals by atmospheric oxygen generates acidity and contaminants in the drainage water. This phenomenon is called acid mine drainage (AMD). In these situations, actions must be taken at the mine site to prevent environmental impacts caused by AMD. The reclamation of mine site constitutes the most important challenge for the mining industry and different techniques have been developed to control the production of AMD.

The materials used in engineered cover used for mine site reclamation can be natural (e.g., sand and silt) or recycled (e.g., non-reactive tailings). In the event where natural, silty materials are not available in the close proximity to a mine site, clayey materials can be used as engineered cover components as a barrier to water infiltration and oxygen migration. This is largely due to the low permeability of clayey materials, which results from their grain-size distribution and mineralogy.

The gold mine of Ity, located in Zouan-Hounien, in the western part of Ivory Coast country during its exploitation will generate reactive tailings that can be considered as potentially generating AMD. Around this mine various materials such as marble and clay materials are available, which could be used as a component of the engineered cover for the reclamation of reactive tailings. However, it is important to first assess their properties and test different reclamation scenarios in the laboratory to select the best scenario for the mine site reclamation.

To evaluate the possible integration of clay materials in the engineered for the mine site reclamation of Gold Ity mine site, physical laboratory models were designed to test three types of covers. These physical models were subjected to several wetting and drying cycles and at the end of each wetting and drying cycle, physical and chemical analyses were carried out on the leachates. Also, continuous measurements of volumetric water content and suction were performed.

This paper presents a description of the used materials, the configuration of the physical models and the instrumentation used to monitor volumetric water content and suction. The results of hydrogeological and hydrochemical behaviour will be presented along with numerical modelling simulations with the objective to evaluate the long term cover performance.

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Co-IMPREGNATED Al-PILLARED CLAY AS CATALYST IN FENTON-LIKE DEGRADATION OF AZO-DYES IN THE PRESENCE OF OXONE

Sanja Marinović, Aleksandra Milutinović-Nikolić, Zorica Mojović, Nataša Jović-Jovičić, Marija Ajduković, Tihana Mudrinić, Predrag Banković*

University of Belgrade - Institute of Chemistry, Technology and Metallurgy, Centre for Catalysis and Chemical Engineering, Njegoševa 12, 11000 Belgrade, Republic of Serbia
*pedja1112@gmail.com ; predragb@nanosys.ihtm.bg.ac.rs

In past decades natural waterbodies have been severely struck by uncontrolled wastewater release. The most harmful water pollutants include different organic compounds, such as synthetic dyes. Catalytic wet peroxide oxidation has been widely investigated as a method for catalytic degradation of organic water pollutants. This is a heterogeneous catalytic process based on the homogeneous Fenton reaction [1,2] that yields hydroxyl radicals capable of disrupting chemical bonds in organic molecules. Sulphate radicals, generated by the conjunction of cobalt with peroxymonosulfate (Oxone), are even more efficient oxidants than hydroxyl radicals. It is due to their higher standard reduction potential comparing with that of hydroxyl radicals [3].

In this work, cobalt impregnated aluminium pillared clay was synthesized, characterized and tested as catalyst in the catalytic wet peroxide oxidation of tartrazine dye in the presence of Oxone reagent. The synthesis consisted of the pillaring of Wyoming bentonite clay (Source Clay Repository of the Clay Minerals Society) with particle sizes of up to 2 μm, followed by the deposition of cobalt oxide species using the incipient wetness impregnation method. Phase compositions, textural and chemical properties of the obtained material were investigated using X-Ray Powder Diffraction, Low Temperature Nitrogen Physisorption, Scanning Electron Microscopy along with Electron Dispersive X-Ray Spectroscopy, as well as Diffuse Reflectance UV-Vis spectroscopy. The optimization of the catalytic degradation of tartrazine dye using the obtained cobalt containing pillared clay was performed regarding heterogeneous catalyst and Oxone concentrations, mixing regime etc. The reaction was monitored with respect to time using UV-Vis spectroscopy. The obtained spectra implied complex mechanism of the reaction that included the degradation of the dye, and the occurrence and subsequent removal of intermediates. Tartrazine degradation using cobalt impregnated aluminium pillared clay and Oxone reagent appears to be efficient since the reaction conditions under which almost complete removal of species detectable by UV-Vis spectroscopy were established.

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DETERMINATION OF ANTIMONY ON CLAY-PVA MODIFIED GLASSY CARBON ELECTRODE

Sanja Marinović, Zorica Mojović, Tihana Mudrinić, Marija Ajduković, Aleksandra Milutnović-Nikolić, Dušan Jovanović, Predrag Banković*

University of Belgrade - Institute of Chemistry, Technology and Metallurgy, Center for Catalysis and Chemical Engineering, Njegoševa 12, 11000 Belgrade, Republic of Serbia
*predragb@nanosys.ihtm.bg.ac.rs; pedja1112@gmail.com

Due to antimony toxicity several methods have been developed for antimony detection including electrochemical [1,2]. In this paper the use of clay-PVA modified electrodes for determination of antimony was studied. Clay from Wyoming deposit was Na-enriched (Na-W) and used for synthesis of clay-poly(vinyl alcohol) composites. Two different poly(vinyl alcohol)-PVA to Na-W ratios were used for composite preparation. The composites were synthesized with 10 wt% and 20 wt% of PVA. The composites were characterized by X-Ray Powder Diffraction and Scanning Electron Microscopy. Both Na-W and composites were dispersed in Nafion® solution prior to depositing on the surface of the glassy carbon electrode (GCE) in order to obtain uniform film [3]. Modified electrodes were denoted as GCE-Naf/Na-W, GCE-Naf/NaW-PVA and GCE-Naf/NaW-PVA2 respectively. For comparison purpose the GCE electrode modified only with layer of Nafion was prepared and designated as GCE-Naf. The applicability of the obtained modified GCE for determination of antimony-Sb(III) concentration was studied.

The square wave voltammograms (SWV) were recorded in the potential window of -0.4 to 0.3 V *vs* Ag/AgCl electrode with following parameters: pulse amplitude = 20 mV, scan increment = 5 mV and frequency = 10 Hz. The electrochemical detection of antimony Sb(III) was performed in acidic environment. The experiments were performed in antimony concentration range from 2.5 to 200 mM. The peak at around -100 mV vs. Ag/AgCl was obtained for all electrodes. Although the presence of clay and clay composites on the electrode surface led to widening of width at half of peak, the currents obtained these electrodes were several times higher than the currents obtained for GCE-Naf in the same concentration range. The presence of clay-PVA composites on electrode surface further improved applicability of GCE in Sb(III) detection. The addition of 10 wt% of PVA in clay composite resulted in increase of peak current and linear response of peak current vs. Sb(III) concentration in broader concentration range. Further addition of PVA up to 20% reduced peak current response, although linearity was preserved in the same concentration range. The dependence of peak current at -100 mV on Sb(III) concentration showed linear behavior in the concentration range of 2.5-100 μM for GCE-Naf/NaW electrode with slope of 0.055 μA/μM. The linear behavior for PVA modified clay was obtained in concentration range of 2.5-200 μM with slopes of 0.118 μA/μM and 0.056 μA/μM for GCE-Naf/NaW-PVA and GCE-Naf/NaW-PVA2, respectively.

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A CLASSICAL POLARIZABLE FORCE FIELD FOR THE STRUCTURE AND DYNAMICS OF WATER AND CATIONS IN CLAYS AND ZEOLITES

Virginie Marry (1), Stéphane Tesson (1), W. Louisfrema (1,2), Mathieu Salanne (1), B. Rotenberg (1), A. Boutin (2), Eric Ferrage (3)

(1) Sorbonne Universités, UPMC Univ Paris 06, CNRS, UMR 8234, PHENIX, F-75005 Paris, France, (2) Ecole Normale Supérieure, PSL Research University, UPMC Univ Paris 06, CNRS, Département de Chimie, PASTEUR, 24 rue Lhomond, F-75005 Paris, France, (3) Univ Poitiers, Ecole Natl Super Ingenieurs Poitiers, HydrASA, CNRS, IC2MP, UMR 7285, F-86022 Poitiers, France

The wide use of clay minerals in industrial applications (catalysis, formulation), energy and ecological engineering (oil recovery, ground water remediation, geological barrier for radioactive waste and CO2) is partly due to their remarkable properties of retention at the mineral surface. In environmental engineering, the role of water on clay permeability and retention properties is crucial. Indeed, the water is the vector of the motion of the species present in the medium, hazardous elements for instance.

Molecular simulations allow a detailed picture of the structure, thermodynamics and dynamics of the fluid at its interface with the clay layers [1,2]. Unfortunately, the numerical results do not always reproduce quantitatively the experimental results, which casts, consequently, a doubt on the validity of simulations interpretations [3]. In particular, the polarizability, which is not taken into account can play a significant role especially when an electric field is present at the interface [4], as it is the case with charged clays.

Therefore we developed a polarizable force field (PIM) based on DFT calculations. The structures of two uncharged clays (Pyrophyllite & Talc) and dry and hydrated montmorillonites with different types of counter-ions (Na^+, Cs^+, Ca^{2+} and Sr^{2+}) were simulated and compared with diffraction data. Then, the polarizable force field was used to study the diffusion of cations and water molecules in montmorillonite. The comparison between the results obtained with PIM and the non-polarizable force field CLAYFF show differences and improvements which encouraged us to extend PIM development to other types of clays and porous media like zeolites [5,6].

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ALKALI ACTIVATION OF KAOLINITE, MONTMORILLONITE AND ILLITE FOR GEOPOLYMER-STABILISED SOIL CONSTRUCTION MATERIALS

Alastair Marsh (1)*, Andrew Heath (1), Pascaline Patureau (2), Mark Evernden (1),
Pete Walker (1)

(1) Department of Architecture & Civil Engineering, University of Bath, Bath, BA2 7AY, UK, (2) Department of Chemistry, University of Bath, Bath, BA2 7AY, UK

The alkali activation of clays in soils to produce geopolymers gives us the potential to produce geopolymer-stabilised soil construction materials, which have lower embodied energy and carbon than current conventional materials. The adoption of this technology is limited by the lack of understanding of how the geopolymerisation reaction differs between the different clay mineral types found in soils.

This study demonstrates the differences in behaviour when activating kaolinite, K10 montmorillonite and illite with sodium hydroxide solution. These three clay mineral types are the most common found in soils. To enable comparison between the clays, a novel approach was used: firstly, that the compositions for the activated samples were calculated using consistent Na:Al molar ratios; secondly, that each sample once mixed with the alkaline solution was at its approximate plastic limit. Na:Al molar ratios of 0.25, 0.75 and 1.5 were used, giving a wide range of alkaline solution concentration up to saturation point. Samples were produced by mixing dry clay powder with a calculated quantity and concentration of sodium hydroxide solution, compacting into a mould, and curing at 80 °C for 24 hours.

XRD patterns, SEM images and bulk sample photos will be presented which show significant differences in phase formation and production phenomena between the clays, under identical production conditions. Most significant is that kaolinite forms a crystalline sodalite product phase, whereas the 2:1 clays K10 montmorillonite and illite form an amorphous product phase. This and other differences are likely to have arisen from the clays' different dissolution rates. From the macro- and microstructural evidence presented, it will be argued that the differences in crystalline structure and composition between clays make the widespread production of geopolymer-stabilised soil construction materials more difficult than previous authors have suggested.

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MINERAL CARBONATION OF CERAMIC BUILDING WASTE AT LOW PRESSURE AND ROOM TEMPERATURE. A SIMULATION STUDY FOR A SUPERFICIAL CO_2 STORE

Domingo Martín*, Patricia Aparicio, Emilio Galán

Departamento de Cristalografía, Mineralogía y Química Agrícola, Universidad de Sevilla (Spain)
*dmartin5@us.es

The increase in average global temperatures since the mid-20th century may be ascribed to the increased emission of anthropogenic greenhouse gases [1]. Generally, human activities result in emissions of four long-lived greenhouse gases (GHGs): CO_2, CH_4, NOx and halocarbons, of which CO_2 is the most important anthropogenic GHG, because it has increased around 40% from the preindustrial era as a consequence of the fossil fuel consumption and the change of soil use [2]. So, technological proposals have been conducted for reducing the emissions into the atmosphere by mean of what is known as carbon dioxide capture, transport and storage. Such strategy involves the development of innovative, available and cost-effective carbon capture and storage (CCS) technologies. One of the options of CCS is the mineral carbonation. The results of this process of fixing are the safest long term, but the main obstacle to mineral carbonation is to do it economically in terms of both money and energy cost.

This research explores the possibilities of CO_2 sequestration on ceramic building materials, in order to propose the injection of CO_2 in a quarry filled with construction wastes as reclamation materials. To approach this possibility a reaction chamber at pilot scale has been designed, which simulates the conditions to carry out the carbonation process in a quarry rehabilitated with materials of construction where the sealing rocks are common clays.

The brick-wastes used were rich in wollastonite, diopside, orthoclase and anhydrite. The behaviour of this material with CO_2 was previously tested, showing the formation of calcite and the partial destruction of silicates and anhydrite. The carbonation was proportional to the reaction time and was independent of the particle-size of the waste. The maximum carbonation was obtained for experiments carried out during 30 days, 10 bar of CO_2, 20wt% of relative humidity (RH) and room temperature. The common clay is composed of calcite, illite and quartz with minor smectite and after carbonation the calcite content also increased [3].

Experimental condition in the reaction chamber were: reaction time 5 months, pressure of CO_2 0,5 bar, RH of brick layer 20 wt%. The experiment was followed by XRD, FRX, BET, SEM, TG, optical microscopy, elemental analyzer and Bernard's calcimeter. In addition the soluble ions (Ca, K) were chemically analyzed by TXRF.

With the CO_2 treatment, wollastonite, diopside and anhydrite were partially destroyed, and calcite precipitated as new phase. Also amorphous materials increased significantly. Chemical analysis of the brick layer showed that calcium decreased, and the RH of the brick layer decreases to a 14 wt%.

On the other hand, the common clay in contact with the brick layer increases RH from 8 wt% at the surface to 20 wt% in contact to the brick layer in deep. The CO_2 produced an increment of calcite content (from 55 to 64 wt%) in the marl, particularly close to the upper part of the brick layer. Nevertheless, as there is not a significant variation of specific surface area of the common clay, no physical retention of CO_2 occurred.

These results are hopeful in relation with the possible mineral carbonation of building ceramic waste in a short time at surface conditions, and opens the opportunity to use those wastes for CO_2 trapping in an appropriate system, as a quarry reclamation.

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VALORISATION OF BYPRODUCTS FROM THE CERAMIC INDUSTRY AS RAW MATERIAL FOR LOW ENERGY BELITE CEMENTS

Sergio Martínez-Martínez (1)*, Dolores Eliche-Quesada (1), Luis Pérez-Villarejo (1), Pedro José Sánchez-Soto (2)

(1) Department of Chemical, Environmental, and Materials Engineering. University of Jaen, Campus Las Lagunillas, s/n, 23071 Jaén, Spain, (2) Materials Science Institute of Sevilla (ICMS), Joint Center Spanish National Research Council (CSIC)-University of Sevilla, c/Américo Vespucio, 49, 41092 Sevilla, Spain

The generation of environmental problems associated with the manufacture of cement, the depletion of raw materials, as well as its high energy demand and the increase of the costs associated with it, are leading to the investigation of new cement materials and to the use in their manufacture, as a raw materials, waste and by-products from other industries.

The cement industry requires a lot of energy. Atmospheric emissions occur primarily from the physical and chemical reactions of raw materials and secondarily from the burning of fossil fuels. Thus, the production of 1 Tm of cement entails the emission of approximately 1 Tm of CO_2 depending on the fuel used. Estimations suggest that cement production is responsible for 5-7% of the worldwide CO_2 emission [1]. Due to the great environmental concern and the great importance of CO_2 emissions by greenhouse effect, different possibilities are posed to reduce emissions in this industry.

On the other hand, the structural ceramic industry generates in its manufacturing process a series of pieces that present breakages and defects. If they are brought to a small particle size, they can be used again in the production process. These residues, such as chamotte, can represent a considerable saving in the consumption of raw materials through its incorporation to produce cement clinker.

For the study of the new formulations of cement clinker, a characterization of the raw materials and chamotte was carried out. Specifically a mineralogical analysis was carried out using XRD and the determination of its chemical composition by FRX. The results of the mineralogical analysis (XRD) of the chamotte allow us to establish that it is mainly quartz with presence of iron oxides (hematite) and hercinite. As for the chemical analysis (FRX), we can see that the content of silica identified in the XRD as quartz predominates, almost 9% of iron in the form of hematite and the aluminum and magnesium present are in the form of hercinite.

For the design of clinker formulations, modified Bogue equations and LSF, SM and AM modules were used. In this way four different formulations of cement clinker have been designed, starting from the composition without chamotte (75.85% limestone - 24.15% mix of red, black and yellow clays) and continue with ranges of variation of 2.5, 5, 10% by weight of chamotte. This type of cement, unlike conventional Ordinary Portland Cement (OPC), contains a higher percentage of belite (C2S) and a lower percentage of alite (C3S). In order to reach the desirable percentages of C2S and C3S, the lime saturation factor (LSF) must be between 78% and 83% [2]. The environmental benefits of the belite type cements over OPC can be summarized as follows: energy saving could rise up to 16%, burning temperatures could be reduced by 6-10% and levels of emitted CO_2 and NO_x could fall [1]. By combining the production of belite cements with alternative raw materials as a substitute for limestone or clay, such as chamotte, additional benefits may be obtained.

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OPTICAL PROPERTIES OF LANTHANIDE IONS INCORPORATED IN HIGH-CHARGE SYNTHETIC CLAYS

Rosa Martín-Rodríguez (1)*, Rafael Valiente (2), Fernando Aguado (3), Ana C. Perdigón (1)

(1) QUIPRE Department, University of Cantabria, Santander, 39005, Spain, (2) Applied Physics Department, University of Cantabria, Santander, 39005, Spain, (3) CITIMAC Department, University of Cantabria, Santander, 39005, Spain

Incorporation of lanthanide ions in synthetic clay minerals is a promising approach to combine the efficient sharp-line emission of lanthanides with the structural stability and biocompatibility of clays [1,2]. Here we report luminescence of Eu^{3+}, Tb^{3+} and Er^{3+} ions, homogeneously distributed in the dispersing inorganic-host high-charge micas $Na_n[Mg_6]^{VIII}[Si_{8-n}Al_n]^{IV}O_{20}F_4$. This aluminosilicate host is a synthetic exchanger layered-clay with unique structural properties and high cation exchange capacity. Despite the forbidden nature of the f-f transition involved, well-resolved lanthanide ions luminescence is observed in the micas, and, contrary to previous results, the use of an antenna for light absorption and transfer to the lanthanide is not required. The fluorinated nature and the absence of iron impurities, together with homogeneous dispersion of lanthanide ions provided by Al^{3+}, makes the high-charge mica an attractive inorganic host. Further evidence of homogeneous distribution and isolation of lanthanide cations in the hexagonal cavities of the mica is provided by spectroscopic luminescence and lifetime measurements. Lastly, since micas are a biocompatible nanomaterial, they represent an ideal inorganic host matrix for lanthanide ions, to be explored in biomedical applications such as drug delivery, biosensing, imaging or diagnosis.

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DETERMINATION OF URANIUM AND THORIUM ISOTOPES IN KAOLINITIC CLAYS BY ICP-MS/MS AND A FIRST APPROACH OF ITS GEOLOGICAL INTERPRETATION

José Luis Mas (1), Patricia Aparicio (2), Emilio Galán (2), Domingo Martín (2), Antonio Romero (2), Adolfo Miras (2), Blanca Bauluz (3), Alfonso Yuste (3), Maria Jose Mayayo (3)

(1) Departamento de Física Aplicada I, Universidad de Sevilla (Spain), (2) Departamento de Cristalografía, Mineralogía y Química Agrícola, Universidad de Sevilla (Spain), (3) IUCA-Facultad de Ciencias, Universidad de Zaragoza, Zaragoza (Spain)

To the best of our knowledges, no exploration has been made on the potential of uranium and thorium isotope ratios to provide further insight on the evolution of kaolinites since their formation. To this aim it should be consider a null hypothesis to verify or reject, which is that all the nuclides from the same radioactive series ($^{238}U/^{234}U/^{230}Th$) are in secular equilibrium, while the $^{238}U/^{232}Th$ isotope ratio mimics that of the local continental crust. Therefore the main aim of this work were: a) establishing the chemical fractionation of uranium and thorium throughout the general method proposed in [1] as adapted for measurement using tandem quadrupole ICP-MS/MS, b) testing the possibilities of the analyses of uranium and thorium isotopes in kaolin samples, c) to apply those results to the evolution of kaolinitic clays after their formation. The studied kaolin materials were sampled in six different outcrops located in the easternmost part of the Iberian Range (NE Spain), the so-called Maestrazgo Basin. This basin was originated during one of the most active stages of the Late Jurassic-Early Cretaceous rifting process. Sample F2Y comes from the Lower Cretaceous (Barremian) Fuentespalda karst bauxite deposit (Teruel), FR9 is a lateritic claystone from the Barremian Artoles Fm. Two samples belong to the Barremian Camarillas Fm: MV36AC, a red claystone, and MV36AR, a medium to coarse white creamy sandstone. Finally, samples AR6 and EST2 are dark grey to black claystones from the Albian Escucha Fm near Ariño and Estercuel (Teruel), respectively. The radiochemical method proposed was applied to certified reference samples in order test uranium and thorium fractionation throughout the procedure. To do that, in several of the steps a small aliquot of the resulting solution were removed, and then were subsequently diluted into 1% HNO3 and measured by ICP-MS/MS for ^{238}U and ^{232}Th concentrations. Fractionations and chemical yields can be calculated by comparing the obtained element concentration with the certified value. The mineralogical analysis shows that F2Y is composed of kaolinite, hematites, gibbsite and boehmite, with traces of anatase and rutile; FR9<2 μm is composed mainly of kaolin minerals (kaolinite and halloysite) with hematites as minor and trace of anatase and chlorite; WMV36AR<2 μm is composed of kaolinite, with minor amount of illite and calcite and traces of quartz and feldspar; WMV36AC <2 μm is mainly composed of kaolin minerals (kaolinite and halloysite), illite and traces of anatase, quartz and feldspar; and those of the Escucha Fm are containing organic matter and EST2 is composed of kaolin minerals (kaolinite and halloysite) with minor vermiculite, whereas AR6 contains kaolinite, pyrite, minor quartz and illite, and traces of calcite, gypsum and goethite. Concerning the isotopes results all the kaolinitic clays, with the exception of sample WMV36AR<2 μm, are showing a clear radioactive disequilibrium. Samples WMV36AC <2 μm, AR6 and FR9<2 μm are close to the line of radiactive equilibrium, MV36AC above and the other two below the line. As values above the secular equilibrium condition could be associated to relatively recent selective removal of ^{234}U as a consequence of weathering, this process could occurred in the case of the bauxite (F2Y). On the other hand, the values below the secular equilibrium could be showing the influence of deposition via adsorption or precipitation (e.g., anoxic environment) of water-carried uranium, which is usually enriched in the lighter isotope as a consequence of the selective leaching. This is situation seems to be very clear in the case of materials from the Escucha Fm, and particularly for EST2.

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THE APPLICATION OF ORGANOMINERAL SORBENTS TO DECREASE THE MIGRATION OF ^{137}Cs AND ^{90}Sr IN RADIOACTIVELY CONTAMINATED SOILS OF BELARUS

Leanid Maskalchuk (1)*, Anatoly Baklay (2)

(1) International Sakharov Environmental Institute of Belarusian State University, Minsk, 23/1, Dolgobrodskaya str., 220070, Belarus, (2) Joint Institute for Power and Nuclear Research - Sosny, NAS of Belarus, Minsk, P.O. Box 119, 220109, Belarus
*maskal@bsu.by; leonmosk@tut.by

The problem of agricultural soils rehabilitation in Belarus, Russia and Ukraine, contaminated in the result of the Chernobyl NPP accident, is well-known and extremely important nowadays. Considering the scale of radioactive contamination of the territory of Belarus and the half-life of the most abundant radionuclides, it is an extremely large amount of cheap and effective organic and/or mineral sorbents that are required to minimize biological uptake of radionuclides from the top soil layer.

One of the perspective solutions of the radioactively contaminated soils rehabilitation problems is theuse of natural raw materials (sapropels) and chemical industry wastes (clay-salt slimes) as radionuclides sorbents. Sapropels are the substances of biogenic origin, which are formed by animal and vegetable remains at the bottom of freshwater lakes where thelack of oxygen is observed. As for determination of sapropels types, the main feature is the content of organic matter. Besides the colloidal structure of sapropels, the big specific surface and considerable cation exchange capacity allow to use sapropels as an effective sorbent of radionuclides. It is indicated that organic sapropels, which are characterized by high values of cation exchange capacity (CEC), are more effective for the sorption of radiostrontium. While the silica, which have the highest Radiocaesium Interception Potential (RIP) values, will be the most effective for the sorption of radiocaesium.

Clay-salt slimes (CSS) are the large-tonnage waste products resulting from the sylvinite ore recycling at JSC “Belaruskali” and represent a suspension of clay particles in a saturated salt solution. The results of the preliminary studies of the physicochemical properties and characteristics of CSS indicate that CSS are clay minerals. CSS main components are calcite, dolomite, montmorillonite, illite, and quartz. The property of CSS is the constancy of morphological features of the original samples; this is a determining factor ensuring a high sorption rate of radionuclides, especially radiocaesium. The CSS fixing ability of ^{137}Cs from multicomponent solutions is about 75-84 wt% of its initial content. The Radiocaesium Interception Potential RIP(K) was studied by the J. Wauters method and is 6631 ± 216 mmol/kg.

A methodological approach based on the quantitative data on the exchange forms of ^{137}Cs and ^{90}Sr, CEC and the exchange potential binding RIP(K) of radiocesium was developed. This approuch allows to carry out the selection of the sorbents of radionuclides with optimal physicochemical and sorption properties. We obtained the analytical expression for evaluating the effectiveness of adsorbents for the reduction of ^{137}Cs migration into the plant from the soil, which is the combination of RIP(K) values of soil, sorbent and dose of sorbent inserted into the soil. It has been estimated that for the reduction of ^{137}Csmigration from soil to plant in 2 times, the RIP(K) ratio of the sorbent and the soil must be not less than 25 (subject to economic feasibility of the insertion of sorbent into the soils in a dose of 1-4 wt. %). The developed method allows to evaluate the efficience of sorbents application for the rehabilitation of soddy-podzolic soils of Belarus contaminated with ^{137}Cs and ^{90}Sr.

On the basis of the developed methodological approach organomineral sorbents (OMS) of radionuclides were obtained on the basis of natural organic material (sapropel) and chemical industry wastes (clay-salt slimes); the effectiveness of their application for reduction of ^{137}Cs and ^{90}Sr migration in a soddy-podzolic sandy and sandy loam soils of Belaruswas showed as well. The results of greenhouse study of the OMSeffect on reducing ^{137}Cs and ^{90}Sr migration in the soil - plant (seedlings rye) shows that the insertion of OMS to the soddy-podzolic sandy loam soil in the amount of 1-4% by weight reduces ^{137}Cs and ^{90}Sr migration in 2-4 times.

The developed mathematical models of ^{137}Cs and ^{90}Sr migration can be used for predicting the long-term radionuclides migration in the soil - soil solution -plant system in case of anuclear and/or radiation accident.

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A COMPARATIVE STUDY OF GLACIOVOLCANIC PALAGONITIZATION OF THOLEIITIC AND ALKALINE SIDEROMELANE AT HELGAFELL, ICELAND AND WELLS GRAY-CLEARWATER VOLCANIC FIELD, BC CANADA

Erica Massey (1)*, John Greenough (1), Benjamin Edwards (2)

(1) University of British Columbia Okanagan, Dept. of Earth and Environmental Science, Kelowna, BC Canada V1V 1V7,
(2) Dickinson College, Dept. of Geology, Carlisle, PA USA 17013
*erica.massey@shaw.ca

Pleistocene glaciovolcanic eruptions occurred frequently beneath continental-scale ice sheets that produced vitric, fragmental volcanic deposits in Helgafell, Iceland (tholeiitic basalt) and Wells Gray, BC, Canada (alkali olivine basalt). The deposits are highly susceptible to hydrothermal alteration that transforms sideromelane (basaltic volcanic glass) into palagonite (early amorphous material) and secondary minerals (e.g. zeolites, clays and sulfides). As an analogue material for Mars, palagonite and the process of palagonitization resulting from glaciovolcanism is an important paleoclimate proxy [1]. Compositional controls, mass transfer and geochemical-textural relationships are investigated by optical microscopy, Electron Microprobe Analysis, Laser Ablation Inductively Coupled Plasma Mass Spectrometry, and geochemical modelling. Helgafell's thinner (6-10 microns) palagonite rims demarcate highly vesicular (30.2%) sideromelane that has more gel-material (18.9%) and secondary minerals (1.4%) than Wells Gray's microlite-rich (12.3%) sideromelane with thicker palagonite rims (10-15 microns). The thicknesses of palagonite rims in one locality are similar whether the sideromelane is unaltered or completely altered and at least two important geochemical-textural relationships are formed during palagonitization (e.g. spherical textures and geochemical-textural trends across palagonite rims).

Multi-dimensional scaling confirms that sideromelane composition, reflecting igneous processes, strongly controls the chemistry of palagonite. Microprobe traverses identified eight prominent geochemical trends across the glass-palagonite interface and palagonite rim, which do not appear to be controlled by sideromelane composition. Several element concentrations decrease in palagonite, including Si (by ~3-10%), Al, Ca and Na, while Ti, Fe and Mg concentrations increase. Locally, the palagonite has an inner Ti-rich zone. The gradual increase in Mg across the palagonite rim may be indicative of changes in solubility and pH.

Mass balance calculations from Gresens' isocons [2] demonstrate that the calculated range of percent mass transfer is significantly affected by assumptions about the concentrations of water inferred to be present in palagonite. The calculations are also most consistent with a two-stage process of mass transfer.

Keywords: palagonite, sideromelane, glaciovolcanism, palagonitization, smectite, basaltic glass.

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ADVANCES IN PORE NETWORK CHARACTERISATION OF NON-CONVENTIONAL HYDROCARBONS RESERVOIRS: CORRELATION OF CORE SCALE POROSITY MAPPING BY AUTORADIOGRAPHY AND MINERAL MAPPING BY BSE SEM MOSAICS

N. Matskova (1)*, D. Prêt (1), S. Gaboreau (2), P. Cosenza (1), C. Fialips (3)

(1) IC2MP/HydrASA, Université de Poitiers, CNRS UMR 7285, Bât B27-TSA 51106, 4, rue Michel Brunet, 86073 Poitiers Cedex 9, France; (2) BRGM - Team D3E/SVP, 3, avenue Claude-Guillemin, BP 36009, 45060 Orléans Cedex 2, France; (3) TOTAL E&P, CSTJF -Avenue Larribau, 64018 Pau Cedex, France

Non-conventional shale reservoir rocks are characterized by multi-scaled pore systems (from micro- to nanometer) and variable spatial distribution of organic matter (OM) and minerals (porous clay matrix and nearly non-porous grains, such as feldspars, carbonates and quartz). The OM and clay matrix bear most of the pore network of the reservoir, controlling the storage areas and pathways forhydrocarbons migration. Porosity evolution within such a complex heterogeneous reservoir, from oil to gas window, is strongly dependent on the relative arrangement and content of non-porous grains and porous matter (clay, OM). Therefore, only a combined multi-technique approach could provide relevantquantitative information on the pore network organisation. Core samples (~7x7 cm) from three different exploration wells of Vaca Muerta formation, in zones with various hydrocarbons types (condensate gas, dry gas and oil) were investigated to characterize the specific porosity of the clay matrix and its spatial distribution.

Autoradiography was performed on large core scale surfaces (~25 cm²) of samples impregnated with a ^{14}C-MMA resin to map and quantify the porosity. An automatic polishing procedure was developed for these large impregnated areas allowing production of porosity maps with limited artefacts and a resolution of ~10 µm over decimetric spatial distribution of the total porosity. Such a quantitative porosity mapping accounts for all the pores regardless of their size, including the interlayer space of swelling clay minerals [1]. Mosaics of SEM Back Scattered Electron images (resolution ~0.5 µm) were acquired for smaller areas of interest, on the same polished surfaces to allow a correlation with the porosity maps at a millimetric-micrometric scale. An advanced image analysis procedure was applied on BSE mosaicsto identify the spatial distribution of the different minerals in order to produce mineral maps controlling the porosity [2]. The superimposition of the mineral and porosity maps with careful correlation of various data sets, revealed the relationships between local porosity values and mineral components, as well as the specific porosity of the clay matrix.

To compare with previous studies, more classical bulk methods for porosity evaluation (nitrogen adsorption with a kinetic control of adsorption equilibrium, mercury intrusion and nuclear magnetic resonance) were applied on sub-samples blocks, previously localized by X-ray µTomography from the same core samples. These methods were performed to allow a direct comparison of the data on pore size distribution of clay matrix with the quantitative porosity maps.

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SYNTHESIS AND SWELLING PROPERTY OF CO-POLY(NIPAAM-SA)-SAPONITE NANOCOMPOSITE GELS

Daichi Matsui*, Kazusa Takahashi, Shin'ichi Ishimaru

Division of Materials Science and Engineering, Graduate School of Engineering, Tokyo Denki University, 5 Senju-Asahicho, Adachi-ku, Tokyo 120-8551, Japan
ishimaru@cck.dendai.ac.jp

In recent years, the desertification is becoming a serious problem. Main reasons for this process are decrease in rainfall due to climate change, over-exploitation of timber resources, influence of grazing and deforestation of agricultural land. Desertification has caused various problems such as food shortage, increase in environmental refugees and decrease in biodiversity. Temperature responsive superabsorbent polymers, such as poly(*N*-isopropylacrylamide) (abbreviated to PNIPAAm), are expected to be a solution for the problem of desertification.

PNIPAAm is commonly utilized in the form of hydrogels that are obtained by copolymerization of NIPAAm with a chemical crosslinker such as *N,N'*-methylenebisacrylamide. The PNIPAAm-hydrogel is known to cause a volume phase transition at $T_c \approx 32$ °C. The polymer absorbs water and forms hydrogel below T_c but releases water and shrinks above the temperature. It is considered to be possible to achieve humidity and temperature control by utilising such temperature sensitive property of PNIPAAm. However, the organic crosslinking hydrogels have some disadvantages, such as low mechanical strength and low optical transparency. Haraguchi showed that the disadvantages of the PNIPAAm hydrogel can be improved by polymerization of NIPAAm monomer by adding laponite without any other chemical cross-linker [1]. This is considered to be caused by the "soft" cross-linking formed by hydrogen bond between amide groups in PNIPAAm and clay surface. Previously, we reported that the amount of water absorbed of clay-PNIPAAm nanocomposites varies with the kind of clay minerals and its amount but the volume phase transition temperature T_c was little affected by them [2].

On the other hand, it is known that the T_c of the PNIPAAm hydrogel can be controlled by introducing a small amount of functional groups which have different polarity from NIPAAm. For example, higher T_c is achieved by copolymerization of NIPAAm with an ionic monomer, sodium acrylate (abbreviated to SA). In addition, the amount and rate of water absorption of the hydrogel are also progressed by introducing SA [3].

In this research, we tried to synthesize new nanocomposite gels consisting of a clay mineral and the co-poly(NIPAAm-SA) polymer to achieve enhancement of the water absorbability. In addition, we investigated the volume phase transition temperature T_c and swelling characteristics at various temperatures of synthesized gels. The samples were synthesized by photopolymerization of the aqueous mixture containing a saponite-type synthetic clay (a reference clay of the Clay Science Society of Japan, JCSS-3501), NIPAAm and SA with different SA contents in the range of the relative proportions of saponite: NIPAAm: SA=1: 1: 0 to 1: 1: 0.15 on weight basis. Homogeneous hydrogels were obtained for the each relative proportion. The transition temperature was determined from microscopic observation of the hydrogel-size with varying temperature. The rate and equilibrium amount of water absorption were determined by the time dependences of the weight of hydrogels immersing in water at constant temperature.

The phase transition was observed around 32, 42, 50 and 53 °C for the gels with the relative proportion of SA = 0, 0.005, 0.01 and 0.05, respectively, and it was not observed for SA = 0.10 below 96 °C, implying that T_c rises monotonically with increase of SA amounts. On the other hand, the swelling ratio W/W_0 of the gels (where W_0 and W are weights of dried nanocomposite and equilibrium swelled gel, respectively) was mostly fixed and was 11±3 below SA = 0.01 but it rapidly increased to 20 and 27 for SA proportions of 0.05 and 0.10, respectively. Each nanocomposite showed pseudo-first order absorption below T_c, but complex swelling behavior was observed above T_c in the hydrogels with high SA contents.

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COMPARISON OF MICROSTRUCTURAL FEATURES OF COMPACTED, WATER SATURATED: MX-80 BENTONITE, SODIUM AND CALCIUM MONTMORILLONITES

Michał Matusewicz*, Markus Olin

VTT Technical Research Centre of Finland Ltd., Espoo, Finland

The repositories of spent nuclear fuel planned in several countries, including Finland, pose significant scientific challenges due to their extremely long lifespan. One of the materials proposed to be used in the Finnish repository is the MX-80 bentonite in compacted, water saturated form. As it is expected that the MX-80 in the repository will undergo the cation exchange process following the composition of the groundwater, the border cases of pure calcium and sodium montmorillonites were included in this study. The clays were studied at different dry densities between 0.7-1.6 g/cm^3.

The structure of the water saturated, compacted clays was investigated using small angle x-ray scattering (SAXS), nuclear magnetic resonance (NMR), transmission electron microscope (TEM). Additionally, atomic force microscope (AFM) was used to obtain size distribution of the montmorillonite platelets. The combination of information obtained from different methods, measuring platelet arrangement (SAXS, TEM), water properties (NMR) and platelet size (AFM), allows a good insight into the structure of the material.

The results clearly show the difference in the structure of compacted MX-80 and pure montmorillonites caused by the purification process, but also between montmorillonites with different exchangeable cations. This is important in case of the repository where sodium bentonite is used and is expected to change its compensation cation composition during the repository lifetime.

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TEXTURAL CHARACTERIZATION AND INTERPRETATION OF Fe-RICH MICROSPHERES IN HOLOCENE CONTINENTAL SEDIMENTS

María José Mayayo*, Alfonso Yuste, Arantxa Luzón, Arsenio Muñoz, Antonio Pérez, María Asunción Soriano

IUCA - Departamento de Ciencias de la Tierra, Universidad de Zaragoza, Spain

The aim of this work is to characterize Fe-rich microspheres occurring in Holocene sediments from the Martín River (NE Spain). Recent research has focused on Fe-microspheres, similar to those described in this work, in relation to their probable microbially-mediated origin and the search of life in other planets, such as Mars (e.g. [1]).

A sedimentary section located in the medium reaches of the Martín River (Teruel, Spain) has been studied. It consists of alluvial and fluviolacustrine Holocene materials. The sedimentary system was fed by surficial waters and by highly mineralized (calcium-magnesium sulphate-bicarbonate) groundwater from the Baños de Ariño spring. In the section (17 m-thick) five lithofacies have been distinguished [2]: gravel, sand, mudstone, marl and tufa. Fe-rich microspheres have been identified in sand and marl lithofacies, related to paleofloods. Sands are orange and were deposited by unidirectional currents referred to the Martín River course. Marls are grey and contain abundant coal fragments, vegetal remains and root traces; they were deposited by settling in the floodplain. X Ray Diffraction (XRD) studies have shown that in both sands and marls calcite is the main phase, coupled by quartz and phyllosilicates, the latter more abundant in marls. In the fine fractions, illite and kaolinite have been identified as the main clay minerals. Some samples also showed the presence of lepidocrocite.

The size of the microspheres, as observed by Field Emission Scanning Electron Microscopy (FESEM), varies from 4 to 30 µ, with an average value of 12.4 µ. Energy Dispersive Spectroscopy revealed that the microspheres are composed only by O and Fe; no S has been detected. Following the observable surficial structure of these microspheres, three different patterns have been distinguished: i) spherical aggregates composed by skeletal octahedral crystals of approximately 1 µm, probably by replacement and dissolution of former pyrite octahedra; ii) spherical aggregates made up of subhedral equidimensional crystals with morphologies close to polyhedra and sizes <0.5 µm, composed by planar anhedral nanoparticles arranged face to face; iii) spherical aggregates showing an internal structure composed by subspherical morphologies 2-2.5 µm in diameter and covered by acicular or lens-shaped nanocrystals that in some zones appear to have radial distribution. In addition, organic structures have been observed in close relationship with the microspheres. These include random clusters of ring-shaped structures frequently covering the Fe-rich microspheres, and chains of subspherical elements. In some cases, the microspheres are nearly covered by a coating of small ellipsoidal capsules (<1 µm), most of them collapsed or perforated. Furthermore, a C-rich soft pliable tissue coating the Fe-rich microspheres surface and fitting the crystals has been observed. These structures are comparable to existing bacterial colonies and extracellular polymeric substances produced by bacteria, including *Leptospirillum ferrooxidans*, which has high capacity to break down the pyrite lattice and oxidize Fe^{2+} to Fe^{3+}.

In view of the above data, we interprete the observed Fe-rich microspheres as framboids and that they were pyrite framboids in origin. Taking into account the presence of coal and vegetable matter in the samples and their close relationship to bacterial signatures, we consider very probable that the transformation of former pyrite framboids into Fe oxides and oxyhidroxides, and even their primary formation, took place through microbial mediation, as [3] and [4] among others have proposed for similar situations.

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CLAY MINERALS IN GEOTHERMAL SYSTEMS: THE CASE STUDY FROM THE CERRO PABELLON PROJECT (APACHETA, CHILE)

Santiago N. Maza, Estefania Camus*, Camila Lizana, Benigno Godoy, Bernardita Alvear Aliaga, Marcela Pizarro, Diego Morata

Adean Geothermal Center of Excellence (CEGA) and Department of Geology, FCFM, Universidad de Chile, Plaza Ercilla 803, Santiago, Chile
santiagomaz@gmail.com

Clay minerals represent one of the most abundant minerals group in geothermal systems, widely used as indicators of physic-chemical conditions, isotope tracing, age and evolution of the heat-flow fields. The central volcanic Andes zone (CVAZ) constitutes an active volcanic environment, with structural settings propitious for the formation of geothermal systems, with heat-flow density values between 50-180 MW/m^2 in the active magmatic arc and the Altiplano [1]. The Cerro Pabellon Project, located to 100 km of Calama in the CVAZ, whose production activities beginning is planned for March 2017, constitutes the first geothermal power plant of South America, with a production of 50 MW and an expected increment to 100 MW. The volcanic belt in this region is characterized by eruptive centres with polygenetic volcanoes of Quaternary age [2], where stratovolcanoes of (Apachecha-Aguilucho) a rhyolitic dome (Cerro Pabellón) could be distinguished. This region is framed within a graben structure with NW-SE orientation and an extension of ~100 km^2. In the central graben region, and linked with the rhyolitic dome, hydrothermal manifestation was not recognized. In the NW and SE sectors and associated with fractures oblique to the graben orientation, surface hydrothermal alteration with a small zone of fumarolic steam near Apacheta volcano crater was identified. In this abstract we present preliminary characterization studies of the hydrothermal alteration minerals. XRD analyses of whole rock powder and clay fraction from the present-day fumarolic zone, surface alteration zones and altered rock core were carried out. The fumarolic zone (~80 °C), contain opal, native sulphur, ferrihydrite accompanied of cristobalite and pyrite, while in the clay phases kaolinite-dickite mixture, smectite and vermiculite were recognized. The surface alteration zone, with whitish-yellowish coloration, contains quartz and alunite as main minerals with smaller proportion of relict plagioclase, while in the clay phases kaolinite-dickite mixture dominates. The surface alteration zone, the greyish coloration, quartz, heulandite and calcite with relict plagioclase were identified, while in the clay phases vermiculite and smectite dominates. The rock core, near the rhyolitic dome, contains plagioclase and pyroxene as main minerals, while in the altered rock quartz, calcite, heulandite and montmorillonite predominates. In the fumarolic zone, the kaolinite-dickite-sulphur association reflects a heated vapors environment, including acid sulphide-enriched vapors. The kaolinite-dickite-alunite mineral assemblage is likely related with old effusive center of fluid acidic-sulphate composition and oxidizing conditions, indicating an estimated temperature ~120 °C. The heulandite-calcite-smectite association could be associated with fluids of neutral-alkaline composition, with estimated temperature ~90 °C. The mineral assemblage of the altered rock core reflects similar fluid composition, with the montmorillonite representing the cap rock composition and show the development of secondary permeability. The fault associated with the graben structure represents an important regional constrain in the formations geothermal resource in ZVAC. The cap rock constitutes a high efficiency lithological control, favoring the fluid migration in a lateral outflow system within the Cerro Pabellon Proyect and without surface hidrothermal manifestation in a blind thermal system. The faults, oblique to the graben structures, exert a secondary control favoring fluid migration as an upflow system, which produce hydrothermal manifestations and fumaroles. We are grateful to the “Fondap-Conicyt project 15090013”, which support our research projects.

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LAYERED MINERALS AS SUPPORTS FOR MAGNETITE NANOPARTICLES AND THEIR USE FOR AQUEOUS As(V) REMOVAL

Paulina Maziarz*, Jakub Matusik

(1) Department of Mineralogy, Petrography and Geochemistry, Faculty Of Geology, Geophysics and Environmental Protection, AGH University of Science and Technology, al. Mickiewicza 30, Krakow, 30 059, Poland
*pmaziarz@agh.edu.pl

Adsorption plays an important role in water purification methods, both in the field of industry and environmental protection. Since adsorption processes often proceed in aqueous solutions, the methods of solid-liquid separation are important and thus constantly developed. Recently, a great attention is focused on synthesis and application of adsorbents possessing magnetic properties which facilitate their separation from wastewater. In present study Fe_3O_4 nanoparticles were synthesized and simultaneously deposited on halloysite (H) and synthetic layered double hydroxide (LDH) surface in order to prepare magnetic adsorbents. The resulting materials were characterized using X-Ray Diffraction (XRD) and Fourier Transform Infrared Spectroscopy (FTIR). Their potential to remove As(V) from aqueous solutions was investigated in detail.

The preparation of synthetic Mg^{2+}/Al^{3+} LDH was in accordance with previously reported procedures [1,2]. The Fe_3O_4 nanoparticles were synthesized on the H or LDH surface via co-precipitation method [3]. The mass ratio of Fe_3O_4 to H or LDH phase was 10% (HFe10, LFe10) and 25% (HFe25, LFe25). The adsorption of As(V) was conducted for initial concentrations (C_{in}) set from 0.1 to 25.0 mmol/L and pH equal to 5.0± 0.2. The solid/solution ratio was 20 g/L. The Langmuir and Freundlich models were employed to quantitatively describe the As(V) uptake.

The XRD analysis of LDH revealed characteristic d values of 7.70 Å, 3.82 Å, 2.60 Å, 1.53 Å and 1.49 Å, which confirmed the successful synthesis. The reflections corresponding to magnetite were found in the XRD patterns of resulting magnetic composites. This indicated that iron nanoparticles were loaded on LDH and H surface. The FTIR bands at 1360 cm^{-1} allowed to identify CO_3 anions in interlayer space of LDH. After coating with Fe_3O_4 the additional bands at 1110 cm^{-1} and 620 cm^{-1} were observed, which indicated the presence of SO_4 anions. Their presence in the interlayer space, was related to iron(II) sulfate reagent used in Fe_3O_4 synthesis. XRD revealed that the presence of SO_4 anions caused an increase of LDH basal spacing to 8.80 Å.

The LDH and LFe10 samples exhibited maximum adsorption capacity at C_{in} of 25 mmol As/L equal to 1294 and 1062 mmol As/kg, respectively. The lowest adsorption capacity was observed for the LFe25. However the adsorption value of 907 mmol As/kg is still very high and promissing. The adsorption experiments on halloysite-based adsorbents revealed, that coating with Fe_3O_4 positively influenced their adsorption properties toward As(V). The results showed, that the HFe10 composite exhibited the highest adsorption ability with a maximum adsorption capacity of 151 mmol As/kg. This adsorption value was about 2.5 times higher than that of H sample, which was found to be equal to 58 mmol As/kg. For the HFe25 sample, the adsorption capacity of 121 mmol As/kg was determined. These results indicated the formation of additional active sites which promoted the sorption affinity of As(V) in comparison to the H sample. For both H and LDH based adsorbents the equilibrium pH decreased with increasing anion concentration, which can result from the anions deprotonation during their uptake. The experimental adsorption data followed the Langmuir isotherm model, with correlation coefficient $R^2>0.99$. The exception was for LDH where the experimental data were fitted to Freundlich model with $R^2=0.90$. The As(V) removal by LDH was via ion-exchange mechanism while in the case of H sample complexation at the particles edge was dominant.

The results proved that the effect of Fe_3O_4 on adsorption processes is highly dependent on the type of mineral supporting phase. The explanation of this behavior requires further studies. However, the study results indicated that the synthesis of Fe_3O_4 on layered minerals surface, allowed not only to obtain magnetically separable adsorbents but also can positively influence their potential of As(V) removal.

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DEVELOPMENT OF GEOPOLYMER-ZEOLITE COMPOSITES

Valentina Medri (1)*, Elettra Papa (1), Elena Landi (1), Mauro Mazzocchi (1), Smail Amari (1,2), Jérémie Manaud (1,3), Patricia Benito (1,4), Angelo Vaccari (1,4)

(1) ISTEC-CNR, Institute of Science and Technology for Ceramics, 48018 Faenza, Ravenna, Italy, (2) Chimie ParisTech, École Nationale Supérieure de Chimie de Paris, 75005 Paris, France, (3) Faculté des Sciences & Techniques de Limoges, University of Limoges, 87000 Limoges, France, (4) "Toso Montanari" Department of Industrial Chemistry, University of Bologna, 40100 Bologna, Italy

Geopolymer-zeolite composites were produced mixing different geopolymer matrices with a synthetic commercial zeolite.

Metakaolin was selected as the main precursor for the geopolymer matrix, because it is the ideal material for the production of geopolymers due to the high reactivity and purity, compared to other starting raw materials as fly ashes and natural clays.

A potassium or sodium silicate activating solution was used for the geopolymerization process and the commercial zeolite Na13X was used as filler.

The microstructure of a metakaolin-based geopolymer consists of nano-particulates separated by micro- and mesopores [1,2]. Moreover, geopolymers can be regarded as the amorphous counterpart or precursor of crystalline zeolites. Indeed, the final geopolymer structure consists of an amorphous network of SiO_4 and AlO_4^- tetrahedral units connected by oxygens and charge-balanced by hydrated alkali cations, while zeolites are crystalline hydrated aluminosilicates with 3-dimensional structures.

The substitution of Al^{3+} for Si^{4+} results in negatively charged aluminosilicate lattice for both the materials, that needs to be balanced by extra-framework cations (generally Na^+, K^+ and Ca^{2+}), resulting movable and exchangeable by other metal ions.

Since zeolite is partially reactive in alkaline medium [3], the production process and the synthesis parameters were investigated to limit the reaction of the zeolite.

In fact, the main goal of the study was to combine the peculiar and defined microporosity of zeolite with the meso- and macroporosity of the geopolymer matrix, together with the possibility to consolidate the zeolite powder. Actually, the requirement of supporting or shaping powdery zeolites is important for industrial applications and often the manufacturing and assembling of supports and zeolites add complexity and cost to the final product.

Because of the high accessibility of pores, these porous composites with 3-dimensionally interconnected and distributed open pores, may be used as catalyst, filters and sorbents, furthermore, zeolites, and in particular zeolite X are largely used for the CO_2 gas adsorption [4].

The selected composites were deeply characterized in term of microstructure, mineralogical composition, porosity and specific surface area, together with the ability to adsorb CO_2, in order to highlight one of the possible functional properties of the new material.

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CLAYS FROM SAGADA, MOUNTAIN PROVINCE, PHILLIPINES: RAW MATERIAL FOR CERAMIC APPLICATION

Aran Khristian A. Mendoza*, Carlo A. Arcilla

Earth Materials Science Laboratory, National Institute of Geological Sciences, University of the Philippines, Diliman, Quezon City, Philippines, 1101
*arankhristian.mendoza@gmail.com

Ceramics are more commonly used as pottery products in the Philippines. The ceramic industry might be greatly improved when sufficient feasibility studies about potential usage of clay materials, both local and global will be conducted. For this study, clay materials collected from Sagada, Mountain Province were examined to characterize and determine its potential application in the production of ceramics in the Philippines. Three stages of analyses on the clay materials were done: Mineralogically, chemically, and physically. Mineralogical characterization was done using X-ray diffraction, Fourier transform infrared spectroscopy, and thermal evolution of clay minerals when fired up to 1000 °C. Chemical characterization was done using X-ray fluorescence spectrometry while physical characterization was done using the plasticity analysis. The sample chemically shows high contents of SiO_2, Al_2O_3, and Fe_2O_3. Chemical composition revealed possible concentration of quartz and smectite in the samples, verified using the X-ray diffraction. X-ray diffraction showed peaks of smectite (15.55 Å) and quartz (3.35 Å, 4.25 Å, and 1.18 Å). To determine if clay materials have characteristics of good ceramic raw, these clays were fired from 900 °C to 1150 °C. Once fired, the fired product was subjected to different analysis to determine its linear shrinkage, water absorption, and bonding strength. The result of this study may contribute to the development of ceramics for not only the pottery industry but for the benefit of the whole business industry. The study has implications on the development of the local ceramic industry as it distinguishes some potential source location of clay materials.

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MOBILITY OF RARE-EARTH ELEMENTS DURING WEATHERING OF ALKALINE FELSIC VOLCANIC ROCKS, GRAN CANARIA

Inmaculada Menéndez (1)*, Esperança Tauler (2), José Mangas (1), Luis Á. Quevedo-González (1), Jorge Méndez-Ramos (3)

(1) Instituto de Oceanografía y Cambio Global (IOCAG), Universidad de Las Palmas de Gran Canaria, Spain, (2) Departament de Mineralogia, Petrologia i Geologia Aplicada, Universitat de Barcelona, Spain, (3) Departamento de Física, Universidad de La Laguna, 38206 La Laguna, Tenerife, Spain
*inmaculada.menendez@ulpgc.es

Gran Canaria Island, a hotspot-derived intraplate oceanic island, holds a variety of alkaline felsic volcanic rocks (e.g. phonolites, trachytes and rhyolites) consisting of lava and pyroclastic flows, dykes and domes, subsequently linked to the development of weathering paleosoils profiles, comprising both preserved B and C (saprolite) horizons. These felsic bedrocks are associated with magmatic Miocene activity of the Tejeda caldera (14.1 - 7.3 Ma) and the Roque Nublo Pliocene stratovolcano (5.5 - 2.9 Ma). Three weathering profiles were collected and analysed for geochemistry (i.e.: FUS-ICP, FUS-MS, TD-ICP, INAA) and mineralogy (petrographic microscopy; XRD; SEM-EDX) in order to assess both the concentration and mobility of rare-earth elements (REE), aiming to find in these weathering profiles a variety of secondary minerals, mainly dominated by REE-bearing species [1]. REE underpin a broad range of emerging technologies in green energy as efficiency enhancement of solar cells and artificial photosynthesis H_2 generation [2], in line with EU Raw Materials Initiative in H2020.

In regards to resulting datasets, the concentration averages of REE in Miocene alkaline bedrocks varied for trachytes (449 ppm), rhyolites (588 ppm) and phonolites (828 ppm). REE are enriched in saprolites of trachytes (480 ppm) and rhyolites (1584 ppm), but depleted in phonolites (388 ppm). Light REE values are an order of magnitude greater than Heavy REE and chondrite-normalised REE plots show the same trend. The phenocrystal proportions in these volcanic bedrocks ranged from 10-30%, while the rest is vitreous and microcrystalline mass. In the rhyolitic saprolite we identified 40 wt% albite, 33 wt% hornblende, 18 wt% smectite (nontronite), 7 wt% hematite, 2 wt % quartz and minor proportion of crystalline and powdery phosphate-silicates observed by SEM-EDX (Fig 1a-b). These minerals were concentrated in Ce (Fig1c-d). We interpret them as secondary phosphates with Si and Al substitutions (e.g.: collophane, frankolite) or/and secondary silicates with P and Ca substitutions (e.g.: allanite).

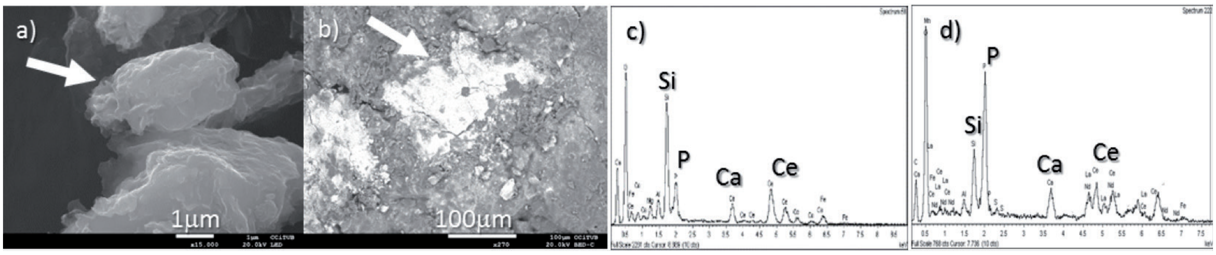

Fig. 1. SEM images (a,b) and EDX spectra (c,d) of the REE-enriched phosphates from trachyte-derived (a,c) and Mn-crust of rhyolite-derived (b,d) saprolites.

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DISTRIBUTION OF DIAGENETIC PRODUCTS CAUSED BY INFILTRATION OF METEORIC WATER AND ITS EFFECTS ON RESERVOIRS EVOLUTION, THE NORTHERN STEEP SLOPE, DONGYING SAG

Wei Meng (1,2), JianhuiZeng (1,2), GuoqiSong (3), XuejunWang (3), Zheng Guo (1,2)

(1) State Key Laboratory of Petroleum Resource and Prospecting, Beijing 102249, China, (2) College of Geosciences, China University of Petroleum, Beijing 102249, China, (3)Shengli Oil field Branch Company, SINOPEC, Dongying, China
18810459786@163.com

The Northern Steep Slope is located in the northern margin of Dongying Sag, and it is showed as two steps under the control of Chennan fault and Shengbei-Tuo94 fault. Alluvial fans, fan deltas, near shore subaqueous fans, and turbidite fans are regularly distributed and well developed in research area. The main objectives of this study were to identify diagenetic products caused by infiltration of meteoric water, conclude the distribution model of those diagenetic products, and summarize the effects of those diagenetic products on reservoirs evolution during burial process. The solution of those questions would be useful to predicate of deep burial reservoirs in petroliferous basins. In order to achieve the aim, 224 samples, which from 37 wells in research area, were collected for stained, and casting (blue) thin sections and SEM based on sedimentary, tectonic characteristics, and core observation. The results show that: (1) the percolating clays, dissolution and kaolinization of aluminosilicate minerals, cementation of authigenic kaolinite and dolomites were caused infiltration of meteoric water. (2) Those diagenetic product regularly distributed in sandstones of different sedimentary facies. (3) The percolating clays mainly distributed in the sandstones of alluvial fans, fan delta plain, and fan delta front. The percolating clays could form relatively complete claddings on the surface of particles. Dissolution and kaolinization of aluminosilicate minerals mainly distributed in the sandstones of pro-fan delta and root fan of nearshore subaqueous fans. Cementation of authigenic kaolinite and dolomites were mainly distributed in the sandstones of middle fan of nearshore subaqueous fans and turbidite fans. (4) The occurrence of percolating clays prevented the diagenetic process during burial process. The primary pores were well preserved and no secondary pores aroused. The dissolution and kaolinization of aluminosilicate minerals greatly declined the compaction resistance of sandstones. The physical properties of sandstones were greatly declined during burial processes, less pores were remained. The cementation of authigenic kaolinite filled in primary pores, without later reformations. The cementation of dolomites greatly improved the compaction resistance of sandstones and could be dissolved during burial process. During burial process the dissolution of dolomites led to the improvement of physical properties for sandstones.

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THE PHYSICAL AND CHEMICAL CHARACTERISTICS OF AUTHIGENIC KAOLINITES IN SANDSTONES AND ITS GENETIC ANALYSIS

Wei Meng (1,2), Jianhui Zeng (1,2), Guoqi Song (3), Xuejun Wang (3), Zheng Guo (1,2)

(1) State Key Laboratory of Petroleum Resource and Prospecting, Beijing 102249, China, (2) College of Geosciences, China University of Petroleum, Beijing 102249, China, (3) Shengli Oil field Branch Company, SINOPEC, Dongying, China
18810459786@163.com

In general, the porosity of sandstones declined with the increasing of depth and ground temperature in continuous sedimentary strata. The dissolution of unstable minerals is the main reason for the arising of high-porosity zone in the deep of petroliferous basins. Predecessors debate on that whether the dissolution and kaolinization of feldspars, which are well developed in sandstones, would lead to the formation of considerable secondary pores. Authigenic kaolinites, which are main diagenetic product result from the transformation of feldspars, maybe can be used to deduce the transformation of feldspars during diagenetic processes. Based on this assumption, Sandstone samples in Dongying Sag are collected for microscope, SEM, EDX and CL. Research results show that there are mainly two kinds of kaolinite. The first kind kaolinite has perfect crystal form, it appears in scaly-vermiform shape under single polar and the tightly packed aggregate of kaolinite occurs as vermiform or booklet under SEM. The crystal form of the second kind kaolinite is not as perfect as the first, and the aggregation appear as feldspar particles. Under the SEM some laminae is curved and the aggregate of kaolinite occurs as accordion which is packed loosely. The first kind authigenic kaolinites have pure elements (just Al, Si and O). On the contrary, the second kind authigenic kaolinites have K(av.1.01%), Fe (av.1.89%), except from Al, Si and O. The first kind of authigenic kaolinites distributed in the depth of 1700m~3600 m, mainly distributed in the depth of 2500~3000 m, with 80-120 °C ground temperature. The second kind authigenic kaolinites distributed in the depth of 2700 m ~3600 m, mainly distributed in the depth of 2900~3300 m, with 110-140 °C ground temperature. Within the depth of the first kind authigenic kaolinites, the feldspars are dissolved and the secondary pores are unfilled, the carbonate cements are well preserved. Within the depth of the second kind authigenic kaolinites, the feldspars are transformed into kaolinites and no secondary pores formed, the carbonate cements are dissolved to form secondary pores. In the process of the formation of first kind kaolinites, organic acids formed and well preserved. Under this situation, the complexing effects of organic acids greatly increase the solubility of Si and Al. All of those lead the Si and Al can migrate for a long distance and precipitated as kaolinites in right place. In the process of the formation of first kind kaolinites, organic acids transformed to CO_2, the solubility of Si and Al greatly declined. Under this situation, the feldspars are transformed to kaolinites, which aggregation appear as feldspar particles.

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X-RAY DIFFRACTION EVALUATION OF PROCESSING METHODS OF ANCIENT CERAMIC MATERIALS FROM POMPEII

Mariano Mercurio (1)*, Celestino Grifa (1), Chiara Germinario (1), Alberto De Bonis (2,3), Vincenzo Morra (3), Piergiulio Cappelletti (3), David Bish (4), Alessio Langella (1)

(1) Dipartimento di Scienze e Tecnologie, Università degli Studi del Sannio, Via dei Mulini 59/A, 82100 Benevento, Italy, (2) Institut für Klassische Archäologie, Universität Wien, Franz Klein-Gasse 1, A-1190 Wien, Austria, (3) DiSTAR, Via Mezzocannone 8, Università degli Studi di Napoli Federico II, 80134 Napoli, Italy, (4) Department of Geological Sciences, Indiana University, 1001 E. 10th St., Bloomington, IN 47405, US

Studies of ancient pottery, particularly extraction of information on ceramic processing methods, benefit from quantitative mineralogical information coupled with an understanding of phase transformations. Several authors have applied powder X-ray diffraction (XRPD) methods to ceramic materials [1-3] to determine quantitative mineralogical information on final ceramic products. These data were also used to draw the paths of pyrometamorphic reactions in ceramic materials, providing insight into the technological skills of ancient craftsmen. However, to-date this approach has not been applied to a full suite of archaeological materials related to different stages of the ceramic production (clayey raw material; temper; unfired, fired and overfired potteries), probably this suite of materials used in the production of ceramics in the same site were unavailable. This is one of the most outstanding aspects of the recent archaeological discovery in Via Dei Sepolcri in Pompeii. Here, a team of French and Italian archaeologists unearthed an ancient workshop that was active until a few of hours before the 79 AD eruption, revealing structures and ceramics that trace the production cycle from raw material procurement to firing conditions. The workshop in 79 AD produced thin-walled pottery, a ceramic class widespread on Roman tables during the Republican period, and production of this ceramic class also existed in Vesuvius environs (Pompeii and Herculaneum). We collected 35 samples at this site, consisting of two clay bodies, one temper, 13 unfired, 13 fired, and six overfired samples of pottery. Quantitative PXRD evaluation was performed using Rietveld-RIR methods determining both crystalline and amorphous phases for all samples; the RIR approach employed profile fitting, which included the quantification of compounds with partial or unknown crystal structure.

The temper, consisting of a locally occurring volcanic sand, contained abundant clinopyroxene and feldspar, with lower amounts of calcite, quartz, illite, analcime, hematite, and amphibole. An amorphous phase (likely volcanic glasses) also occurs. The mineralogy of unfired samples is identical to that of clay bodies, both representing the required mixture of clayey raw material and volcanic grains added as temper (up to ~ 10%). They contained primarily poorly ordered phases (smectite, illite, kaolinite, chlorite) up to 35 wt.%, along with quartz, feldspars, calcite, clinopyroxene, and an amorphous component, the latter from the addition of volcanics.

Fired vessels lacked smectite, chlorite, and kaolinite, all of which broke down upon firing, thereby increasing the amorphous components (up to 59 wt.%). Quartz and feldspar persisted, whereas, calcite increased from ~ 25% to 10 wt% in unfired to fired samples, respectively. Clinopyroxene increased from ~8% to 25%. The absence of gehlenite, a typical newly formed phase in high-CaO clayey raw materials (CaO ranges from 10 to 18 wt%), is noteworthy [4]. Hematite is present in low amounts.

XRD data for overfired samples revealed a marked increase in feldspar and clinopyroxene contents, counterbalanced by a decrease in calcite (present only in trace) and the highest amount (62%) of amorphous components. The occurrence of hercynite indicates the presence of a reducing atmosphere in the furnace.

Quantitative mineralogical data for the materials from this unique archaeological site, where it was possible to collect ceramic materials along with their unfired counterparts, shed new light into the firing dynamics of these potteries by precise evaluation of phase transitions and amorphous phase development.

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MICROBIAL COMMUNITY ANALYSIS OF URANYL NITRATE TREATED BENTONITE MICROCOSMS FOR DISPOSAL OF RADIOACTIVE WASTE PURPOSES

Margarita Lopez-Fernandez (1), Ramiro Vilchez-Vargas (2), Marius Vital (3),
Fadwa Jroundi (1), Ivan Sanchez-Castro (1), Dietmar H. Pieper (3), Ines Martin Sanchez (1),
Mohamed L. Merroun (1)*

(1) Department of Microbiology, University of Granada, Campus Fuentenueva 18071, Granada, Spain, (2) Department of Gastroenterology, Hepatology and Infectious Diseases, Otto-von-Guericke- University, Magdeburg, Germany, (3) Helmholtz Centre for Infection Research, Microbial Interactions and Processes (MINP), Research Group, Braunschweig, Germany
*merroun@ugr.es

Deep geological repository (DGR) is one of the internationally accepted options to dispose radioactive wastes. Bentonite formations from Almeria, Spain, were selected as reference material for artificial barriers for the future Spanish repository. However, the safety of this long-term disposal could be compromised not only by physico-chemical factors but also by microbial processes. To simulate a scenario where the mobilization of uranium from the repository to the host formations may occur, long-term microcosms were studied. After being treated with uranyl nitrate for 5 months the response of the bentonite microbial community to the addition of this radionuclide was evaluated. High throughput 16S rRNA gene sequencing revealed that the structure of the microbial community after the uranyl treatment differs to that of the control microcosms. The microbial diversity was dominated by Firmicutes and Proteobacteria. Moreover, after the uranyl nitrate treatment *Paracoccus* and *Bacillus* were highly enriched. The effect of uranium in the microbial diversity described in this work should be incorporated into a reactive transport modelling to evaluate the performance of the engineered barrier system for future DGR. Further analyses are required to fulfil the knowledge about the metabolic potential of the microorganisms involved in the uranium bioprecipitation for future DGR.

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INVESTIGATION OF BENEFIT REUSE OF DREDGED SEDIMENTS AS ECO-GEO-MATERIALS

Mesrar Laila (1,2), Benamar Ahmed (1), Panté Anne (1), Jabrane Raouf (2)

(1) Normandie University, UNIHAVRE, CNRS, LOMC, 76600 Le Havre, France, (2) Department of Earth and Science, Laboratory Georesources and Environment, Fez, Morocco

Aquatic ecosystems are precious ecological resources that cover almost 70% of the earth's surface, and are key targets of European resource management policies. Coastal zones offer many advantages in terms of fishing, maritime transport and tourism. These reasons explain why about 3 billion people live within 200 km of coastline; this represents almost half of the world's population. The continuous augmentation of anthropogenic activities (urbanization, industrialization, agriculture) is associated with a strong expansion of contaminant releases (organic and inorganic) into the aquatic environment. Over time, these free contaminants can undergo transformations and adsorb on clays and fine sand particles that make up marine sediments [1]. Sedimentation has become a real problem for the infrastructures of ports. Deposited in large quantities in waterways (harbors, access roads, estuaries, canals and rivers), the sediments interfere or prevent the movement of vessels. The benefit reuse of dredged sediments is a very interesting challenge which is part of the sustainable development policy, aiming both at the release of materials impeding port activity and the exploitation of these resources (sediments) in several fields consuming earth materials.

The aim of this work is to investigate how dredged and deposited sediments of the estuary and port areas can be used as an alternative raw materials for the heavy clay industry, and so reducing the dredging activities. The characterization of these sediments in their raw state shows that their chemical and mineralogical compositions are fairly close. Moreover, their low content of clay minerals (6.6%) and their high carbonate (25.2%) content constituted a limitation to the use in ceramic industry.

The geochemical analysis reveals that major elements of sediment samples are mainly composed of silica (50.2%) and carbonate (25.2%). The technical properties such as rheological parameters, have been investigated and tests were conducted in the objective to demonstrate the extent to which sediments provide assets to suit the heavy clay industry.

Keywords: dredged sediments, benefit reuse, raw material, heavy clay, geochemical, mineralogy.

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HYDROTERMAL ILLITES OF A MINERALIZED REGION IN SOUTH BRAZIL

Denise Canarim, André Mexias*, Ana Maria Misuzaki

Universidade Federal do Rio Grande do Sul, Programa de Pós Graduação em Geociências, Porto Alegre, 91501-970, Brazil
denise.canarim@ufrgs.br

The Camaquã Mines (consisting of the Uruguay, São Luiz and Santa Maria Mines) are former producers of Cu, Pb and Zn. They arelocated on the southern edge of Brazil (in the Sul-Rio-Grandense Shield region) in the Camaquã Basin (Neoproterozoic to Early Paleozoic volcano-sedimentary deposits) (Paim et. al. 2000). The Camaquã Mines region is classically known as the “BomJardim Window” and has been the subject of many studies. The latest-studies indicate that the Camaquã Mine may be considered as a hydrothermal- epithermal type deposit, resulting of a mixture of a magmatic fluids and meteoric waters, and a temperature varying from 350 to 80 °C (Renac et. al., 2014). Mineralization occurs in faults and as disseminations in the sandstones and conglomerates of the Santa Bárbara Group of this Basin. The sulfides of Cu present include the paragenesis composed of chalcopyrite, bornite, chalcocite and pyrite, with Au and Ag appearing as the main byproducts (Laux et. al., 2005). The presence of a conglomerate with zoned pebbles of granitic composition resulting from the hydrothermal alteration processes acting on these rocks is highlighted in the Uruguay Mine. Samples from these pebbles were collected from drill cores and analyzed by petrography, x-ray diffraction and scanning electron microscopy. They show hydrothermal alteration of illitic composition, mainly in the innermost portion of the pebbles. Thus, in 4 samples collected from different boring depths, different particle-size fractions were separated (<0.1, <0.2, <0.3, $>0.1<0.4$, <0.4 µm). All this particle-size fraction were analyzed with x-ray diffractionwhere it was identified 1Mt illites, which according to Drits & McCarty 1996 can be hydrothermal or diagenetic origin, characterizing a temperature lower than 280 °C. It is compatible with the existing hydrothermalism proposals for the region. These fractions, which were rich in illite, were dated by the ^{40}K-^{40}Ar method, and different ages were obtained (507.41 ± 10.37, 486.74 ± 9.96, 466.23 ± 9.54, 465.92 ± 9.48, 396.84 ± 8.1 and 250.61 ± 5.38 Ma), resulting in the recognition of the following three age groups:

- 507.41 ± 10.37 to 465.92 ± 9.48 (Cambro-Ordovician),
- 396.84 ± 8.1 (Devonian),
- 250.61 ± 5.38 (Triassic).

The first group was related to the hydrothermal processes generating the ore in the region, showing ages consistent with existing geochronological data. The second and third groups were interpreted as records of tectonic activity marked by the faulting existing in the entire region or the reactivation of these faults. It is mainly a response to a burial process suffered by the Paraná Basin (north area). These findings demonstrate that ^{40}K-^{40}Ar dating of hydrothermal illites results in data that are significant for the interpretation of mineralized regions.

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MINERAL CHEMISTRY OF MAGMATIC AND HYDROTHERMAL ALTERATION PHASES AND CLAY MINERALS FROM SEIVAL MINE COPPER DEPOSITS, CAMAQUÃ BASIN, NEOPROTEROZOIC OF SOUTHERN BRAZIL

Rodrigo W. Lopes (1,2), André S. Mexias (1)*, Christophe Renac (2), Eduardo Fontana (1,2), Márcia E. B. Gomes (1)

(1) Universidade Federal do Rio Grande do Sul, 91501-970, Porto Alegre, Brazil, (2) Université Cotê D´Azur, 06560, Valbonne, France

Seival Mine copper deposits [4] are hosted by a Neoproterozoic sequence of volcanic rocks included in the Lavras do Sul Shoshonitic Association, Hilário Formation, in the post-collisional Camaquã Basin. Field and drill-core samples consist of pyroclastic, vesicular lava, porphyritic lavas and andesitic dikes with apparent preserved magmatic minerals and altered ones described as post-magmatic albitization and meteoric-hydrothermal alteration [2]. Whit this premise, the chemical compositions of minerals were determined in thin sections by electron microprobe. Clay minerals with light green colours consist of flake particles (10 to 100 μm) surrounded of andesine-labradorite, albite and augite. Theses clay minerals are dominantly trioctahedral smectite and interlayered chlorite/smectite, chlorite-rich chlorite/smectite, chlorite and corrensite, associated with calcite, titanite, quartz and hematite. Chlorites compositions is Mg-chamosite in pyroxene alteration, hydrothermal vein and matrix of andesite dike. The hydrothermal system started in out gassing, partially segregated into vesicles, which have deposited mainly pyrite and chalcopyrite. The albitization started at temperatures from 600 to 350 °C, and subsequent cooling at ca. <251 °C led to crystallization of titanite and Mg-chamosite. Chloritization continued at ca. 183 °C [3] Mg-saponite and saponite/chlorite mixed layers formed at lower-temperature (150 to 80 °C) [3].

The Mg-chamosite of lavas and pyroclastic rocks may be indicative sulfide bearing hydrothermal vein in Seival Mine area. Saponite, chlorite/smectite and different types of Mg-chamosite may represent mixture of magmatic and meteoric waters [1] or phase reflecting chemical metastability with decreasing temperatures and the intensity of hydrothermal alteration. Clay mineralogy and chemistry do not derive from local equilibrium, but rather from composition of volcanic rocks, water activity, temperature and Al, Si, Fe and Mg chemical changes. Moreover, mass balance calculations [2] have pointed out that hydrothermal alteration occurred in closed chemical systems with respect to Si, Al, Fe and Mg with additional hydrous carbonic fluids. Mg-chamosite formation was probably related with Cu-sulfide and Fe oxide formation.

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VAPOR TRANSPORT IN A POROUS SMECTITE CLAY: FROM NORMAL TO ANOMALOUS DIFFUSION

Leander Michels (1), Yves Méheust (2)*, Mario A. S. Altoé (3), Henrik Hemmen (1), Roosevelt Droppa Jr. (4), Giovanni Grassi (3), Jon O. Fossum (1), Geraldo J. da Silva (3)

(1) Department of Physics, Norwegian University of Science and Technology - NO-7495, Trondheim, Norway, (2) Geosciences Rennes (UMR CNRS 6118), Rennes, France, (3) Instituto de Física, Universidade de Brasília, 70.919-970, Brasília - DF, Brasil, (4) Centro de Ciências Naturais e Humanas, Universidade Federal do ABC, 09.210-580, Santo André - SP, Brasil

Smectite clays possess a connected mesoporous space in the micrometer range, and nanopores inside the mineral grains. The grains are stacks of individual 1 nm-thick clay particles (the *layers*) with the ability to swell by incorporating H_2O molecules (or other molecules such as CO_2) in-between the layers, depending on the ambiant temperature and on the relative humidity (RH) present in the mesoporous space surrounding the grain. Imposing a gradient of RH along a temperature- controlled dry sample of smectite clay, we investigate the diffusive transport of water molecules in vapor phase through the material. As water molecules diffuse through the mesoporous space, (i) some of them intercalate into the nanopores, (ii) causing the grains to swell and the separation of clay grains into particles of smaller thickness. From (ii) results a change in the geometry of the mesoporous space, with a decrease in the mesoporous volume available for vapor diffusion. These two effects (i and ii) render the transport process potentially anomalous. We monitor it using space- and time-resolved X-ray diffraction at a synchrotron source. Indeed, water absorption into the nano-layered grains changes the interlayer repetition distance (*d*-spacing) of the stacks, which is seen in the diffraction data [1]. A separate calibration experiment allows mapping this monotonous evolution of *d* as a function of the RH. By measuring *d* in space and time in the transport experiments we thus record the time evolution of RH profiles along the direction of the initial RH gradient [2]. To model the data we consider a 1D effective diffusion process described by a fractional time diffusion equation with a diffusion coefficient that depends on the RH. It is possible to rescale all RH profiles onto a single master curve as a function of $(x/t)^{\gamma/2}$, where γ is the exponent characteristic of the fractional derivative. We observe that when the clay sample is prepared with sodium cations intercalated in the nanopores, vapor transport is normal (γ=2), while if the interlayer cation is lithium the transport is strongly subdiffusive [3]. This is explained by the different dynamics of cation intercalation in these two clays. In both cases we also obtain the dependence of the effective diffusion coefficient on relative humidity.

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INTERACTION BETWEEN SWELLING CLAY MINERALS AND DNA. A STRUCTURAL INVESTIGATION

Laurent J. Michot (1)*, Patrick Davidson (2), Erwan Paineau (2), Nobuyoshi Miyamoto (3)

(1) Physicochimie des Electrolytes et Nanosystèmesinterfaciaux, PHENIX CNRS Sorbonne Université, Paris VI, 75005 Paris, France, (2) Laboratoire de Physique des Solides UMR CNRS Université Paris Sud Bât 510 Orsay France, (3) Department of Life, Environment, and Materials Science, Fukuoka Institute of Technology, Japan

The interaction between nucleic acids and mineral surfaces has been of prime importance throughout geological time. Presently, significant amounts of nucleic acids are present in soils where they are used by microorganisms for gene exchange or transfection [1,2]. Nucleic acids are retained on mineral surfaces that protect them from degradation, whether enzymatic or UV-mediated [1,3]. Furthermore, during Earth's early time, the interaction between mineral surfaces and organics, especially nucleic acids, may have played a crucial role in the origin of Life as first hypothesized by Bernal as early as in 1951 [4]. In that frame work, understanding the interaction between swelling clay minerals and DNA-building molecules [5,6] or DNA is certainly worthwhile. In the present study, we have analyzed the interaction of two dispersions of swelling clay minerals, beidellite and montmorillonite, with both a short and a long DNA. Optical observations reveal that the presence of DNA significantly affects the phase diagram of both clay minerals strong differences being observed between the short length DNA and the long one. Furthermore, Small Angle X-ray Scattering (SAXS) experiments reveal that the presence of DNA modifies the interactions between clay platelets leading to interplatelets distances that are significantly shorter that those measured in water [7]. The origin of such behavior will be discussed in this presentation.

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POLYAMIDE/POLYSTYRENE COMPATIBILIZATION BY MONTMORILLONITE NANOCLAY: EFFECT ON MACROPOROSITY OF GAS DIFFUSION LAYERS FOR PROTON EXCHANGE MEMBRANE FUEL CELLS

Frej Mighri (1)*, Nafaa Athmouni (1), Said Elkoun (2)

(1) Research Center for High Performance Polymer and Composite Systems, CREPEC. Department of Chemical Engineering, Laval University, Quebec, G1A 0A6 CANADA, (2) Department of Mechanical Engineering, Université de Sherbrooke, Sherbrooke, QC, G1K 2R1 CANADA

The aim of this work was to improve the porosity of gas diffusion layers (GDLs) for proton exchange membrane fuel cell electrodes by using small amounts of Cloisite 30B montmorillonite (MMT) clay. GDL films were developed by twin-screw extrusion process from electrically conductive formulations composed of polyamide11 (PA11)/Polystyrene (PS) system as the polymeric matrix phase and an appropriate mixture of carbon black (CB) and graphite (GR) as the conductive additives. Final GDL film porosity, especially its macroporosity, was generated by selective extraction of the PS phase using adequate solvents. Since the generation of film porosity was found to be directly related to PA11/PS blend's morphology, several blend compositions were studied and small amounts of MMT clay were used as compatibilizer to improve the dispersion of PS inside the PA11 polymeric phase. It was observed that the incorporation of 2 to 6 wt% of MMT clay was found to improve significantly the pore specific surface area of the GDL film, whatever the composition of PA11/PS phase. However, the best improvement of porous properties of the GDL film was obtained with the incorporation of 2 wt% MMT. Although GDL volume porosity was not or slightly affected by the addition of MMT compatibilizer, its pore specific surface area was clearly increased. For GDL films made from a blend composed of 65wt.-% of PA11/PS (30/70) and 35 wt% of GB/GR (57/43), an increase of GDL specific surface area from 53 m^2/g (without MMT) to around 75 m^2/g (with 2 wt.-% MMT) was obtained. This improvement within the addition of MMT compatibilizer was attributed to the modification of the dispersion state of the PS phase inside PA11.

The localization of MMT compatibilizer normally depends on its compatibility with PA11 and PS. The MMT cloisite 30B used in this study was chosen because of is exfoliability in polyamides [1]. Moreover, when introduced in small percentage in PA11/PS blends, MMT preferential localization should be at the interface between PA11 and PS phases [2]. This was confirmed by TEM characterization that clearly shows MMT stacks situated at the PA11/PS interface (see picture), which confirms that MMT compatibilization of the PA11/PS based blends took place. Such compatibilization led to a higher connectivity of pores and consequently more accessibility to the micro/mesopores of CB and GR.

The most significant modification obtained with the addition of MMT clay was on pore size distribution, especially in the micropore/mesopore range. It was observed that, depending on MMT content, pore size distribution in this range was shifted to smaller or higher values. This means that, by controlling the amount of the MMT compatibilizer, this technique should be considered as interesting routes to tailor GDL porosity.

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MIXED-LAYER CLAY MINERALS ON MARS AND IMPLICATIONS FOR WIDESPREAD DIAGENESIS

Ralph E. Milliken (1)*, David L. Bish (2), Vivian Z. Sun (1)

(1) Brown University, Providence, RI, USA, (2) Indiana University, Bloomington, IN, USA

Orbiter and rover missions have provided a wealth of information about the presence, diversity and distribution of hydrated minerals, including clay minerals, on Mars. A wide range of clays have been inferred from orbital near-infrared reflectance spectroscopy data, including smectites, illite, chlorites, and kaolin-serpentine phases [1,2]. More recently, in situ X-ray diffraction measurements by the CheMin instrument on NASA's Curiosity rover have confirmed the presence of clays, and smectites in particular, within Gale crater [3,4]. The persistence of smectites in terrains on Mars that are billions of years old is in sharp contrast with the oldest smectites on Earth, which may be on the order of several hundred million years, and has been suggested to indicate limited water-rock interaction after initial smectite formation [5]. However, mixed-layer clay minerals produced during diagenesis (e.g., chlorite/smectite) may be spectrally similar to certain smectites at near-IR wavelengths, and it is possible that such phases have been overlooked in previous studies of martian clays.

To address this issue we have carried out laboratory reflectance measurements of a variety of natural mixed-layer clay minerals of different hydration states for comparison to Mars data, and we have used these lab data to establish empirically-based methods for distinguishing between mixed-layer C/S, smectite, and physical mixtures of discrete smectite and chlorite. When applying these methods to orbital near-IR reflectance spectra of martian clay deposits we find that the majority of occurrences are consistent with mixed-layer C/S. Occurrences of smectite are also observed but they are not as numerous and are most common in several locations, including Mawrth Vallis, Gale Crater, and Nili Fossae. These clays may represent products of burial diagenesis that have been brought to the surface by impact crater excavation or, alternatively, they may have formed in martian soil/regolith at the surface. In either case the presence and persistence of water is implied, as basin or crustal fluids in the first case or as water/thin films in surface sediments in the latter. In addition, global analyses of clay deposits associated with central peaks of martian impact craters reveals that chlorite abundance increases with depth [1,6], a trend that is expected if smectite is converted to chlorite with progressive burial depth.

Together, these observations indicate that mixed-layer clay minerals, and C/S in particular, are common on Mars and indicate that diagenesis was widespread prior to ~3 Ga. Though much of this diagenesis may have occurred in the warmer subsurface where liquid water is likely to be more stable, we cannot rule out C/S formation in the near-surface environment due to intermittent interaction of thin films of water with sediment integrated over billion year timescales. Detailed spectral analysis of martian clays thus reveals a more complex story of water-rock interaction on early Mars, though the preponderance of Fe/Mg clays over late-stage weathering products such as kaolinite and gibbsite suggests total chemical weathering was still not as advanced as is commonly found on Earth. Because of their diversity and great antiquity, clay-bearing deposits on Mars may provide novel information about clay evolution on timescales not accessible in Earth's rock record. As such, martial clay deposits provide excellent locations for future in situ measurements and/or sample return.

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EVALUATION OF CERAMIC PROPERTIES OF BAUXITIC MATERIALS FROM SE OF IBERIAN RANGE

Adolfo Miras (1), Domingo Martin (1), Isabel Guerrero (1), Antonio Romero (1), Patricia Aparicio (1), Blanca Bauluz (2), Alfonso Yuste (2), Maria Jose Mayayo (2)

(1) Departamento de Cristalografía, Mineralogía y Química Agrícola, Universidad de Sevilla (Spain), (2) IUCA-Facultad de Ciencias, Universidad de Zaragoza, Zaragoza (Spain)

One of the most important traditional refractory materials are made of aluminum-rich raw clays and bauxites. After firing the structure of the material consists of needle-like mullite crystals in a siliceous and vitreous matrix with some impurities, being the mullite the responsible of the refractory properties. The aim of this study is to analyze ceramic properties of some bauxites to evaluate their use as refractories.

Four samples were selected for the study come from Lower Cretaceous karst bauxite deposits that outcrop to the SE of the Iberian Range (Maestrazgo zone) [1,2,3]. Bauxites constitute bodies filling karst cavities developed in Jurassic limestones. Samples were characterized determining mineralogical and chemical composition, thermal analysis and kaolinite structural order by XRD and DTA and high-temperature optical microscopy. On the other hand, a set of 5 mm-diameter cylinders were made with the milled raw clay by pressing, and then heated from 1000º to 1400 ºC and some physical properties such as dilatometry, linear contraction, water absorption, density and mechanical resistance and color, have been evaluated in order to evaluate their use as refractories. Also the evolution of the mineralogical composition was quantified by XRD using zincite as internal standard.

Two samples (F4-4 and F2X) are composed mainly of kaolinite with traces of anatase, rutile and hematites, F3-1R contains kaolinite and gibbsite with minor amount of hematites and traces of anatase and rutile, finally F2Y is composed of kaolinite with minor amount of hematites, gibbsite and boehmite, and traces of anatase and rutile. Chemical composition is according with this mineralogical composition. The kaolinite present a high structural order. The mineralogical composition of the firing samples is composed mainly of mullite and cristobalite associated with amorphous phase.

The evaluation of the ceramic properties shows:

- Sample F2Y presents the best refractory behaviour because his high mechanical resistance and low cristobalite content avoid thermal dilatation. The quality as refractory would be better if iron content is reduced by magnetic separation or chemical leaching.
- Sample F2X, which has higher cristobalite content than F2X, presents low mechanical resistence at 1350 ºC. This sample could be used as refractory at 1200º or 1300 ºC, but with medium number of heating cycles.
- Sample F4-4, although the low iron content could be indicate a better refractory behaviuor, presents a very high cristobalite content, so its quality as refractary material will be poor with low number of heating cycles.
- Finally sample F3-1R could not be used as silicum-alumninum refractory.

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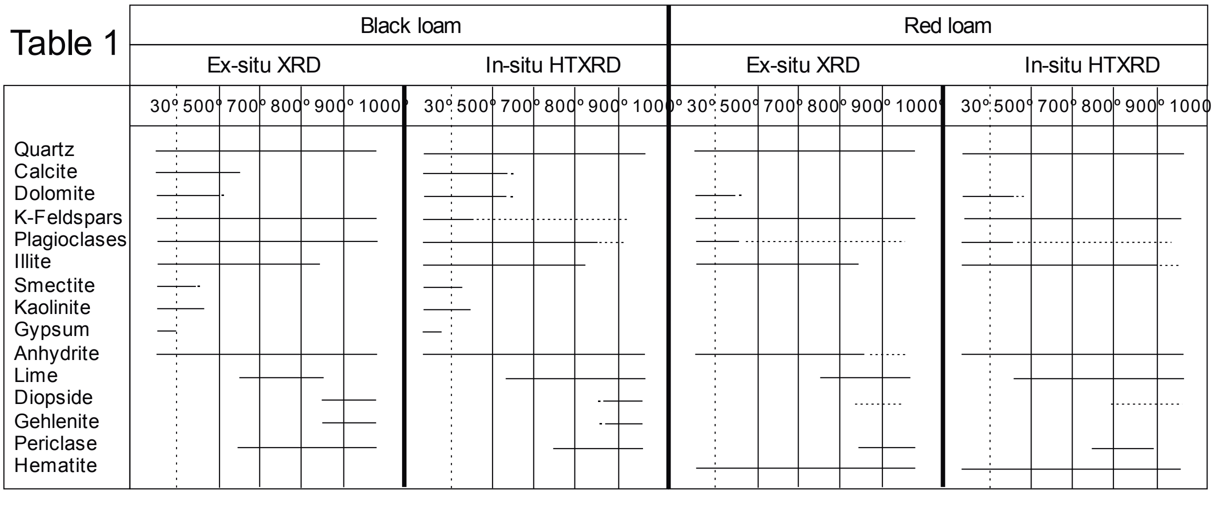
STUDY OF THE MINERALOGICAL EVOLUTION OF CERAMIC CLAYS DURING HEATING BY "IN-SITU" HIGH TEMPERATURE X-RAY DIFFRACTION (HTXRD)

Adolfo Miras*, Antonio Romero, Isabel González, Emilio Galán, Paloma Campos

Dpto. de Cristalografía, Mineralogía y Química Agrícola. Universidad de Sevilla (Spain)

High temperatures tests are often performed in ceramics bodies to determine their physical properties which are largely dependent on the new phases formed. Usually such technical determinations and the phase characterization are carried out on test pieces prepared on laboratory heated at the most suitable temperatures, according to the composition of the raw material and the ceramic product to be fabricated. However, these studies do not allow to follow the evolution occurring during heating and foresee what is the most appropriate temperature to heat the ceramic bodies in order to obtain the better ceramic product and to save energy. In the last years has become of widespread interest the use of "in-situ" High Temperature X-Ray Diffraction (HTXRD)for the measurement of crystallographic parameters, and to follow the evolution of the crystalline phases under controlled temperature. The aim of this contribution is to compare the results obtained with this technique with those deduced from the classical approach to optimize the possible temperature of the finished products manufactured from two raw materials commonly used for making bricks in ceramic industries. Those clays are locally called "black loam" and "red loam", according to their respective colors, at the brick industry of SE Spain. The "in-situ" HTXRD analysis was carried out using a powder diffractometer (Bruker DISCOVER D8) equipped with a chamber (MTC-FURNACE) with corundum sample holder and a fast response/high sensibility detector (Bruker, LYNXEYE-XE). The temperature during the heatingwas increased at a rate of 25 ºC·min^{-1} from room temperature (RT) up to 500 ºC, and at 5 ºC·min^{-1}from 500 to 1000 ºC. The classic "ex-situ" XRD experiments were performed on ceramic pressed disks fired at 500, 700, 800, 900 and 1000 ºC in a Bruker D8I Advance diffractometer. For a better comparison the mineral phases found with the two procedures and their evolution with the temperature they are shown in Table 1. From the HTXRD analysis only the phases identified for the same temperatures than those deduced from the study of test pieces by XRD are indicated. According to the HTXRD results: a) dolomite is ever destroyed at higher temperature, b) lime appears at lower temperature and at 1000 ºC it is not totally consumed to form diopside and gehlenite, c) periclase also appears at lower temperature, if it comes from the dolomite destruction, but it is worn out at less than 900 ºC to form diopside, d) diopside is detected later than in other study, e) not all the illite is destroyed when it is the only one clay mineral (red loam), and it remains up to a higher temperature. These differences between the results obtained from the two studies can be because the "in-situ" experiments were carried out at a higher speed than the others and the equilibrium was not achieved, because of the kinetic of reactions. On the other hand there are some difficulties for a good identification of high-temperature phases due to the expansion of the mineral structure parameters. In addition, a quantification approach is practically impossible presently. Nevertheless, the HTXRD investigations of ceramic materials can save time respect to XRD study of test-pieces heated at different temperatures, and give immediate information of the transformation occurring on heating, which can be useful to improve the most suitable firing temperature in the industry.

Table 1



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DEVELOPMENT OF NEW CARBON/CLAY COMPOSITE ELECTRODES FOR THE ELECTRO-FENTON PROCESS

Simona Melania Miron (1), Jocelyne Brendle (1), Lionel Limousy (1)*, Fabienne Fourcade (2), Abdeltif Amrane (2)

(1) Institut de Science des Matériaux de Mulhouse, UMR CNRS 7361, ENSCMu, Université de Haute Alsace, Mulhouse, 68093, France, (2) Equipe Matière condensée et systèmes electroactifs, UMR CNRS 6226, Université de Rennes 1, Rennes, 35042, France
*Lionel.Limousy@uha.fr

The electro-Fenton process is an electrochemical advanced oxidation process which presents some advantages comparing to other ones: low chemical products consumption, *in-situ* production of oxidant reagents, and low production of iron sludge compared to classical Fenton processes [1]. Mineralisation of persistent organic compounds (hormone derivatives, pesticides, antibiotics) can be achieved by coupling this process with a biologic treatment (activated sludge) [2]. The only drawback concerns the necessity to add iron chloride to the raw solution to be treated.

The novelty of our approach stands in the development of a new type of electro-Fenton electrodes containing iron. A series of innovative composites combining carbon felt and aminoclay (with a talc-like structure containing Fe or Fe and Mg) or montmorillonite was prepared to that purpose. The main complexity of this work was to find and set the synthesis conditions necessary to obtain a continuous and thin film of clay at the surface of the carbon fibres. The different samples were characterized by SEM-EDX (Figure 1), TGA, FTIR, Chemical analysis (by X-ray wavelength fluorescence (XRF)) and nitrogen adsorption-desorption experiments.

Figure 1.SEM pictures of carbon/aminoclay composites containing Fe(a) and Fe/Mg(b)

The evaluation of the catalytic properties of iron (present in the clay framework) is underway. These new electro-Fenton electrodes can be an effective approach for overcoming the challenges of Fenton-like reactions.

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PEG-PE/CLAY COMPOSITE CARRIERS FOR DOXORUBICIN: EFFECT OF COMPOSITE STRUCTURE ON RELEASE, CELL INTERACTION AND CYTOTOXICITY

Hagay Kohay (1), Rupa Sawant (2), Can Sarisozen (2), Aditi Jhaveri (2), Vladimir P. Torchilin (2), Yael G. Mishael (1)*

(1) The Robert H. Smith Faculty of Agriculture, Food and Environment, The Hebrew University of Jerusalem, Rehovot, Israel, (2) Center for Pharmaceutical Biotechnology and Nanomedicine, Northeastern University, Boston, MA, USA

A novel drug delivery system for doxorubicin (DOX), based on organic-inorganic composites was developed. DOX was incorporated in micelles (M-DOX) of polyethylene glycol-phosphatidylethanolamine (PEG-PE) which in turn were adsorbed by the clay mineral, montmorillonite (MMT). The nano-structures of the PEG-PE/MMT composites of LOW and HIGH polymer loadings were characterized by XRD, TGA, FTIR, size (DLS) and zeta measurements. These measurements suggest that for the LOW composite a single layer of polymer intercalates in the clay mineral platelets and the polymer only partially covers the external surface, while for the HIGH composite two layers of polymer intercalate and a bilayer may form on the external surface. These nanostructures have a direct effect on formulation stability and on the rate of DOX release. The release rate was reversely correlated with the degree of DOX interaction with the clay mineral and followed the sequence: M-DOX>HIGH formulation>LOW formulation>DOX/MMT. Despite the slower release from the HIGH formulation, its cytotoxicity effect on sensitive cells was as high as the “free” DOX. Surprisingly, the LOW formulation, with the slowest release, demonstrated the highest cytotoxicity in the case of Adriamycin (ADR) resistant cells. Confocal microscopy images and association tests provided an insight into the contribution of formulation-cell interactions vs. the contribution of DOX release rate. Internalization of the formulations was suggested as a mechanism that increases DOX efficiency, particularly in the ADR resistant cell line. The employment of organic-inorganic hybrid materials as drug delivery systems, has not reached its full potential, however, its functionality as an efficient tunable release system was demonstrated.

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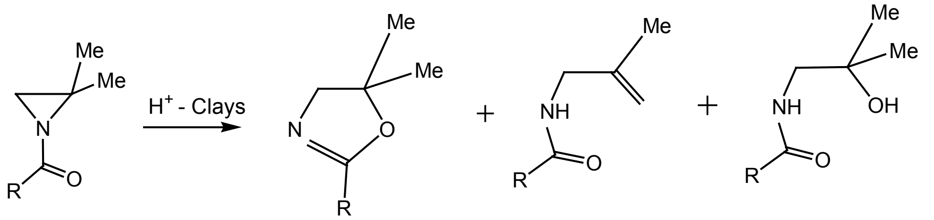
ACID ACTIVATED CLAYS EFFECT ON N-ACYL-2,2-DIMETHYL AZIRIDINES: MECHANISTIC ELUCIDATION

Djallila Missaoui (1)*, Ali Rahmouni (1), Okkacha Bensaid (2), Neji Besbes (3)

(1) Laboratoire de Modélisation et de Méthodes de Calcul, Université Docteur Moulay Tahar de Saida, 20002, Saida, Algérie, (2) Laboratoire des Substances Naturelles et Bioactives, Université de Tlemcen, 13000, Tlemcen, Algérie,(3) Laboratoire Physico-Chimie de Matériaux Minéraux et leurs Applications, Centre National des Recherches en Sciences des Matériaux, 2087, Soliman, Tunisie
*missaoui_chem@yahoo.fr

Tunisian acid activated clays have been used for the rearrangement of N-acyl-2,2-dimethylaziridines 1 (Scheme 1) into a mixture of N-methallylamides 2, oxazolines 3 and amidoalcohols 4 at room temperature for three days[1-3]. The results show that the yields of these products depend strongly on the nature of acyl group carried by nitrogen of aziridine cycle (1a: propanoyl, 1b: benzyloyl and 1c: benzoyl) and the physicochemical characteristics of acid activated clays used. The structures of the different stationary points of these reactions have been optimized by the DFT calculation method with the 6-31G* level using the GAUSSIAN 09. Frequency analysis was performed to determine the nature of each stationary point. The mechanism of the competitive transformation catalysis of N-acyl-2,2-dimethylaziridines 1 by Bronsted sites located at the active surface of these clays are performed using quantum chemistry methods. Geometries of reactant 1, intermediaries I and II, transition states TS1 and TS2, protonated intermediaries 2', 3' and 4' and products 2, 3 and 4 have been also optimized [4].



1 2 3 4

1a: R= C_2H_5
1b: R= $PhCH_2$
1c: R= Ph

Scheme 1 . Acid activated clays effect of N-acyl-aziridines 1a-c

Keywords: acid activated clay, N-acylaziridine, theoretical calculation, acid catalysis.

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ADSORPTION-DESORPTION OF CESIUM ONTO LAMINAR SILICATE MINERALS AND CHARACTERISTICS CHANGE BY HEAT TREATMENT

Takuya Miura (1)*, Atsushi Sasaki (2), Masatoshi Endo (1)

(1) Yamagata University (Graduate School of Science and Engineering), Yonezawa, 992-8510, Japan, (2) Yamagata University (Faculty of Engineering), Yonezawa, 992-8510, Japan
*t.miura1230@gmail.com

The adsorption-desorption characteristics of cesium onto minerals are affected by many different factors. Cesium ions are adsorbed by ion exchange in soils and in the pores of the zeolite minerals. The interlayer of micas having water-swelling can be swollen to several tens of times its original size with water. Micas are common in soils of Fukushima (Japan), and the mineral is important for decontamination efficiency of cesium. In this study, the adsorption-desorption behaviour of cesium onto laminar minerals, natural/artificial zeolite and soil reference materials was investigated. Additionally, the heat treatment of mineral for the inhibiting cesium desorption was experimented.

Mica, bentonite, vermiculite, natural zeolite, artificial zeolite, geochemical reference samples in Japan (basalt: JB; soil: JSO) and as laminar compounds were used for the cesium adsorption experiments. Cesium solutions (200 or 2000 mg/L) were prepared from ^{133}CsCl. The cesium solution (50 mL) and mineral sample (0.5 g) were placed a 200 mL polystyrene container and stirred for 2 h. After equilibration, each sample solution was filtered through a membrane filter (0.20 μm), and the saturation amounts of adsorbed cesium were determined by the cesium concentrations in the filtrates measured by ICP-MS. The desorption solution {HCl, HNO_3, H_2SO_4, $(COOH)_2$:oxalic acid, $(CH(OH)\ COOH)_2$:tartaric acid, $C_6H_4(COOH)_2$:phthalic acid } (25mL) and the mineral containing adsorbed cesium (0.25 g) were added to each polystyrene container for desorption experiments. The desorption procedure was similar to the adsorption procedure. In addition, the minerals were calcined at 400, 600, 800, 1000-degree C and then used in the cesium adsorption and desorption inhibition tests.

Cesium adsorption amount onto laminar silicate mineral (mica, bentonite and vermiculite) and zeolite (11~200 mg/g) were larger than geochemical reference samples (0.57~5.3 mg/g). Adsorption characteristics of cesium were influenced by the minerals skeleton structure and their cation exchange capacity. Zeolite has porous structure with many adsorption sites and high cation exchange capacity, so cesium adsorption amounts was largest. Mica and bentonite of the laminar structure had larger cesium adsorption capacity than vermiculite. This result has related to water-swelling, so cesium ions were intercalated between soil layers. From adsorption characteristics onto all mineral samples, cesium adsorption stability and ability were higher the uniform skeleton structure minerals (mica and zeolite) than the nonuniform skeleton structure minerals (other minerals). The mineral adsorbing large amount of cesium ions had a low cesium desorption ratio. Cesium desorption ratio on minerals with an intercalation structure were high using the combination of acids and NH_4^+. Acids dissolved the mineral structure, the condition with low pH and the expanded interlayer. Additionally, the high desorption ratio of cesium with NH_4^+ is probably due to a strong chemical attraction of NH_4^+ which has ionic radius similar to that of cesium ion. Adsorption and desorption ratio of cesium ions decreased in accordance an increasing with calcined temperature. The number of adsorption sites was decreased by structural changes and the combustion of organic substances during calcination. Calcination of minerals changed the soil interlayer and pore structures, melting the mineral, and trapping the exchangeable cations at the ion exchange sites. The heat treatment methods of mineral are effective for the final treatment of contaminated soil.

Keyword: laminar silicate mineral, cesium, adsorption and desorption.

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MORPHOLOGY, REACTIVITY AND DISPERSIBILITY CONTROLS OF COPPER NANOPARTICLES WITH LAYERED CLAY MINERALS

Masaya Miyagawa*, Akane Shibusawa, Hideki Tanaka

Department of Applied Chemistry, Chuo University, Tokyo, 112-8551, Japan
*miyagawa@kc.chuo-u.ac.jp

Cu nanoparticles (Cu NPs) have recently attracted much attention due to their optical and catalytic properties. However, their low oxidation resistivity has been a critical problem to the application. In addition, multistep procedures have often been required in chemical reduction method to remove excessive amounts of a capping agent and a hazardous reducing agent. In contrast, our research group has reported regenerative Cu NPs by environmentally-friendly photoreduction method [1]. Considering that layered materials have been a promising supporter due to stable nanostructures, we have believed that syntheses of the Cu NPs with layered clay minerals by the photoreduction method would give novel viewpoints in both fields of the clays and the metal NPs. In addition, unlike previous studies using the chemical or photocatalytic reduction [2], we have assumed that the Cu NPs could be synthesized simply by UV irradiation to a clay dispersion containing a Cu salt. Furthermore, it may be possible to control morphology and reactivity of the Cu NPs by difference in physicochemical properties of the clays such as adsorption and exfoliation. From these backgrounds, we have developed a novel synthetic method of the Cu NPs with two different clays, and investigated differences in the morphology and the reactivity. Kaolinite (KL, Kanpaku mine, Japan) and synthetic saponite (Sapo, Kunimine Ind. Co.) were dispersed in water, respectively. Copper acetate aqueous solution and ethanol were added to the dispersion drop by drop. The mixed solution was irradiated by UV light. Other experimental detail is described elsewhere [3]. When the KL suspension was irradiated by UV light, it turned reddish brown. Since the color was deeper than that of spherical Cu NPs [1], production of anisotropic Cu NPs was suggested. As expected, SEM observation revealed production of Cu nanodisks (Cu NDs) with a diameter of 80 nm on KL. Oxidation state and resistivity of the nanocomposite (Cu ND−KL) were evaluated with XRD. As a result, Cu ND−KL was found to contain no oxides, and the powder sample did not get oxidized even after 6-months air exposure. We assume that this extremely high oxidation resistivity originates from the relatively large Cu NDs and firmly-stacked kaolinite. Production mechanism of Cu ND−KL was elucidated from time-dependent UV-vis spectra and XRD patterns. As a result, it was found that the photoreduction of Cu^{2+} to Cu^0 was stepwise via Cu_2O: The first step reduction from Cu^{2+} to Cu_2O occurred in the solution, followed by adsorption on KL to produce Cu_2O NDs. The second step reduction to Cu NDs occurred on KL. It is noted that the reduction started from the electron transfer from CH_3COO^- to Cu^{2+}. Ethanol was reacted as the sacrificial reagent. The total photoreaction mechanism is summarized and discussed in detail elsewhere [3]. Since the Cu_2O nanocrystals were formed in the solution without capping agents, the obtained Cu NDs were relatively large. In addition, even though the Cu ND−KL solution showed high oxidation resistivity, the back reaction to copper acetate occurred slowly on exposure to air. Contrary to KL, small spherical Cu NPs in the aggregated Sapo (Cu NP−Sapo) were observed by STEM observation. It is probably because Cu^{2+} was adsorbed and isolated on Sapo, suppressing particle growth greatly by the photoreduction of Cu^{2+}. Their diameter could be controlled from 3 to 24 nm not only by $[Cu^{2+}]$ and [Sapo] but also by the drop rate of the copper acetate solution. Because larger Cu NPs were obtained by adding the solution quickly, it was implied that Cu^{2+} was segregated on Sapo, which induced the particle growth after the photoreduction. In addition, dispersibility of Cu NP−Sapo was also controlled by $[Cu^{2+}]$, [Sapo] and the drop rate, suggesting that the dispersibility is determined by the size of the aggregated Sapo. Contrary to Cu ND−KL, the Cu NP−Sapo solution showed high reactivity: it quickly turned yellow by the air exposure. We confirmed production of Cu_2O with XRD and UV-vis spectroscopy after the exposure. STEM observation revealed unexpected formation of Cu_2O NP clusters. The diameters of the clusters and the constituent Cu_2O NPs were about 1 μm and 100 nm, respectively. Therefore, it was suggested that the Cu NPs moved by the air exposure to form the large Cu_2O NPs followed by the clusters in the aggregated Sapo. In conclusion, we developed the synthetic method of the Cu NPs with KL and Sapo by photoreduction. In the former case, the Cu NDs were obtained with the high oxidation resistivity. In the latter case, the small spherical Cu NPs were obtained with the high reactivity to produce the Cu_2O NP clusters by the air exposure.

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ANISOTROPIC COMPOSITE GEL OF FLUOROHECTORITE NANOSHEET LIQUID CRYSTAL

Takumi Inadomi (1), Kenji Urayama (2), Nobuyoshi Miyamoto (1)*

(1) Department of Life, Environment and Materials Science, Fukuoka Institute of Technology, Fukuoka 811-0295, Japan, (2) Department of Macromolecular Science and Engineering, Kyoto Institute of Technology, Kyoto 606-8585, Japan
*miyamoto@fit.ac.jp

Lyotropic liquid crystals (LCs) of inorganic nanosheets [1] are emerging as new-type LC materials with rich electric and optical functionalities inherent to inorganic materials, very low isotropic/LC transition concentration, fluidity, and capability of forming organic-inorganic nanohybrids. We recently demonstrate the utilization of inorganic nanosheet LCs to facilely synthesize hydrogels with anisotropic structures and anisotropic properties [2]. Here, we demonstrate electric-field-assisted synthesis of a cm-scale monodomain gel (7 cm x 7 cm at maximum) of exfoliated LC clay/ polymer composite adsorbed with dye. The gel shows a photo-induced anomalous deformation behaviour [3].

The gels were synthesized by photo-polymerization of *N*-isopropylacrylamide (NIPA) dissolved in the liquid crystalline fluorohectorite clay colloid in a cell. The alignment of the nanosheet LC is achieved by applying in-plane or out-of-plane AC electric field during photo-polymerization. When the LC clay/pNIPA composite gel is observed between crossed polarizers, it showed a uniform interference color due to birefringence, indicating the formation of the large oriented monodomain gel. In the stretching test from two orthogonal axes, the anisotropic gel showed the larger tensile modulus along the direction parallel to the oriented nanosheet plane than the perpendicular axis.

A photoresponsive pattern was printable onto the gel with μm-scale resolution by adsorbing a cationic dye through a pattern-holed silicone rubber. When the gel is irradiated with light, only the colored part is photothermally deformed; the deformation is anisotropic due to the oriented nanosheets in the gel. Interestingly, the photo-irradiated gel shows temporal expansion along one direction followed by anisotropic shrinkage, which is an anomalous behavior for a conventional PNIPA gel.

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ADSORPTION BEHAVIOR OF RARE EARTH ELEMENTS ON CLAY-POLY(*N*-ISOPROPYLACRYLAMIDE) NANOCOMPOSITE

Hirotaka Mizuno*, Shin'ichi Ishimaru

Division of Materials Science and Engineering, Graduate School of Engineering, Tokyo Denki University, 5 Senju-Asahicho, Adachi-ku, Tokyo 101-8551, Japan
ishimaru@cck.dendai.ac.jp

Rare earth elements are widely important resources for various applications, such as high power magnets, emitting materials and catalytic substances. Recycling metals from used devices attract attention because main producer of the metals is limited by the reason of costs and the fluctuations in market price are large. Methods for recovering metals from aqueous solutions can be classified into coprecipitation and ion-exchange techniques, but they have some problems, e.g., difficulties in separating of each metal for the former technique and the high cost of ion exchange resins that are used in the latter method. New ion-exchange materials, which are low cost and have easy desorbility of metals are needed.

Clay minerals are the natural ion-exchanger that are available in abundant amounts. They can be considered to be materials with high environmental harmony and superior cost. However, clay minerals are very fine particles, and they are difficult to separate from the solution. We previously reported synthesis procedures [1] and adsorption properties for Cu(II) and Zn(II) [2] of nanocomposite materials clay-P(NIPAAm) that consisted of clay minerals and hydrophilic polymer, poly (*N*-isopropylacrylamide). These nanocomposites showed superior mechanical strength and good separative performance while keeping clay's cation exchange capacity.

In this study, we evaluated the adsorption-desorption behaviour of Sc(III), La(III), Ce(III) and Pr(III) on clay-P(NIPAAm) nanocomposites in aqueous solution. The clay minerals used for synthesis of nanocomposites were fluorohectrite and saponite-type synthetic clays, sourced from Co-op Chemical Co. Ltd. and the Clay Science Society of Japan, respectively. Each clay was dispersed in pure water and added with aqueous solution of NIPAAm monomer and the initiator dissolved in a small amount of acetone, then the mixture was stirred under bubbling nitrogen gas to remove oxygen. The nanocomposites were synthesized by photopolymerization under UV irradiation with nitrogen gas flow. Clay contents in the obtained nanocomposites were determined by TG-DTA and ignition loss. Adsorption behaviour of four rare earth elements was investigated by observing the change in the metal ion concentration in the aqueous solutions at various pH and the initial concentration. The concentration of metal ions was determined by absorption photometry using chlorophosphonazo-III as a coloring reagent. Chlorophosphonazo-III forms a 1: 1 blue complex with the lanthanoid and shows an absorption maximum arround 670 nm.

The adsorption amounts increased with pH elevation in the range from 2 to 6, but hydroxides precipitated at higher pH than 7 for all metals investigated. These results imply that the appropriate pH of adsorption for these metals is in the range from 4 to 6. The maximum adsorption amounts for lanthanoids were 70-100% of the expected cation exchange capacity of clay minerals including the nanocomposites for a trivalent cation. On the other hand, it reached to 150% for Sc(III) at pH 6. This is because the dominant chemical species is $[Sc(OH)]^{2+}$ rather than Sc^{3+} at this pH. Recovery of the whole metal ions was successfully achieved by a treatment of the nanocomposites after adsorption using a mildly acidic solution.

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CATALYTIC HYDROGENATION OF AQUEOUS BROMATE WITH Pd AND Pt SUPPORTED ON Al-PILLARED CLAYS

Carmen B. Molina*, Alejandro H. Pizarro, Carolina Belver, Juan J. Rodriguez

Universidad Autónoma de Madrid, Cantoblanco 28049, Madrid, Spain
*carmenbelen.molina@uam.es

Bromate is a by-product detected in drinking water from disinfection of bromide-containing source waters. It is a potential carcinogen to human beings, identified as a 2B substance by the International Agency for Research on Cancer. The World Health Organization (WHO) has recommended a maximum bromate concentration of 0.01 mg L^{-1} in drinking water. Bromide occurs in water due to natural and anthropogenic sources including seawater intrusion, pesticide run-off, industrial waste and impurities in road de-icing salt [1]. The heterogeneous catalytic hydrogenation of different water pollutants using metallic catalysts has demonstrated its high efficiency but bromate reduction has not been extensively studied in the literature. Among the materials used for this process monometallic materials supported on activated carbon [2], Pd/mesoporous carbon nitride [3] or mono and bimetallic ZSM5 [4] can be found. In the last few years pillared clays have shown their potential as catalytic supports for the removal by hydrogenation of different aqueous pollutants: chlorophenols [5], chloronitrogenated aromatic compounds [6], cresols [7], nitrate [8] and azo and triarylmethane dyes [9] using precious metals as active phase. The aim of this work was to study the hydrogenation of bromate in aqueous phase under ambient-like operating conditions using own-prepared catalysts based on Pd and Pt supported on Al-pillared clay. The effect of the previous reduction stage of the catalysts and the pH of the reaction medium were studied.

The catalysts used were synthesized by impregnation of Al-pillared clay calcined at 350ºC. The impregnation of Pd or Pt was carried out with a $PdCl_2$ acidic solution in the case of Pd and an aqueous H_2PtCl_6 solution in the case of Pt. Further calcination at 500 ºC was accomplished in order to fix the active phase to the support. The metallic loads tested were 1% wt. Surface area values greater than 170 m^2/g were achieved in all cases. The catalytic activity experiments were performed in a batch stirred glass jacketed reactor (25ºC, 1 atm, 100 mg/L BrO_3^- initial concentration, 1 g/L catalyst) using a continuous H_2 flow (50 mL/min). A previous reduction step of the catalysts was carried out for 2 h at temperatures ranging between 25 and 200 ºC under hydrogen flow. The pH of the solutions was adjusted to values between 2 and 8. The hydrogenation process was followed from the evolution of the concentration of the reactant (bromate) and reaction product (bromide) measured by ionic chromatography.

Hydrogenation of bromate with the catalysts prepared at 25 ºC and 1 atm reached the complete removal of bromate in both cases. Bromide was detected as the only final product of this process. Pt showed a higher catalytic activity than Pd. The effect of the pH of the reaction medium was very important with both catalysts, being pH 2 the optimum in both cases. From these results, Pt catalyst was selected to test the effect of the temperature of the previous reduction stage of the catalyst. Reduction at 90 and 200 ºC yielded the best results being preferable 90 ºC for the economy of the process.

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DECOLORATION OF TRIARYLMETHANE DYES BY CATALYTIC HYDROGENATION WITH PILLARED CLAYS

Carmen B. Molina*, Alejandro H. Pizarro, Carolina Belver, Juan J. Rodriguez

Universidad Autónoma de Madrid, Cantoblanco 28049, Madrid, Spain
*carmenbelen.molina@uam.es

The synthesis of organic dyes represents a very important activity of the chemical industry and two-thirds of their world-wide production is consumed by the textile and plastic industries. Azo and triarylmethane compounds are, by far, the most widely used synthetic colorants. The discharge of dyes is forbidden by the EU legislation due their carcinogenic potential. Destructive and non-destructive technologies have been used for the removal of these compounds from industrial effluents including wet air oxidation, advanced oxidation processes, adsorption or coagulation-flocculation [1]. The main drawback of these treatments is the formation of highly toxic species, even more harmful than the original ones, especially nitrogenated or chloronitrogenated compounds [2]. The use of reductive processes for aqueous dyes removal has been reported which can overcome the drawbacks of the oxidation technologies [3]. Among reductive treatments catalytic hydrotreatment has been studied in the reduction of different dyes with different catalysts based on Ni, Au or Ag nanoparticles [4], Pd on polypropylene membranes [5] and also zerovalent Fe or Zn [6]. In the last years pillared clays have shown their potential as catalytic supports for the removal by hydrogenation of different aqueous pollutants: chlorophenols [7], chloronitrogenated aromatic compounds [8] and also azo and triarylmethane dyes with Pd as active phase [9]. The aim of this work was to study the removal of a triarylmethane dye (Fuchsine (Merck, 632-99-5)) by hydrogenation in aqueous phase under ambient-like operating conditions using own-prepared catalysts based on Pd, Pt, Rh and Ru supported on Al-pillared clay. The effect of reaction temperature was also tested.

The catalysts used were prepared by impregnation of Al-pillared clay calcined at 350 ºC. The impregnation of Pd, Rh or Ru was carried out with $PdCl_2$, $RhCl_3$ or $RuCl_3$ acidic solutions while an aqueous H_2PtCl_6 solution was used in the case of Pt. Further calcination at 500 ºC was accomplished in order to fix the active phase to the support. The metallic loads tested were 1% wt. Specific surface area values greater than 130 m^2/g were achieved in all cases. The catalytic activity experiments were performed in a batch stirred glass jacketed reactor (25 ºC, 1 atm, 100 mg/L dye initial concentration, 1 g/L of catalyst) using a continuous H_2 flow (50 mL/min). A previous reduction step of the catalysts was carried out for 2 h at 90 ºC under hydrogen flow. The hydrogenation process was followed from the evolution of the concentration of the reactant (fuchsine) measured by spectrophotometry.

Hydrogenation of fuchsine with the catalysts prepared at 25 ºC and 1 atm reached its complete removal only in the case of Pd catalyst. Pt catalyst yielded a removal percentage of the dye around 90% while Rh and Ru only reached around 65% of its removal. Parallel adsorption experiments showed that elimination of fuchsine by adsorption represented less than 30% in all cases. The effect of reaction temperature was carried out with the Pt catalyst. Complete dye removal was obtained at a reaction temperature of 40 ºC.

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VALORIZATION OF MUSSEL AND OYSTER SHELLS TOWARD METAKAOLIN-BASED ALKALINE ACTIVATED MATERIAL

Monneron-Gyurits Matthias (1), Joussein Emmanuel (1), Soubrand Marilyne (1), Fondaneche Patrice (1), Rossignol Sylvie (2)

(1) Université de Limoges, GRESE "Groupement de Recherche Eau Sol Environnement", Limoges, France, (2) Université de Limoges, SPCTS, Limoges, France

The valorization of oyster or mussel shells toward metakaolin-based geomaterials was investigated by XRD, SEM, FTIR and leaching tests. The aim is to better understand the feasibility and the reaction involved during the incorporation of shells (natural or calcined) into a metakaolin-based alkaline solution. Mixtures are realized by (i) the substitution of metakaolin aluminosilicate source by shells raw material (from 0 to 100% weight) or (ii) addition up to 50% weight. Substitution of metakaolin by shells was conducted without structure loss up to 40% and 30% addition, whether the used of oysters or mussels, thermally treated or not. In each addition or substitution, the results highlight the duality between both reactions i.e. polycondensation versus hydration. (i) using natural shells, only polycondensation reaction occurs due to the unreactivity of shells (interaction of shells with matrix by surface binding: role of aggregates or fillers); (ii) using calcined shells, coexistence of polycondensation in first followed (or stopped) by hydration reaction: presence of portlandite and C-(A)-S-H. Then the results show the role of calcium form (carbonate versus lime; reactivity) in metakaolin-based materials. The combination with geochemical leaching approach made it possible to obtain a better sensitivity than the structural methods ones by apprehending the reactions for low substitution or addition rates. Finally, the potential reuse of shells in alkaline activate material is quite effective and promising.

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NEW NANOFLUIDS BASED ON CLAY MINERALS AS PROMISING HEAT-CARRIERS FOR ENERGETICS

Vasily Moraru

The Department of Gas-Thermal Process and Nanotechnology, Gas Institute of National Academy of Science of Ukraine, 39, Degtyarivska Str., 03113 Kiev, Ukraine
vasily.moraru@gmail.com

The ability to increase the intensity of heat transfer, especially during boiling, is one of the most remarkable properties of “nanofluids” (NFs). Nevertheless, the thermal properties of clay minerals nanodispersions did not receive much attention by researchers for a long time. However, the so-called natural aluminosilicates - water based NFs exhibit a remarkable heat transfer capacity, particularly during boiling, so that they can be promising coolants for Energetics, than many other types of NFs such as oxides, carbides, etc, due to their superior heat engineering parameters. For example, the specific heat flux (SHF) at boiling of water-aluminosilicate NFs may increase to 300-400% compared to ordinary water and reach values q_{max} = 3-4.10^6 W/m^2, and the heat transfer coefficient (HTC) can exceed 40,000 W/m^2K [1-7].

Prior to the preparation of nanofluids from natural aluminosilicates (clays) for heat transfer purposes there their thermo-physical properties and heat engineering tests were first proposed and conducted [1-7]. The purpose of this work was to highlight some results of the heat transfer enhancement studies during boiling of NFs, based nanodispersions of Ukrainian natural aluminosilicates in water.

In an automated installation powered by DC [3], the boiling curves and HTC-dependencies on the superheat values (ΔT) under free convection conditions for the water nanodispersions of four natural aluminosilicates - hydromica, montmorillonite, palygorskite and mixtures of the latter two were obtained. In addition, the effect of some factors on pool boiling heat transfer was also studied [1-5].

A strong influence of the shape and anisotropy of nanoparticles (NPs) to the heat transfer parameters of NFs was detected. The maximum values of SHF and HTC were shown by NFs, which consist of NPs mixtures with various shapes and high anisotropy and which form at the boiling surface of the most delicate nanostructure with the most developed surface area, porosity and roughness. It is most likely that high heat transfer is due to the maximum density of vaporization centers and the area of heat exchange surface formed in these nanostructures [5].

The effect of a deflocculant on the heat transfer characteristics (SHF and HTC) at boiling of aluminosilicate nanofluids was also studied. Depending on the crystal structure of the nanoparticles and the type of electric heating current (AC or DC), the effect may be both positive or negative [1,2,5].

The “architecture” of nanostructures deposited on the heater surface during boiling of the nanofluids, plays an important role in the enhancement of heat transfer and in avoiding boiling crisis [5].

This study showed the effectiveness of aluminosilicate nanofluids for extra emergency cooling of overheated surfaces of powerful equipment in the event of the sudden onset of the boiling crisis [6,7].

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MANUFACTURING OF LIGHTWEIGHT AGGREGATES USING ORNAMENTAL ROCK SLUDGE, SEPIOLITE REJECTIONS AND CARBON FIBER WASTES

José Manuel Moreno-Maroto (1)*, Beatriz González-Corrochano (1),
Jacinto Alonso-Azcárate (1), Luis Rodríguez (2), Anselmo Acosta (3)

(1) University of Castilla-La Mancha. Department of Physical Chemistry, Faculty of Environmental Sciences and Biochemistry, Avenida Carlos III, s/n, 45071 Toledo, Spain, (2) University of Castilla-La Mancha. Department of Chemical Engineering, School of Civil Engineering, Av. Camilo José Cela, 2, 13071 Ciudad Real, Spain, (3) University of Castilla-La Mancha. Department of Physical Chemistry, Faculty of Chemical Sciences and Technology, Av. Camilo José Cela, s/n, 13071 Ciudad Real, Spain

Recycling processes have long been researched in the ceramic industry, contributing this way to diversify the offer of raw material and reducing in turn the costs of production [1]. Lightweight aggregates (LWAs) are granular materials of great porosity and low density, which are widely used in construction materials, agriculture, environmental and civil engineering purposes. Even though LWAs can have a natural origin, a meaningful number of studies have demonstrated that LWAs can be artificially manufactured from wastes [2].

In the present study, three different residues have been assessed for LWA manufacturing: granite and marble sludge as main component (COR), sepiolite clay rejections (SEP) and carbon fiber wastes (FC). As the sample COR was essentially non-plastic, the addition of a relatively low proportion of SEP clay had positive effects in the workability of the paste. Thus, the mineral base was comprised in all cases by a mixture of 10% SEP with 90% COR (w/w). In turn, 0, 2.5, 5 and 10% (w/w) of FC in the form of powder <500 μm was added to check its suitability as a bloating agent. The mixtures were milled, kneaded with water, extruded, shaped into pellets, oven-dried and finally fired at 1100, 1125 and 1150 °C for 4, 8 and 16 minutes in a rotary kiln. The sintering behavior observed was different depending on the composition. Thus, in the case of those specimens not containing FC, neither bloating effect was observed. Despite this, the LWA sintered without FC at the minimum time (4 min) and temperature of firing (1100 °C) presented the higher value of water absorption (24.2%). A water suction capability test pointed out that this LWA could be suitable in hydroponics and/or water filtration systems, even better than the commercial LWA Arlita G3, due to its microporous structure.

Concerning those aggregates containing FC, the behavior of granules during firing varied depending on the proportion of FC and the temperature, but in any case, all of them were lightweight. Furthermore, the addition of FC not only implied lightness and expansiveness, but also the development of a singular internal structure in which unburnt carbon fibers were embedded, exerting an extra reinforcing effect. Thus, at 1100 °C even though no important changes in density were observed, enhancements in mechanical strength (values around 10 MPa) were achieved mainly with 5% and 10% of FC in the mixture. At 1125 °C pore formation was promoted especially with 2.5% and 5% of FC, and meaningful compressive strength measurements were recorded in some varieties (>10 MPa). Only two sorts of LWAs could be sintered at 1150 °C because FC fostered melting at this temperature. These two ones were fired for 4 min with 2.5% and 5% of FC, achieving a significant bloating effect linked to a great porosity and a very low density. A large number of these LWAs hold excellent properties to be used in concrete manufacturing.

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HYBRID NANOCOMPOSITS CONTAINING POLYMERS OF TETRONICS AND CLAY: PLATFORM FOR ANTI-CANCER THERAPY

Gabriel Bezerra Motta Câmara, Yane Paiva Bruna Galvão, Fernanda Nervo Raffin, Túlio Flávio Accioly de Lima e Moura*, Raquel de Melo Barbosa*

Department of Pharmacy, Federal University of Rio Grande do Norte, 59010-180 Natal, RN, Brazil

Lapacholis a natural product, chemically identified as anaphthoquinone, extracted from various species of plants of the *bignoniciae* family; found in the Brazilian northern and northeastern regions. β-lapachone (βLAP), is a drug that has antiviral, antiparasitic, antitumor and anti-inflammatory properties showing promising potential in various biomedical applications[1]. However, βLAP(0.038 mg mL^{-1}) has low water solubility that limits its systemic administration and clinical applications *in-vivo*. Nanocomposite (NC) hydrogel nanoparticles within a hydrated, polymeric gel matrix, are offering increasing uses in the biomedical field, which may simply arise from the added properties of the bulk and the dispersed phase, but also based on specific features imparted by the additional junction points formed as the polymer chains adsorb onto the nanoparticle surfaces, leading to new characteristics such as improved mechanical properties, elasticity and the sol-gel transition. Tetronic®, or poloxamine is an amphiphilic four-arm (X-shaped) block copolymer of poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) (PEO-PPO-PEO) with a pH-sensitive central ethylene diamine spacer[2, 3]. Tetronics focused on here are T1304, T904 and T90R4 (reverse Tetronic®), varying in EO/PO ratios. Laponite nanoparticles are disk-like synthetic clays, with an empirical formula of $Na^{+}_{0.7}[(Si_8Mg_{5.5}Li_{0.3})O_{20}(OH)_4]^{-0.7}$. Laponite surfaces exhibit negative charges whereas the edge charges are pH dependent[4].

The objective of this project was the development of a multifunctional platform to be used as a nanotechnological system using polymeric micelles prepared with the copolymer Tetronic® with or without the presence of LAP. Thus, different Tetronics were used in varying in proportions of EO/PO and Laponite RD (LAP), a synthetic clay widely used as a rheological modifier.

Samples were prepared by simple mixing or dispersion of components with different concentrations of the polymers, T904, T90R4 e T1304 (1 to 20% (w/w))with or without 3% (w/w) LAP. The parameters studied were: (i) structural description of Tetronic® micelles and formulations with or without Laponite, being evaluated the Phase behavior (in the interval of 20 - 80 °C) and analysis of physico-chemical aspects, through the evaluation of the hydrodynamic radius and polydispersity index (PDI) by Dynamic Light Scattering; (ii) partitioning of the ß-LPC in thehybrid and micellar systems. The ß-LPC was quantified by spectrophotometry in *UV*/*VIS* at 25 7 nm. The results showed a strong influence of the temperature and concentration of the polymer in the formation of the giant micelles and the hybrid hydrogels. At high temperature, it was observed the formation of gels associated with an increased size of the micelles. Tetronics® are capable of modulating the gelation of the formulations in the presence of LAP, because the polymer chains are adsorbed onto their surfaces. However, samples containing reverse Tetronic® (T90R4), with the PPO units in the outer portion of the structure, and the direct Tetronic® T1304, in presence of the LAP promoted the formation of stronger samples than others. Additionally, the samples containing a mixture ofT1304 with 3% de LAP demonstrated greater ß-LPC solubilization capacity in all concentrations evaluated at natural pH. The solubility was increased33.4x when compared to water´s solubility. It is believed that all aspects of this study are relevant to the potential development of therapies based on Tetronic® and hybrid systems prepared with Tetronic® 1304 and LAP. Thus, it intended to prove that Tetronic® associated with LAP or not could be an attractive multifunctional platform for cancer therapy using ß-LPC.

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MODELING AQUEOUS SOLUBILITY OF SODIUM CHLORIDE IN CLAYS AT THERMODYNAMIC CONDITIONS OF HYDRAULIC FRACTURING BY MOLECULAR SIMULATIONS

Filip Moučka (1,2)*, Martin Svoboda (1,2), Matin Lísal (1,2)

(1) Laboratory of Aerosols Chemistry and Physics, Institute of Chemical Process Fundamentals of the CAS, v. v. i., Prague, Czech Republic, (2) Department of Physics, Faculty of Science, J. E. Purkinje University, Ústí nad Labem, Czech Republic

To address a high salinity of flow-back water during hydraulic fracturing we study equilibrium partitioning of NaCl and water between bulk saturated solution and clay pores. We use an advanced Grand Canonical Monte Carlo (GCMC) technique [1] based on fractional exchanges of dissolved ions and water molecules. We consider a typical shale gas reservoir condition of 365 K and 275 bar, and we represent clay pores as neutral pyrophyllite and Na-montmorillonite (MMT) slits of the width ranging from about 0.7 to 2.8 nm. We employ the Joung-Cheatham model for ions [2], SPC/E model for water and CLAYFF [3] for the MMTs. We first determine chemical potentials of the ions and water in the bulk phase using Osmotic Ensemble Monte Carlo simulations [4]. The chemical potentials are then used in GCMC to simulate adsorption of ions and water molecules in the clay pores, and in turn to predict the salt solubility, i.e., ion concentrations, in the confined solutions. Besides thermodynamic properties, we evaluate the structure and in-plane diffusion of the adsorbed fluids, and conductivities of ions.

Our molecular simulations show that the overall concentrations of adsorbed ions in the clay pores are lower with respect to the bulk phase. The Na-MMT with hydrophilic pore walls can adsorb more water than the slightly hyrophobic pyrophyllite. On the other hand, the Na-MMT pores exhibit lower concentrations of adsorbed ions when compared with the pyrophyllite pores of the same width due to the presence of compensating sodium ions on the Na-MMT surface. Atomic density profiles used to investigate the distributions of ions and water molecules in the clay pores show a progressive formation of one-layer, two-layer, and two-layer plus bulk-like layer structures depending on the width of the pores. For wide pores with the bulk-like layer in the middle, the ion concentration can be expressed as a sum of contributions from the surface and bulk-like layers proportional to the relative widths of these layers. As regards diffusion of ions and water, in pyrophyllite, it tended to be slightly faster than in the bulk phase; in Na-MMT, the effect is opposite due to the presence of compensating sodium ions on the clay surface. Ion conductivities then reflect combined effects of variation of the ion self-diffusion coefficients and ion concentrations.

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CLAY MINERALS OF UPPER VISEAN AGAB OU ISSAWI FORMATION (CENTRAL MOROCCO): DIAGENETIC, CLIMATE AND TECTONIC SIGNATURES

Hassan Mounach*, Mostafa Berkhli, Hafsa Tourab, Amal Hachimi

University of Moulay Ismail, Faculty of sciences, Department of geology. PO. Box 11201 Zitoune, Meknès - Maroc
m.berkhli@fs-umi.ac.ma

The Jebel Agab Ou Issawi Formation is exposed in the eastern part of central Morocco. It's located at the North of Mrirt city, less than two kilometers to the east of secondary road S331 connecting Meknes to Khenifra. This Formation rests in angular unconformity on the Devonian series. It is composed of diversified facies, argillites, olistoliths, limestone tempestites, polygenic conglomerates and sandy limestones. These facies vary laterally and vertically [1]. The aim of this work is to determine the clay mineral composition of these deposits and to specify their diagenetic, climatic and tectonic signatures.

The qualitative and semi-quantitative analysis of the X-ray diffractograms shows that these samples are composed of simple clay minerals, illite, chlorite, kaolinite, vermiculite and mixed layer clay minerals, illite-chlorite and illite-vermiculite.

Towards the top of the section, the distribution of the various Clay minerals shows the abundance of inherited clay minerals (illite, kaolinite), which can be interpreted as the result of surface alteration of the silicate minerals of a back land which feeds a carbonate platform under a tropical climate, warm and humid, during the Upper Viséan.

To the depth, the gradual increase in pressure and temperature conditions favors the effects of burying diagenesis, which on the one hand causes the disappearance of sensitive kaolinite under such conditions, and on the other hand allows the appearance of mixed layer clay, illite-chlorite and illite-vermiculite which are more stable under these new conditions.

The representation of the illite crystallinity as a function of the ratio I002 / I001 of the illite on the Esquevin diagram show that the majority of points are localized in the diagenesis and anchizona area, indicating that the degree of metamorphism that affected this Formation is too low. Exceptionally, on the same diagram, four samples are located in the epizona area, indicating an increase in pressure and temperature probably related to the tectonic activity of the faults. Such a transformation was, however, at the origin of the disappearance of the minerals sensitive to the increase of pressure and of temperature like the kaolinite and the appearance of new clay minerals stable under these conditions. Moreover, the ratio I002 / I001 of the illites is greater than 0.3, indicating a aluminous character of the illites and a strong evolution of the sediment [2].

The study of the evolution of the clay minerals assemblage along the Agab Ou Issawi Formation (Bouchbel, central Morocco) shows that the sedimentary stacking of this Formation took place in a tropical climate, warm and humid, and evolved under low diagenetic conditions indicating a low burial (<4000 m).

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LITHIUM MODIFIED CLAY NANOPARTICLES FOR INJECTABLE OSTEOGENIC STEM CELL MICROENVIRONMENTS

Mohamed Mousa, Nick Evans, Richard O. C. Oreffo, Jon Dawson

B & J Research Group, Stem Cells & Regeneration, Institute of Developmental Sciences, University of Southampton, Southampton, SO16 6YD, United Kingdom

Despite being still in its infancy, research exploring the potential of clay nanoparticles in regenerative medicine is currently receiving a growing interest and suggests new unexplored opportunities for biomaterial design and enhanced tissue regeneration. For instance, recent studies have demonstrated the ability of Laponite-clay nanoparticles to self-organize into injectable microenvironments able to host and stimulate stem cell growth and differentiation for tissue regeneration [1,2]. Furthermore, it has been shown that Laponite nanoplatelets alone can induce *in vitro* osteogenic differentiation of human bone marrow mesenchymal stem cells (hMSCs) and human adipose derived stem cells (SSEA-4+hASCs) without the need of any external growth factors such as BMP-2 or dexamethasone [3,4]. However, relatively little attention has been given to the role of clay mineral structure/composition in influencing such clay - stem cell interactions. Regarding Laponite, its degradation products: $Si(OH)_4$, Mg^{2+}, and Li^+, are each known to influence osteogenic cell function. Lithium, in particular, is known to modulate the canonical Wnt signalling pathway through the inhibition of GSK3β and stimulates osteogenic differentiation of responsive population [5].

In this work, various Li^+-modified Laponite formulations have been successfully generated in collaboration with BYK-ALTANA. The XRD, XRF, AAS and chemical analysis confirmed that standard, low and high structural Li^+ Laponite clay have been successfully synthesized, followed by efficient Li^+ exchange reactions producing Laponite nanoparticles with Li^+ content ranging from 0 to 9.9 g/kg. Modified clay formulations were biologically investigated to shed the light on clay-enhanced osteogenesis. Human bone marrow stromal cells (HBMSCs) were cultured in contact with various concentrations of the tailored clay nanoparticles, as culture media additives, and assessed for cell viability, proliferation and osteogenic differentiation in response to structural and cation-exchanged lithium modifications of Laponite.

The effect of Laponite nanoparticles, dispersed in tissue culture media, on HBMSC viability and proliferation was evaluated via the WST-1 assay and showed high cytocompatibility at concentrations of dispersed Laponite up to 1 mg/ml. Addition ofunmodified Laponite nanoparticles in the tissue culture media (up to a concentration of 100 μg/ml) increased expression of the osteogenic genes (ALP, RUNX2, Collagen I, Osteocalcin, Osteopontin and Osteonectin), increased alkaline phosphatase enzyme activity and enhanced calcium phosphate deposition. Interestingly structurally modified Laponite formulations slightly attenuated osteogenic differentiation of clonal (CFU-F) cultures of HBMSCsirrespective of Li^+ content suggesting a mechanism independent of the Li^+ content of the clay mineral. Other clay chemistries such as surface charge, particle size and Cation Exchange Capacity may play a role in modulating the osteogenesis of hMCSs. Such studies seeking to elucidate the mechanism behind clay-enhanced stem cell ostegenesis are ongoing.

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CERAMICS IN TUNISIA

Béchir Moussi (1), Mondher Hachani (1,2), Walid Hajaji (3), Fernando Rocha (4), Alberto Lopez Galindo (5), Johan Yans (6), Michele Dondi (7), Fakher Jamoussi (1)

(1) Georessources Laboratory, CERTE, 273, 8020 Soliman, Tunisia, (2) ISE Borj Cédria, Tunisia, (3) Natural Water Treatment Laboratory, CERTE, (4) Geobiotec, Geosciences Dept, University of Aveiro. 3810-193 Aveiro. Portugal, (5) (IACT), CSIC-University of Granada, Aveda. Palmeras 4, Armilla, Granada, Spain, (6) University of Namur, 61, rue de Bruxelles, 5000 Namur, Belgium, (7) Institute of Science and Technology for Ceramics Faenza, Italy
fjamoussi@yahoo.com

The ceramics sector in Tunisia includes 49 brick manufacturing plants, 101 artisanal bricks plants, 15 earthenware factories and 10 sanitary units. The consumption of clay in Tunisia in this activity is about 9 million tons per year distributed among the brick, earthenware, sanitary, refractory, binders and artisanal pottery sectors. Tunisia mines the sedimentary clay levels extending from the Triassic to the Pliocene and imports almost 149 thousand tons of clay per year, to meet this demand.

We have carried out research from the South to the North of Tunisia covering the entire stratigraphic series (Jamoussi, 2001, Hajjaji et al., 2010, Hachani 2011, Moussi et al., 2011).

The clay levels of the sedimentary series which contain illite, kaolinite, halloysite and which are likely to be used in ceramics are: clays of the Triassic of the Saharan platform, clays of the Lower Cretaceous over all Tunisia, clays of the Oligocene and Eocene of northern Tunisia and some clays of the Mio-Pliocene of northern Tunisia.

We performed a large sampling in the studied levels. These clays have undergone a physic-chemical identification including a mineralogical, geochemical study of the major elements, infrared spectroscopy, DTA-TGA and the determination of plasticity. We have also carried out ceramic tests with the studied clays. In this way, we have prepared bricks and ceramics on the scale of the laboratory, on which we have performed ceramic tests including the determination of the Bigot curve, the dilatometric curve, bending tests, compression tests and porosity tests on the manufactured parts.

The laboratory and semi-industrial technological tests were moreover carried out on the clays in order to decipher their ceramic potential. These analyses show that the Paleocene, Eocene and Oligocene clays give very satisfactory results in the production of bricks. The Triassic and lower Cretaceous clays are used for the manufacture of ceramic tiles. Some of them have given good results in both the production of bricks and the manufacture of ceramic tiles.

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EFFECT OF CLAY MINERALS ON THE COLOR OF COBALT BLUE/CLAY MINERAL HYBRID PIGMENTS

Bin Mu*, Anjie Zhang, Xiaowen Wang, Aiqin Wang

Key Laboratory of Clay Mineral Applied Research of Gansu Province, Center of Eco-material and Green Chemistry, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, PR China
aqwang@licp.cas.cn (A. Wang)

Cobalt blue ($CoAl_2O_4$) is an eco-friendly inorganic colored pigment with an intense blue color prepared by sintering cobalt(II) oxide with alumina at high temperature [1]. Due to the high refractive index, good chemical stability, excellent weather ability and thermal stability, cobalt blue is widely applied in the various fields of ceramics, plastics, paint, rubber and glass [2]. However, the high production cost of cobalt blue severely limits their wide applications owing to the scarcity in nature of cobalt ores. In addition, cobalt blue prepared by traditional solid-phase method is always associated with undesired by-products, [3] which decrease its color property and environmental stability. In recent years, substrate-based inorganic hybrid pigments have received much attention based on the hybrid principle between inorganic pigments and inorganic substrates [4-6]. Due to the abundance in nature, low-cost, non-toxic and unique structure features, clay minerals can be served as a excellent substrate materials for loading of inorganic nanoparticles. Thus our groups firstly prepared cobalt blue hybrid pigments incorporating of clay minerals by co-precipitation method followed a calcination process [7,8]. It confirmed that the incorporation of clay minerals was a feasible strategy to decrease the production cost of cobalt blue hybrid pigments, but the introduction of clay minerals affected the chroma of cobalt blue. Therefore, it is necessary to study this negative effect to fabricate the high-grade cobalt blue pigment with low-cost and excellent color performance.

In this work, we systematically investigate the effect of different clay minerals on the color property of cobalt blue, including attapulgite, sepiolite, halloysite, kaolin, illite-smectite clay, montmorillonite, and mullite. It was found that the characteristic diffraction peaks of clay minerals disappeared from the XRD patterns of the hybrid pigments, and the diffraction peaks located at $2\theta = 31.1, 36.8, 44.8, 49.0, 55.5, 59.2, 65.2$ corresponded to (220), (311), (400), (331), (422), (511) and (440) plane of spinel $CoAl_2O_4$, [9] indicating that the type of clay minerals almost had no effect on the crystalline phase of $CoAl_2O_4$. In addition, the cobalt blue nanoparticles with a diameter of about 10~20 nm were well coated on the surface of clay minerals. It suggested that the introduction of clay minerals could effectively prevent from the agglomeration and the size increase of cobalt blue nanoparticles during high temperature crystallization process. However, the color property of hybrid pigments was dependent on the type of clay minerals, which was mainly ascribed to difference in the composites and thermal stability of clay minerals. The high aluminum content of clay minerals is favor of enhancing the color property of hybrid pigments, and the value of b^* could reach -55, which was superior to the reported ones. It is expected to prepare the high-grade cobalt blue with low-cost and excellent color property by incorporating of the appropriate clay minerals.

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INFLUENCE OF CLAY-BOUND SODIUM-DODECYL SULFATE ON ELECTROCHEMICAL BEHAVIOUR OF NICOTINE

Tihana Mudrinić*, Zorica Mojović, Aleksandra Milutinović-Nikolić, Nataša Jović-Jovičić, Predrag Banković, Sanja Marinović, Dušan Jovanović

University of Belgrade - Institute of Chemistry, Technology and Metallurgy, Centre for Catalysis and Chemical Engineering, Njegoševa 12, 11000 Belgrade, Republic of Serbia

In this study, electrode coating based on sodium dodecyl sulfate (SDS) bound to smectite clay was synthesized and characterized. In order to enable SDS bonding to clay surface, the acid modification of clay was previously performed at 90 ºC for 2 h. The acid modification changed surface charge of smectite into positive, thus enabling electrostatic interaction with negative sulfate ions from SDS. The presence of SDS in SDS/acid modified smectite (SDS/AMS) structure was confirmed by elemental analysis. SEM analysis revealed the morphology of the obtained sample. Glassy carbon electrode (GCE) was modified with a suspension of the synthesized SDS/AMS and Nafion® solution (GCE-SDS/AMS) and a uniform film was obtained [1]. The electrochemical behaviour of nicotine was tested with modified GCE using cyclic voltammetry. It has been shown previously that the electrochemical response of nicotine on carbon based electrodes can be improved by adding SDS into electrolyte solution [2]. On the other hand, clays have the ability to preconcentrate analytes because of their porous structure and the presence of potential active sites [3]. Acid activated clays can be modified with SDS [4]. Therefore, the aim of this study was to investigate the influence of SDS bound to smectite on the electrochemical behaviour of nicotine. Britton-Robinson (BR) (0.1 M) supporting electrolyte buffer solutions in the pH range from 2.0-10.0 was used for preparing the supporting electrolyte of nicotine. The influence of the pH of the supporting electrolyte, scan rate and accumulation time were investigated and discussed. The GCE-SDS/AMS exhibited similar electrochemical behaviour in comparison with the bare GCE but with the differences in the intensity and position of peak corresponding to nicotine oxidation. The intensity of the oxidation peak was lower on the GCE-SDS/AMS that on the bare GCE. In contrast, the onset and peak potentials were significantly shifted towards less positive values on the GCE-SDS/AMS comparing with the bare GCE. On the other hand, the nicotine peak intensity increased gradually as the accumulation time increased. Therefore, selecting the appropriate accumulation time the sensitivity of the GCE-SDS/AMS can be improved. The above results demonstrate the possibility of use the synthesized SDS/AMS in the nicotine electrooxidation process.

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FORMATION OF TURBOSTRATIC BRUCITE AND ITS NANOSHEETS BY REVERSIBLE MODIFICATION WITH DIPODAL LIGANDS

Keisuke Muramatsu (1)*, Yoshiyuki Kuroda (2), Atsushi Shimojima (3), Hiroaki Wada (3), Kazuyuki Kuroda (3,4)

(1) Department of Advanced Science and Engineering, Faculty of Science and Engineering, Waseda University, Tokyo, 169-8555, Japan, (2) Waseda Institute for Advanced Study, Waseda University, Tokyo, 169-8050, Japan, (3) Department of Applied Chemistry, Faculty of Science and Engineering, Waseda University, Tokyo, 169-8555, Japan, (4) Kagami Memorial Research Institute for Materials Science and Technology, Waseda University, Tokyo, 169-0051, Japan
kuroda@waseda.jp

Brucite-type metal hydroxides, composed of various divalent transition metal cations, are promising precursors for nanosheets with diverse functions; however, their intercalation and exfoliation are relatively difficult because of their nonexistent or very low layer charges. Recently, we have reported that interlayer modification of brucite-type metal hydroxides with tripodal ligands, such as tris(hydroxymethyl)aminomethane ($H_2NC(CH_2OH)_3$; Tris-NH_2) through a tridentate alkoxy bonding, being stable to hydrolysis even in water [1]. The hybrid metal hydroxides can intercalate various organic molecules and can be exfoliated in water because of weakened interlayer interactions, though the immobilized organic groups seem to prohibit adsorption of substrates directly on inorganic sheets, which is disadvantageous for their use as catalysts, adsorbents, and so on. Thus, it is better to remove surface functional groups after the formation of hybrid nanosheets, and we have also reported that a bidentate alkoxy bonding is formed in organic solvents and the bidentate bonding is hydrolyzed in water [2]. Here, we report *reversible* modification of brucite layers with a dipodal ligand. The ligand can be immobilized in an organic solvent and removed in water. We also found for the first time that turbostratic brucite, which is also exfoliated in water, is obtained after the removal of dipodal ligand from the hybrid nanosheets. Dimethyl sulfoxide (DMSO) containing a small amount of H_2O was used for the synthesis of brucite modified with a dipodal ligand (2-amino-1,3-propanediol; $H_2NCH(CH_2OH)_2$;Bis-NH_2). The solutions of $MgCl_2 \cdot 6H_2O$ and Bis-NH_2 were mixed and stirred at specified temperature. The gelled product was separated by filtration, washed with methanol twice, and dried at 80 ºC for 12 h (Mg-Bis-NH_2). The dipodal ligand was removed from Mg-Bis-NH_2 by dispersing it in deionized water, followed by centrifugation. Mg-Bis-NH_2 has a pseudo-hexagonal lattice with a turbostratic structure because the powder XRD pattern is almost the same as that of the hybrid magnesium hydroxide modified with Tris-NH_2 reported previously by us [1]. The^{13}C CP/MAS NMR spectrum showeda downfield shift of the signal due to methylene carbon of Bis-NH_2, indicating the formation of the bidentate alkoxy bonding with brucite layers. In contrast, when the same reaction was conducted in water, only non-modified brucite was formed, indicating the critical role of the controlled amount of water to suppress the hydrolysis of alkoxy bonds. WhenMg-Bis-$NH_2$was dispersed in water, the dipodal ligands were hydrolyzed and completelyremoved from the layer surface of brucite. The amount of nitrogen, related directly to the amount of Bis-NH_2, decreased from 4.7 wt% to the level underthe detection limit. Although 2.1 wt% of carbon was detected even after the treatment, this carbon was probably ascribed to adsorbed carbonate ions because C-O stretching vibrations due to carbonate were observed in the FTIR spectrum. Consequently, Bis-NH_2 was completely removed by the treatment. Interestingly, a new diffraction peak was observed, even though most of the diffraction peaks are attributable to conventional brucite (JCPDS #44-1482). The new peak at d = 0.51-0.52 nm, slightly larger than the normal basal spacing of brucite (0.48 nm), should be attributed to the basal spacing of the product. Also, the ED pattern of the Mg-Bis-NH_2 treated with water was ring-like, suggesting turbostratic stacking of brucite nanosheets. When brucite has the usual basal spacing, surface hydroxy groups are regularly interdigitated; however, the interdigitated configuration should not be formed when they are randomly stacked. Thus, the slight increase in the basal spacing is reasonable. This compound composed of randomly stacked brucite nanosheets was easily swollenin water. In addition, theywere re-exfoliated in water via ultrasonication. The AFM images of spin-coated brucite nanosheets showed a sheet-like particle with the thickness of ca. 0.5 nm. In conclusion, dipodal ligand is a useful organic modifier for brucite-type metal hydroxides. It is immobilized on it in organic solvents, and removed in water. These processes lead to the formation of turbostratic nonmodified brucite which is swollen with water and exfoliated into nanosheets. The behaviour is totally different with conventional brucite, which open a new field of layered metal hydroxides.

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INTERACTION OF SUGAR CANE VINASSE AND CLAYEY SOIL IN THE NORTHWEST OF URUGUAY

Marcos Musso (1)*, Lyliam Loperena (2), Verónica Saravia (2)

(1) Instituto de Estructuras y Transporte, (2) Instituto de Ingeniería Química, Facultad de Ingeniería, Universidad de la República, Montevideo, Uruguay

Since the middle of the 20th century, sugar cane has been cultivated in Bella Unión, Uruguay. Initially only sugar was produced, but recently approved fuel government policy promotes and regulates ethanol addition to fuel. Alcohol production generates 10 to 15 vinasse per litre of ethanol. This sugar industry efluent contains organic matter as well as K, N, and P among other elements, so could be used as a soil nutrient source. Some experience using vinasse fertigation was developed in tropical soils in Cuba and Brasil, among others. However in temperate (?) climate soil less research has been published. In particular in Uruguay this technique has been implemented recently for the first time. The environmental protection agency of Uruguay has demanded research about soil response to vinasse fertigation.

The research was developed in two typical soils in the sugar cane area. One of them (L1) is a clayey soil, with an argillic B horizon, developed over Quaternary sediments of the Libertad Formation. The second soil (B1) is a clayey sand soil, developed over Cretaceous basalt of the Arapey Formation. These kinds of soils occupy 30 percent of the sugar cane area. Four sites of each soil were selected to spread vinasse in different concentrations by hectare: 0, 150 m^3, 300 m^3, 450 m^3. Before vinasse was spread, soil samples were collected for physical and mineralogical analysis in laboratory. Hydraulic conductivity in field using double ring methods was measured and soil solution was collected with lisimeter at 20 cm and 40 cm deep to analyse cations, pH and electrical condutivity (EC) as base line. After vinasse application, 4 to 6 soil and soil solution samples were collected for 12 months to evaluate chemical transport through the soil. In laboratory, the soil physics, cation exchange capacity (CEC) and X-ray diffraction (XRD) mineral analysis were performed. Hydraulic condutivity was developed in constant head with water.

The L1 sandy clay loam to clay soil with 1.6%(?) of organic matter in A horizon contains CEC values of 13 to 24 $cmol_c$/kg with calcium and magnesium as main exchange cations. Clay mineralogy is a mixture of smectite and illite with a low amount of kaolinite. The B1 clay loam to sandy clay loam with 3.9%(?) of organic matter in A horizon contains CEC values of 24 to 31$cmol_c$/kg, also with calcium and magnesium as main exchange cations. Clay mineralogy is mainly smectite with low amounts of illite. Hydraulic conductivity in field was $1x\ 10^{-7}$ m/s to $5\ x10^{-8}$ m/s and $1x\ 10^{-7}$ m/s to $8\ x10^{-7}$ m/s for L1 and B1 respectibility. In laboratory, L1 and B1 hydraulic conductivities were lower than 10^{-10} m/s. In L1 sites, pH values were between 6 and 7 in all sites during the test. The EC values in the different L1 sites were greater than base line values, but within a few months the values of the different sites were similar to 0 vinasse application site. In B1 sites, soil pH values were between 6.5 and 7 in all sites during the test. The EC values in the different B1 sites had greater values than baseline, but these values were lower than the L1 site values. Like L1, after a few months the pH and EC values of the different sites were similar to the 0 vinasse application site. The medium to high CEC and the clay content were responsable for cation adsorption and low transport through soil horizont.

The soils analysed had different behaviours caused by differences in inorganic composition. After one year application no increase was observed in K concentration, hydraulic conductivity or pH. To evaluate long time effects of vinasse fertigation in physical and chemical soil properties, monitoring should be continued.

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Keywords: vinasse, clay soil, adsorption, hydraulic conductivity.

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LIBERTAD CLAY: POTENTIAL USE IN ENVIRONMENTAL CLAY BARRIER

Marcos Musso (1)*, Ramiro Rodriguez (1), Gonzalo Bango (1), Alfonso Flaquer (2)

(1) Instituto de Estructuras y Transporte, (2) Instituto de Mecánica de los Fluidos e Ingeniería Ambiental, Facultad de Ingeniería, Universidad de la República, Montevideo, Uruguay

Clay barriers have been frequently used in environmental protection in the last decades and clayey formations are used as alternative or complement to develop wastewater treatment lagoons and landfill. Hydraulic conductivity lower than 10^{-9} m/s and granulometric size without cobbles are the main properties required by environmental legislation in different countries. However, there are no recommendations about clays composition or adsorption clay capacity. Clayey soil areas are explored to obtain raw material or to locate landfill and treatment lagoons.

Libertad formation is a Quaternary clayey and silty clayey sediments very common in the south of Uruguay which overlay Precambrian (igneous and metamorphic) rocks, sedimentary rocks and Cenozoic sediments. Libertad formation was studied in the last decades because it shrinks when dry and swells when wet. This behaviour produced damage to civil infrastructures generating economic losses. Libertad clay is mainly composed of smectite, with small amounts of illite and little kaolinite. With this initial knowledge, we evaluated the behaviour of Libertad formation for its use as a natural and compacted clay barrier.

Two different sites near Libertad city were analysed. Samples were taken using an auger at every 0.5 m until 3 m depth. Undisturbed samples were obtained at 1, 2 and 3 m depth. Soil clasificacion using Soil Unified Classification System was developed and dry unit weight, porosity, moisture, specific gravity were determined. Clay mineralogy was determined using X-ray diffraction and cation exchange capacity (CEC) by acetate ammonium method. Hydraulic conductivity was determined in the laboratory by the constant head method.

At Site 1, all samples have low sand content (1-3%) and similar silt (43-61%) and clay (36-55%) contents. Soils are Lean clay CL, Fat clay CH, Elastic silt MH. CEC soil values were 25 to 41cmol/kg and the clay fraction was composed of smectite and illite. At Site 2, all surface samples have low sand content (2-4%) which increased with depth up to 15%. Silt content (58-61%) was higher than clay (39-48%). Soils in different depths are Lean clay CL. CEC soil values ranged from 23 to 33 cmol/kg and clays were composed of mostly smectite, with medium to low illite content. Hydraulic conductivity values at both sites are lower than 10^{-9} m/s as is required by differents environmental regulations. Today Libertad formation is used as barrier, but it has not data published about hydraulic properties or perfomance. Then, the values obtain in this research show that the Libertad clay has hydraulic conductivity and adsorption capacity that it could be used as clay barrier in order to protect soils and groundwater.

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ORIENTATION OF NIOBATE NANOSHEETS LIQUID CRYSTALS BY RADIATION PRESSURE OF A LASER BEAM: DEPENDENCE OF ORIENTATION ON POLARIZATION DIRECTION OF THE LASER BEAM

Takashi Nagashita (1)*, Yuki Higashi (2), Makoto Tominaga (3,4), Yasutaka Suzuki (1,2,3), Jun Kawamata (1,2,3), Takuya Kumamoto (5), Teruyuki Nakato (5)

(1) Graduate School of Sciences and Technology for Innovation, Yamaguchi University, Yamaguchi 753-8512, Japan, (2) Faculty of Science, Yamaguchi University, Yamaguchi 753-8512, Japan, (3) Graduate School of Medicine, Yamaguchi University, Yamaguchi 753-8512, Japan, (4) Research Fellow of Japan Society for the Promotion of Science, Tokyo 102-0083, Japan, (5) Department of Applied Chemistry, Kyushu Institute of Technology, Fukuoka 804-8550, Japan
j_kawa@yamaguchi-u.ac.jp

We have found the orientation of colloidally dispersed inorganic nanosheets can be changed by radiation pressure of a focused laser beam [1]. However, the induced orientation of nanosheets are still not clear. In this study, we systematically investigated the orientation of the inorganic nanosheets at a focal point.

Nanosheet colloids consisting of niobate nanosheets with a lateral size of ~1.6 mm were prepared at concentrations of 2.5, 5.0 and 10 g/L. The colloids were mixtures of isotropic and liquid crystal phases. Niobate nanosheet colloid sample was injected to a thin-layer cell which made by a glass slide and a cover glass with a spacer of 100 μm. A linearly polarized laser beam ($\lambda = 532$ nm, 100 mW) was irradiated to the samples mounted on a polarized microscope through an objective (x25, N.A. = 0.4). The polarization direction of the irradiated laser beam was controlled by rotating a half wave plate. The orientation of niobate nanosheets at a focus was evaluated from the brightness of polarized microscope images

When the angle between polarization directions of a laser beam and polarizer or analyser was 45°, the bright spot was observed at a focal point. This observation indicated that the niobate nanosheets were directed to 45° with respect to the polarizer or analyser of polarized microscope by polarization of laser beam. On the other hand, when the angle was rotated to be 0°, the focal point became dark. The dark spot means the niobate nanosheets are oriented to be 0° to the polarizer or analyser of polarized microscope [2]. The niobate nanosheets were found to align along the polarization direction of incident laser beam. During rotating the polarized direction of light, the bright and dark spots were alternatively appeared at every 45°. Such phenomena were observed from all samples treated in this study.

When the rotation speed of polarization direction of the laser beam was slower than 2π rad/min, the orientation change of colloidal niobate nanosheets with a concentration of 2.5 g/L followed the rotation of polarization of the laser beam. When the concentrations were 5 g/L and 10 g/L, the maximum rotation speeds which can induce the orientational change of niobate nonasheets were π rad/min and $1/2\pi$ rad/min, respectively. Thus, the slower rotation speeds were required for the orientational change of higher concentration of the colloidal niobate nanosheets, namely higher viscosity of the colloids.

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THE EVOLUTION OF ELECTRICAL RESISTIVITY OF CLAYS DURING ELECTRO-OSMOSIS

Milad Naghibi (1)*, Hossam Abuel-Naga (2), Rolando Orense (1)

(1) Dept. of Civil and Environmental Engineering, Univ. of Auckland, Auckland 1142, New Zealand, (2) La Trobe Univ., Plenty Rd. and Kingsbury Dr., Melbourne, VIC, Australia

Electro-Osmosis (EO), which is a subgroup of electro-kinetic processes, is defined as the water movement in the fine-grained soil body due to external electrical potential gradients (voltage). EO is applied in many fields of science and technology, such as in geology, geotechnics, ground improvement, treatment of hazardous materials and dewatering of clays. Generally, the volume of transported water, efficiency and also the distribution of current and voltage in the soil during EO are controlled by the soil's electrical resistivity. In the absence of electric gradient, the electrical resistivity of the soil depends on numerous factors, such as void ratio, behaviour of pore solution and soil mineralogy. Once the voltage is applied, depending on boundary conditions, Electro-Hydro-Mechanical (EHM) and/or Electro-Chemical (EC) processes occur which highly affect the laboratory-measured electrical resistivity of the soil. In this paper, the effect of EHM and EC are separately investigated. Then the interactions of both processes are studied under the framework of EO consolidation where EHM and EC take place concurrently. It was found that, neglecting EC processes, EHM processes, which lead to reduction of void ratio, increase the soil electrical resistivity progressively. In that case, the clay surface conductivity becomes an important parameter. In addition, in the absence of EHM processes, EC processes will lead to generation of various zones in terms of electrical resistivity which are modelled using electric circuits. The electrical resistivity of identified zones increases with time, which results in reduction of the effective voltage up to 50% in total for the tested EO system. Finally, the effect of EHM and EC are integrated and it was concluded that, taking the potential loss at the pre-defined zone into the account, the level of EHM processes decreases and therefore the rate of reduction in electrical resistivity will decrease.

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TRANSFORMATION OF CLAY SEDIMENTS IN PRESENCE OF BURIED ARTHROPODS: EXPERIMENTS AND CAMBRIAN LAGERSTÄTTEN

Elena Naimark (1)*, Natalia Boeva (2), Maria Kalinina (3), Alexandr Shokurov (3)

(1) Paleontological Institute RAS, Moscow, 117647, Russia, (2) IGEM RAS, Moscow, 119017, Russia, (3) IPHCHE RAS, Moscow, 119071, Russia

Lagerstätten are localities with exceptionally preserved soft-bodied organisms. The most spectacular Lagerstätten date back to the Cambrian Period. Their dominant lithology is characterized by clayey mudstones and siltstones; fossils are often thin carbon films mineralized with aluminosilicates [1] including chlorites and kaolinites.

In order to reveal the mechanisms of soft-bodied fossil formation we performed long-term experiments which imitated catastrophic deposition, a process believed to guide Lagerstätten formation. *Artemia salina* (Crustacea, Branchiopoda) nauplii were buried in marine sediments of kaolinite or clinochlore. After 12-18 months the carcasses were exhumed from the sediments. At the end of the experiment, we estimated: (1) the degree of preservation compared to that in marine water without sediments, (2) pH of the media and sediments at different depth, (3) mineralogical composition of the sediments.

We found that the degree of preservation in sediments is much higher than in marine water: kaolinite enhanced the preservation 14-20-fold, chlorite - 2-2.5-fold. Excellent preservation in kaolinite is coupled with unusual morphology of nauplial carcasses: empty cuticular sacs with well-preserved fine anatomy of appendages, setae and filter apparatus, but with gut completely decayed. Burying in chlorite resulted in much fewer specimens with such peculiar morphology; there were no such specimens in marine water control. The results imply that clay sediment, especially kaolinite, facilitates the reinforcement of external tissues. Stabilized external tissues arrested decay, providing wider time window for mineralization of soft tissues, and higher probability of preservation of taxonomically important features.

*p*H in both sediments with decaying carcasses dropped to 6.6-6.2 from 7.8-8.2 (water) or 6.8-6.9 (sediments without nauplii). The decrease in *p*H appeared to be larger in comparison with control (nauplii in marine water: pH 6.8-6.9). We conclude that both kaolinite and chlorite sediments form and/or maintain acidic environment around decaying carcasses.

The intriguing feature of the model system is the rise of *p*H at the water-sediment interface. Such peaks were found in both kaolinite and chlorite (water 5 cm above sediment:water-sediment interface:sediment: 7.0:7.1:6.6 in kaolinite; 6.9:8.5:6.3 in chlorite). Similar pattern was also detected in freshwater and brackish kaolinite sediment with nauplii (7.3:7.6:6.9; 7.6:8.1:7.5), while there were no such peaks in the sediment controls without nauplii. Steep pH gradients point to the complex chemical processes in clays triggered by the presence of organic remains. These processes also manifested themselves in the transformations of experimental sediments.

The acidic environment promotes accelerated dissolution of clays. This process is confirmed by the appearance of new very fine crystalline phase (TEM, DCA+TGA), amorphous products, allophane, and gibbsite (SEM, DCA+TGA) in the case of kaolinite, and by the separation of Fe- and Mg-containing mineral phases (DCA+TGA) in chlorite. The carcasses in chlorite seems to include Mg-ions in their elemental composition (SEM-EDX). Conversely, the formation of $CaCO_3$ is possible at the water-sediment interface but not inside the sediment with decaying remains. Indeed, many Lagerstätten have been known to form calcite cement on top of fossiliferous layers [2]. Acidic environment, enriched by Al-ions which are known to possess tanning properties, may retard decay. Moreover, high concentration of cations released through acidic hydrolysis of clay favours mineralization of organic remains.

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PHASE-SEPARATED STRUCTURES OF LIQUID CRYSTALLINE BINARY COLLOIDAL OXIDE NANOSHEETS

Teruyuki Nakato (1)*, Atsushi Takahashi (2), Shinya Terada (1), Shogo Yamaguchi (1), Emiko Mouri (1), Yusuke Yamauchi (3), Morio Shintate (4), Nobuyoshi Miyamoto (4)

(1) Department of Applied Chemistry, Kyushu Institute of Technology, Kitakyushu, Japan, (2) Graduate School of Bio-Applications and Systems Engineering, Tokyo University of Agriculture and Technology, Koganei, Japan, (3) National Institute for Materials Science, Tsukuba, Japan, (4) Department of Life, Environment and Materials Science, Fukuoka Institute of Technology, Fukuoka Japan

Inorganic layered materials can be converted to colloidal liquid crystals (LCs) through exfoliation into inorganic nanosheets [1]. Among nanosheet LCs, binary nanosheet systems are interesting because of their rich structures based on phase-separation of the two nanosheet species. Theoretically, entropically driven demixing of the two colloidal particles results in phase separation of the binary LCs typically exemplified by coexistence of different LC phases. Computational studies of plate-plate systems have indicated three-phase coexistence of one isotropic and two LC phases. Nevertheless, this has not been realized by experimental systems consisting of binary plates including nanosheets with different chemical compositions. Here we show our experimental studies of binary inorganic nanosheet LCs. We have developed two binary nanosheet systems: one is the mixture of niobate ($K_4Nb_6O_{17}$) and smectite-type clay nanosheets, and the other is that of titanate ($H_{1.07}Ti_{1.78}O_4$) and clay nanosheets.

For the niobate-clay binary system, the two nanosheets are phase-separated only at a microscopic scale [2]. Although this system is apparently homogeneous at a macroscopic scale, our recent small-angle X-ray scattering (SAXS) measurements indicate the niobate nanosheets form a lamellar LC phase, which is separated from an isotropic phase of clay nanosheets. The LC phase is compressed by the coexisting isotropic phase, as evidenced by shrinkage of the basal spacing of the lamellar structure. Variation in the lateral size of clay nanosheets (from several tens of nanometers to a few micrometers) little affects the basal spacing of the lamellar LC phase. Such a phase-separated structure is visualized in a real space by confocal laser scanning microscopy (CLSM). CLSM images of scattered light reflect the location of the niobate nanosheets while those of fluorescence can monitor the location of clay nanosheets adsorbed by a cationic dye. CLSM observations clarify that the niobate nanosheets form domains with the size of several tens of micrometers and the domains are located in a lamellar manner. Some voids are observed between the niobate domains, and the voids are occupied by the clay nanosheets.

On the other hand, the titanate-clay system exhibits phase separation at a macroscopic scale [3]. Naked-eye observations clarify phase separation characterized by the emergence of both of the isotropic-LC biphasic and isotropic-LC-LC triphasic coexistence. This phase behavior is different from the niobate-clay binary system, although the titanate and niobate nanosheets have lateral length of micrometers and similar chemical properties. In addition, the clay nanosheets tend to destabilize the colloids to induce heterocoagulation of the two nanosheet particles. The results indicate that the multiphase structures of the multicomponent colloidal LCs depend on the chemical components even though the dispersant particles have similar shapes and properties.

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FACTORS CONTROLLING THE DIVERSITY OF MANGANESE OXIDES IN THE NATURAL ENVIRONMENT

Seonyi Namgung, Giehyeon Lee*

Dept. of Earth System Sciences, Yonsei University, Seoul, Republic of Korea

Manganese (Mn) is ubiquitous and abundant in the Earth's crust. It is the the 3rd most abundant among the transition metals. Because of this abundance, Mn is a common minor constituent of soil as well as natural waters. It readily participates and dissolves, and thus controls many important biogeochemical reactions. Especially, it forms a wide variety of Mn (oxyhydr)oxides (collectively refered to as Mn oxides), which are among the most reactive minerals in the environment by controlling the fate and transport of various nutrients, contaminants, and other elements. It has been reported that over 30 different types of natural Mn oxides exist in the natural environment. Each mineral possesses its characteristic atomic arrangement, crystallinity, and the valence of structural Mn, which account for a wide range of chemical reactivity. There have been extensive studies on the reactivity in relation to sorption and redox reactions of specific Mn oxides with various contaminants. However, the geochemical processes controlling the diversity of Mn oxides formation in the dynamic environmental settings have not been clearly understood yet. We have investigated the factors controlling the formation and phase transformation of diverse Mn oxides by various redox reactions of dissolved- or solid-phase Mn under environmentally relevant conditions

Homogeneous or heterogeneous Mn(II) oxidation under varying conditions was examined to identify the types of Mn oxides and to assess the factors contorlling the diversity of Mn oxide formation. For homogneous Mn oxidation, varying concentrations of dissolved Mn ($[Mn(II)]_0$ = 50 - 994 µM) were oxidized in 50 mM $NaNO_3$ electrolyte at pH 7, 8 or 9 using a buffer (10 mM MOPS for pH 7; 50 mM MOPS for pH 8; or 50 mM CHES for pH 9). For heterogeneous Mn(II) oxidation, 8.0 mM Mn(II) was reacted with 1.0 g/L birnessite at pH 7.0 - 9.0 under anoxic or oxic conditions. In addtion, effects of solid substrate on the heterogeneous Mn(II) oxidation were evaluated by reacting 1.0 mM Mn(II) with 1.0 g/L $Cr(OH)_3$(s) using the same pH range and atmospheric conditions. The results showed that the major types of Mn oxides formed under different conditions were all different, indicating that every factor tested in this study such as the reaction time, solution pH, presence or absence of dissolved oxygen, and the type of solid substrate for heterogeneous systems was responsible for the diversity of Mn oxides formation. For example, homogeneous Mn(II) oxidation at pH 9.0 open to the atmosphere produced hausmannite (Mn_3O_4), whereas heterogeneous Mn(II) oxidation produced mainly Mn oxyhydroxides such as manganite (γ-MnOOH), feitknechtite (β-MnOOH), groutite (α-MnOOH) and hausmannite. These results suggested that various Mn oxides can be formed under widely vayring natural conditions, and the factors controlling the formation and the phase transformation of various Mn oxides should be further investigated.

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APPLICATION OF MONTMORILLONITE-POLY(COBALT ACRYLATE-CO-ACRYLIC ACID) NANOCOMPOSITES IN SYNTHESIS OF OXIDE CATALYSTS FOR TOTAL OXIDATION OF TOLUENE

Piotr Natkanski*, Anna Rokicinska, Barbara Dudek, Piotr Kustrowski

Department of Chemical Technology, Faculty of Chemistry, Jagiellonian University, Ingardena 3, 30-060 Krakow, Poland

Recently, natural layered aluminosilicates, representing a large group of raw minerals, have become attractive and functional materials in many fields of chemistry and material engineering. Nowadays, clays are used on a large scale as fillers in polymer-inorganic composites, improving the properties of polymers, such as: mechanical strength, thermal stability or biocompatibility [1,2]. On the other hand, polymers may be used for the modification of properties of aluminosilicates. Intercalation of polymeric hydrogels into the interlayer spaces of clay can lead to the improvement of adsorption capacity of metal ions. Furthermore, the ions introduced into the clay interlayers can result in partial delamination and structure opening manifested by an increase in porosity and specific surface area [3].

In order to produce Co_3O_4/clay materials characterized by expanded surface area and high dispersion of transition metal species, we synthesized a series of montmorillonite-poly(cobalt acrylate-co-acrylic acid) nanocomposites (MT-P(CoA-co-AA)) in this work. Such approach allowed us to omit the additional step of synthesis of Co_3O_4-containing catalysts based on Co^{2+} ion adsorption, which was previously used for the modification of hydrogel-clay composite precursor [4]. In this simplified procedure, the MT-P(CoA-co-AA) composites were obtained by copolymerization of AA and CoA at various molar ratios (AA/CoA = 2:1, 3:1, 4:1 and 5:1) carried out in an aqueous suspension of MT (15 wt.%) in the presence of 2,2'-azobis(2-methylpropionamide) dihydrochloride (AIBA) as an initiator (2% mol. in relation to monomers). The (CoA-AA)/MT mass ratio was constant and equal to 1:1. The resulting precursors were calcined at elevated temperature in air flow in order to remove of polymeric template.

The structure of the obtained materials at each stage of the synthesis (after polymerization and after thermal treatment) were studied by means of X-ray powder diffraction. The composition of the catalyst precursors and catalysts was determined by infrared spectroscopy (DRIFT), UV-vis-DR spectroscopy, thermogravimetry, elemental analysis and X-ray fluorescence. The thermal analysis coupled with infrared spectroscopy (TGA-IR) was used in examination of the mechanism of thermal decomposition of the composites and for selection of optimal conditions for the calcination process. The results of low-temperature nitrogen adsorption measurements for the calcined precursors showed an increase in specific surface area compared to the raw aluminosilicate, as well as the presence of slit pores. The obtained oxide materials appeared to be active catalysts in the process of the complete oxidation of toluene. For the best samples 100% conversion of the substrate was achieved at about 300 °C.

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ON THE ENANTIOSELECTIVE SEPARATION OF CHIRAL DRUGS BY PEPTIDE METAL ORGANIC FRAMEWORKS

J. Navarro-Sánchez (1), A. I. Argente-García (2), Y. Moliner-Martínez (2), D. Roca-Sanjuán (1),*
P. Campins-Falcó (2), M. J. Rosseinsky (3), C. Martí-Gastaldo (1)

(1) Instituto de Ciencia Molecular, Universidad de Valencia, Catedrático José Beltrán, 2, 46980, Spain, (2) MINTOTA research group, Departament de Química Analítica, Facultat de Química, Universitat de Valencia, Doctor Moliner, 50, 46100 Burjassot, Spain, (3) Department of Chemistry, University of Liverpool, Crown Street, Liverpool, L697ZD, UK.

We report a joint theoretical and computational study on the ability of a chiral Cu(II) 3D MOF based on the tripeptide Gly-L-His-Gly (GHG) for the enantioselective separation of metamphetamine and ephedrine. Monte Carlo simulations were initially performed to provide an initial guess on the differential binding properties of the enantiomers. Whereas no significant separation was estimated for metamphetamine, a large difference in the absorption energies of (+)- and (-)-ephedrine was obtained. The theoretical findings suggest that chiral recognition is linked to preferential binding of one of the enantiomers mainly as the result of additional H-bonds with the framework that lead to energetically more stable diastereomeric adducts. The experiments shows that Cu(GHG) is capable of separating more than 50% of one enantiomer from a racemic mixture of ephedrine in only four minutes when used as a chiral solid phase extraction (SPE) cartridge. The present combination of theory and experiment might help addressing the problem of chiral recognition by producing more complex chemical environments able to maximize enantiomeric resolution for particular drugs.

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CLAY-BASED CERAMIC FOAMS AS GREEN BUILDING MATERIALS

María Linarejos Navío-González, Rosendo J. Galán-Arboledas, Salvador Bueno*

Fundación INNOVARCILLA, Bailén, Spain

This work presents a set of researching lines oriented to develop novel green building materials from traditional ceramic clays. They focus on manufacturing macro porous clay-based ceramic foams, with a total porosity greater than 50%. This microstructure, similar to that of porous materials in nature, improves insulation features, compared to those of traditional ceramic building materials. This, together with the possibility of incorporating waste in their formulation, is of great interest in the current trends of sustainable construction. However, even if fundamentals of these developments have been described for several advanced applications [1-3], this knowledge has not had a relevant impact on the technological innovation on new materials achieved by the traditional clay-based ceramics industry.

In the present study the starting materials were a highly-carbonated illite-smecttite clay from Bailén (Jaén, Southern Spain) and a kaolinite clay from Extremadura (South-west Spain), both used in the manufacture of ceramic bricks and pottery, and with the intention of covering different rheological and sintering behavior[4].

From these raw materials, it is proposed the development of different types of ceramic foams by using several processing routes such as the replica method by impregnation of polymer sponges or the direct foaming of ceramic slip and its subsequent consolidation by gel-casting. Thus, porosity is mainly achieved using biopolymers through biomimetic strategies.

Dynamic sintering studies were performed in order to establish optimum firing cycles and thus reduce environmental impact. Furthermore, this study offers an alternative approach to this topic, which shows how to obtain porous materials mainly based on unfired clays, similar to traditional materials such as adobe bricks.

The main technological properties determined were bulk density, open and close porosity, thermal conductivity and modulus of rupture. These properties were analyzed and discussed in terms of processing parameters and developed microstructures, in order to maximize samples size. Thus, the present work contributes to a systematic feasibility study on the technical implantation and repercussion of these new methods of material processing for building applications.

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IN SITU CLAY BUILDING AND DIGITAL FABRICATION

Matjaž Nekrep Perc, Andrej Tibaut

University of Maribor, Maribor, Slovenia

Automated manufacturing systems will undoubtedly expand and find their place in the future way of building. Digital fabrication will play significant role in near future AECOO (Architecture, Engineering, Construction Ownership and Operation) industry.

Additive manufacturing has potential to be “the next big step forward”, because it allows advanced and brave design and free-form constructions inspired by nature. Design phase will significantly intensify the importance of embedded building details while in the construction phase less human intervention will be needed. Future research directions are further parameterization of the interoperability demand function, BIM maturity, automation of workflow models, application of structural engineering results into models’ infill structure and new approaches for engineering of embedded building elements.

Traditional construction materials as clay will be used differently. Advanced micro structure geometry is generated to achieve optimum material to performance ratio which leads to minimizing material consumption. Elements appear the same but their internal micro-structure is what sets them apart. Integral design of all building accessories like internal heating, ventilation, and air conditioning (HVAC), water supply, and drainage network installations is essential when applying additive manufacturing. Important benefit of digitally fabricated building can be internal topological optimization of building elements like walls and slabs for thermal insulation and structural capabilities.

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MODELING WATER - SWELLING CLAY MINERAL INTERACTIONS IN SOILS AND THEIR EFFECTS ON SORPTION CHARACTERISTICS

Tibor Németh (1)*, Viktória Kovács-Kis (2), Péter Sipos (3)*, István Dódony (1)

(1) Eötvös Loránd University, Department of Mineralogy, Budapest, Hungary, (2) Institute of Technical Physics and Materials Science, Centre for Energy Research, Budapest, Hungary (3) Institute for Geological and Geochemical Research, Research Centre for Astronomy and Earth Sciences, Budapest, Hungary

Aqueous wetting and subsequent drying is a common process in temperate zone soils. These soils are characterized by various swelling clay mineral assemblages containing different smectites, vermiculites and mixed-layer clay minerals. Our previous results suggest that cyclic WD modifies only swelling clay minerals, which can incorporate water in the interlayer space, but has no significant effect on non-swelling clay minerals. The aim of this study is to show the effect of cyclic wetting and drying (WD) on the physico-chemical properties on the swelling clay minerals.

Smectites with different layer charge and interlayer cations (Na, Ca, K, heavy metals), soil smectite, vermiculite and pedogenic chlorite-vermiculite were submitted to numerous (up to 140) WD cycles in the laboratory. The mineralogical, structural and chemical features of the intermediate and end products were studied by XRD, ATEM, FTIR and thermal analysis. Additional sorption experiments (metals and water vapour) were carried out to characterise the properties of the clays.

The most striking change during subsequent WD is the significant decrease of the thickness of the clay crystallites and of the lateral dimension of the clay particles. Additionally, this physical modification is accompanied by the change of the chemical composition. Generally, the clay particles after several WD cycles contain more silicon. Contrary to K-smectites, Na-smectites preserve their expansion capacity during WD cycles. Within the smectite layer charge range, high charged smectites lose their swelling ability, and their metal adsorption capacity also decreases. Basal reflection of high charged K-smectite falls to 10 Å with WD cycles. On the contrary, vermiculites become more expansive after numerous WD cycles indicating smectitization. Our results suggest that cyclic wetting and drying may be one of the causes explaining why clay minerals are fine-grained in soils, and that WD has a significant contribution to pedogenic clay mineral alterations.

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KINNEKULLE K-BENTONITE MIRRORING HEAT IMPACT ON THE CLAY MINERAL COMPOSITION OF BUFFER CLAY FOR ISOLATING HIGH-LEVEL RADIOACTIVE WASTE IN REPOSITORIES

Lan Nguyen-Thanh (1)*, Roland Pusch (2), Jörn Kasbohm (3,4), Thao Hoang-Minh (5),
Nga Pham-Thi (5), Rafael Ferreiro Mählmann (1), Sven Knutsson (2)

(1) Technical University of Darmstadt, Germany, (2) Luleå Technical University, Sweden, (3) University of Greifswald, Germany, (4) Jörn-Kasbohm-Consulting, Germany, (5) VNU University of Science, Vietnam

In Permian age, a diabas flow has affected the 90 m thick underlying Kinnekulle K-bentonite of Ordovician age, consisting of three units: Bed A (thickness 30 cm), Bed B (200 cm) and Bed C (18 cm) (borehole Mossen-3). They have been investigated with respect to the mineralogical composition by XRD, TEM, FTIR and XRF, as well as determination of the CEC. The profile has been considered as a possible natural analogue of processes in clay isolation of canisters with heat-producing radioactive waste, because the maximum temperature is estimated to have been 140 °C (Pusch et al., 1998).

Mineralogical composition: 3- 50% of two types of randomly interstratified illite-smectite mixed layers (IS-ml) with Ca-dominated (not found in beds A and C) and K-dominated interlayer cations (in all three beds), holding 3-20% illite, 4-30% $2M_1$ muscovite, 0-40% quartz, 0-15% chlorite, <5% albite, 0-10% lepidocrocite and traces of Ca-Si-bearing phases constitute the mineral matter and visualize the high quantitative variability of this composition. The highest amount of IS-ml, nearly 55% is at the bottom of 2 m thick bed B. This part also has the lowest expandability in the profile (%S <55%). The highest expandability (up to S% ~ 80%) was recognized in the upper part of bed B.

Geological processes: The mineral and chemical composition and the distribution of clay minerals in the profile suggest the following geological processes: (i) impacts of early diagenesis at the interface water/sea bottom (*e.g.* by K- & Fe-enrichment in chlorite and mica-phases), (ii) impacts of late diagenesis/burial (*e.g.* by illitization), (iii) heat impact of Permian diabas flow and (iv) and of additional dissolution processes. They can have taken place in particular in the bottom parts of beds contacting limestone, and in the bentonites during diagenesis and also by impact of heat, yielding reduction of smectite phases. The heat impact (iii) caused (A) dissolution of IS-ml as indicated by the lowest amount of phases with the highest % S-values, and (B) cementation of mineral particles by silica (Si-precipitation in IS-ml at the top), and (C) smectitization of survived IS-ml in the upper parts of beds - all by assumed interaction with a reactive plume of pore solution.

Role of open/dynamic chemical system: Thin beds A + C (lower than 30 cm) and the upper 30 cm of 2 m thick bed B (dominated by dissolution processes) show complete different mineralogical evolution in comparison to deeper parts of bentonite bed B, which is characterized by solid state transformations only. Large mineralogical alterations characterize the upper 30 cm. In contrast, the high amount of smectite phases and their expandability is conserved at depths of more than 1.5 m from the top of bed B. This large thickness is only limiting the transport of pore solutions and dissolution products under the prevailing conditions.

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COMPETITIVE REACTIONS DURING THE UREA SYNTHESIS OF LAYERED DOUBLE HYDROXIDES

Ulla Gro Nielsen (1)*, Line Boisen Staal (1), Suraj S.C. Pushparaj (1), Claude Forano (2), Vanessa Prevot (2), Dorthe B. Ravnsbæk (1)

(1) Department of Physics, Chemistry and Pharmacy, University of Southern Denmark, 5230 Odense M, Denmark, (2) CNRS and Institute de Chemie, University Blaise Pascal, F-6300 Clermont-Ferrand, France

Layered double hydroxides (LDHs, $(M(II)_{1-x}M(III)_xA\ nH_2O)$ find wide-spread applications as e.g., energy materials, and catalysts as well as in drug delivery and environmental remediation due to their anion-exchange properties and layered structure. Pure LDHs of well-defined size and morphology is essential to control and optimize these applications, as impurities and structural defects can lead to undesired by products. Thus, the so-called urea synthesis [1] is commonly preferred as highly crystalline LDHs can be prepared. Co-precipitation, the second common synthesis approach, gives pure, smaller and less crystalline LDH particles. However, LDHs prepared by urea synthesis contain large quantities of poorly crystalline by-products and LDH may not be the main component [2]. These elusive impurities are not easily detected by powder X-ray diffraction and electron microscopy, two commonly preferred characterization techniques. Furthermore, elemental analyses sometimes indicate excess M(III) ions, but large quantities of impurities are still present with a bulk composition of M(III) ions below the maximum content ($x<1/3$). Both solid state NMR (SSNMR) and vibrational spectroscopy (IR and Raman), which are probes of the local environment, suggested the presence of non-LDHs environments with only 25-60% of Al in the LDH-phase based on ^{27}Al SSNMR. Previous ^{27}Al SSNMR studies of LDHs prepared by the urea method have earlier reported additional ^{27}Al resonances[3-6], but this has been ascribed to e.g., hydrogen bonding [3].

We have performed a detailed study of the urea synthesis for ZnAl-LDHs using time-resolved PXRD in combination with a series of samples prepared at different reaction times, which were characterized ex-situ in depth using a combination PXRD, SSNMR, TEM, and vibrational spectroscopy as well as elemental analysis. Furthermore, the synthesis conditions were systematically varied and the impact on the quality of the LHD product assessed. This provided detailed insight into the mechanism of formation of LDHs during the urea synthesis as well as the origin and nature of the other phases formed. Furthermore, results from studies of MgAl LDHs prepared with different Al content by the urea method will also be presented.

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CHEMICAL LAKE RESTORATION ON THE MOLECULAR LEVEL - PHOSPHATE SEQUESTRATION BY A MODIFIED CLAY AND ZEOLITE

Ulla Gro Nielsen (1)*, Kasper Reitzel (2), Line Dithmer (1,2), Line Würtz Bæk, Sara Ane Zachhau, Thor Kolath Jensen (2)

(1) Department of Physics, Chemistry and Pharmacy, University of Southern Denmark, 5230 Odense M, Denmark, (2) Biology Institute, University of Southern Denmark, 5230 Odense M, Denmark

Phosphorus (P) is a non-renewable resource that is extensively used as phosphatic fertilizers in agriculture in order to ensure sufficient food supply. About 15-20% of the phosphate applied to fields is leached into the aquatic fresh water systems, which along with phosphate from domestic sewages, causes eutrophication (algae bloom) in lakes. Thus, immobilization of legacy phosphate to comply with EU regulations is needed.

Chemical lake restoration uses an approach were P is immobilized to insoluble and (hopefully) geologically stable inorganic phase in the sediment. Two common approaches that are used for phosphate removal are the addition of Phoslock©, a La^{3+} exchanged bentonite, and Al(III)hydroxides. To study the effectiveness of the restoration products knowledge on the formed P compounds is needed. It is very difficult to characterize phosphate phases, as they are complex and have low crystallinity. ^{27}Al, ^{31}P, and ^{139}La solid-state NMR (SSNMR) in combination with La EXAFS spectroscopy were used to monitor phosphate sequestration and to characterize the phosphate phases formed. Furthermore, the effects of humic substances and lake conditions were investigated. The phosphate sequestration mechanism was established based on laboratory studies [1]. Subsequently, adsorption experiments using water and sediment were performed and sediment samples from 16 European lakes previously treated with Phoslock© were investigated [2,3].

A new zeolite-based product was recently introduced, which addresses some of the current issues with Al(III) and Phoslock©. Here we present preliminary results combining adsorptions studies and solid state NMR spectroscopy to unravel the mechanism of phosphate sequestration and how the chemical conditions of the lake influence the phosphate sequestration.

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REMOVAL OF *E.COLI* AND TOTAL BACTERIA FROM WATER BY GRANULATED MICELLE- CLAY COMPLEXES: FILTER REGENERATION AND MODELING OF FILTRATION KINETICS

Ayelet Kalfa, Nadya Rakovitsky, Mordechay Tavassi, Mark Ryskin, Julius Ben-Ari, Hanoch Etkin, Uri Shuali, Shlomo Nir*

Dept. Soil and Water Sciences; The Hebrew University of Jerusalem, The R.H. Smith Faculty of Agriculture, Food and Environment, Rehovot 76100, Israel

Minimizing the risk of an outbreak of waterborne diseases in humans or animals requires to reduce the concentration of pathogenic microorganisms in water. Removal of pathogenic microorganisms by filtration may provide safe water, and decrease the risk from harmful disinfection by products. The micelle-clay complexes produced have a relatively large surface area; they include large hydrophobic fractions and are positively charged to about half of the cation exchange capacity of the clay, which is useful in the removal of microorganisms whose external surfaces are net negatively charged. The employment of micelle-clay complexes in powdered form (1), demonstrated in batch and filtration experiments, the removal from water of several types of Gram negative and Gram positive bacteria and *Cryptosporidium parvum*. However, in a filter the powdered complex had to be mixed with excess of a granulated material, such as sand, whereas the granulated complex could be included exclusively in filters, which enabled upscaling (2).

Granulated micelle-clay composites (0.3 to 2 mm) formed from Na- bentonite and the organic cations Octadecyltrimethylammonium (ODTMA), or Benzyldimethylhexadecylammonium (BDMHDA) were employed to remove from water by filtration (**a**) *Escherichia coli* S-17 and (**b**) total bacteria count (TBC).

(**a**) Filters included 4g to 27 g of complex mixed with sand, and bacteria numbers were $6.4 \bullet 10^5$ to $5 \bullet 10^6$ per mL. Filter lengths were 20 cm and in certain experiments two filters were operated in series. Mixing with sand was just for shortening duration of experiments. A model which considered convection, adsorption, and desorption simulated the filtration results and yielded predictions. Estimates of capacity (for emerging bacteria <1 per 100 mL) have been generated for removal of similar bacteria by a large filter (1 m long) at a flow velocity of 10 m/h. For a filter filled exclusively with BDMHDA-clay granules the capacities varied between 5 and 100 m^3 per kg of complex when the water included $5 \bullet 10^6$ to 1000 bacteria/mL, respectively.

(**b**) Removal of TBC. The capacity of filters was smaller than in (**a**), 2 or 3 m^3 per kg of ODTMA, or BDMHDA complex, respectively, but the technology enables to avoid using UV lamps in domestic filters.

In both **(a)** and **(b)** bacteria capture by filtration was independent of the complex used, but BDMHDA complexes were superior in reducing numbers of emerging bacteria, due to a larger biocidal, or biostatic effect of released cations. Placing a layer of activated carbon after the micelle-clay filter reduced the released cations to 1μg/L.

Regeneration of used filters was by: (**i**) passing a solution of 0.1% NaOCl, or 0.01 M of HCl, or (**ii**) heating in a furnace at 105 °C for 2.5 h. Capacities for removal of bacteria after first and second regenerations by (**i**) were 86% and 57% of those with fresh granules, respectively. It is suggested that the technology can provide a **safe** and **economical treatment** for drinking water contaminated by pathogenic bacteria.

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ADSORPTION OF FORMALDEHYDE BY GEOPOLYMERS FROM AQUEOUS SOLUTIONS

Liudmila Novikova (1), Dmitry Bogdanov (1), Larisa Belchinskaya (1), David Kolousek (2), Barbora Dousova (2)

(1) Department of Chemistry, FSBEI HE «Voronezh State University of Forestry and Technologies named after G.F. Morozov», 8 Timiryazeva str., 394087, Voronezh, Russia, (2) Department of Solid State Chemistry, University of Chemistry and Technology in Prague, Prague, Czech Republic
novikov-la@yandex.ru

Clay-based sorption materials have been extensively used in industrial applications at the stage of waste waters and/or emissions treatment. Depending on the contaminant chemical nature, physical-chemical activity, concentration, adsorption characteristics, clays and other aluminosilicate based materials have been targeted for various types of modification, pre-treatment or activations. In particular, alkaline activation of aluminosilicate materials (e.g. fly ash, natural clays, zeolites, feldspars) may produce a new family of synthetic materials called geopolymers, which are environment benign (no CO_2 emissions) and cheap. Similar to zeolites the structure of geopolymers comprises two- and three-dimensional frameworks of silica and aluminum-oxygen tetrahedra, however, it is largely amorphous and includes admixtures of zeolitic phases the fraction of which strongly depends on the conditions of synthesis.

High adsorption capacity of geopolymers towards heavy metals ions has been successfully used for disposal of industrial waste. The ability of geopolymers to adsorb other classes of industrial toxic substances constitutes current research interest.

The present work was aimed at studying adsorption properties of geopolymers in aqueous solutions of formaldehyde, the main component of wastewaters from woodworking, furniture, paint and varnish and construction industries.

Geopolymer sorbents (GS) were prepared by hydrothermal synthesis from the following components (wt.%): 1) G-14/100 - metakaolin (41%), $NaAlO_2$ (41%), water (18%), t = 100 °C (14 h); 2) G-3/130 - metakaolin (41%), $NaAlO_2$ (41%), water (18%), t = 130 °C (3 h); 3) G-Clin-3/130 - metakaolin (39%), $NaAlO_2$ (41%), water (18%) and natural clinoptilolite (originating from Slovakia) (2%), t = 130 °C (3 h). The sorbents were characterized by XRF, N_2-BET and SEM methods, and the data are presented in Table 1. The adsorption behavior of the GS was studied using 0.064-0.366 M aqueous formaldehyde solutions after equilibrating for 1 h. and using a sulphite method for quantitative determination.

The physical chemical characteristics of geopolymer sorbents illustrate their lower specific surface area and higher cation-exchange capacity values compared to the natural clinoptilolite sample. The change of geopolymers morphology under different synthesis conditions determines the accessible surface for adsorption of sorbate molecules. Formaldehyde adsorption increased for GS (Na^+-form) prepared at higher temperatures and/or when a filler of natural zeolites was used. Additionally, as followed from adsorption isotherms, the state of formaldehyde in equilibrium solution has changed when shifting to higher concentrations due to stronger "sorbate-sorbate" interactions yielding dimers, trimers, etc. of formaldehyde.

Table 1. Characteristics of physical chemical properties of aluminosilicates samples and adsorption of formaldehyde from aqueous solutions

Samples	$\frac{SiO_2}{Al_2O_3+Fe_2O_3}$	S_{BET}, m^2/g	Pore volume, $V*10^3$, cm^3/g		Pore diameter, D, nm	CEC, $mmol_c/g$	Adsorption of formaldehyde, mmole/g		
							Ionic form		
			V_{micro}	V_{Σ}			Na^+	Cu^{2+}	NH_4^+
G-14/100	0.9	14	2.0	71.9	3.9	2.03	0.81	1.69	1.69
G-3/130	0.9	n.d.	n.d.	n.d.	n.d.	2.67	1.06	1.31	1.94
G-Clin-3/130	0.9	22	2.4	97.3	3.9	2.72	1.94	1.06	2.94
Clin	5.0	31	-	107.0	16.2	0.82	1.56(Ca^{2+})	3.94	1.00

The largest amount of formaldehyde was adsorbed by geopolymer sorbents in NH_4^+-form, obviously, due to contribution of chemical sorption mechanism and large number of adsorption sites (NH_4^+-ions), whereas the least adsorption was observed for Clin-sample. A reverse order of adsorption was found for sorbents in Cu^{2+}-form: the highest adsorption for clinoptilolite and the lowest one for G-Clin-3/130. Probably, formation of large coordination complexes of Cu^{2+} and formaldehyde hydrates was easier within wider pores of clinoptilolite.

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OPTIMIZATION OF BENTONITE ACTIVATION WITHIN TOBIT MODELLING

Jaka Nugraha (1), Is Fatimah (2)

(1) Statistic Department, Universitas Islam Indonesia, Kampus Terpadu UII, Jl. Kaliurang Km 14, Sleman, Yogyakarta, Indonesia 55584, (2) Chemistry Department, Universitas Islam Indonesia, Kampus Terpadu UII, Jl. Kaliurang Km 14, Sleman, Yogyakarta, Indonesia 55584
jnugraha@uii.ac.id

Clay material is one of interesting material in adsorption process for water treatment. Based on some reports, physical and chemical treatment of clay material are usually performed in order to increase specific surface area as well as material adsorptivity to specified water contaminant and for this purpose a modeling related to optimization is usually used. In this paper, optimization of bentonite treatment was conducted. Clay activation was conducted by acid treatment, calcination and their combination refer to the application for chromate and rhodamine B adsorption. For such situation on the variables of clay treatments, many reports utilize logit, probitand model complementary log model but the models can not be implemented easily. In this research, a new model, Tobit model was applied for the case of clay activation over acid reflux and calcination at varied acid concentration and temperature of calcination. The model is proofen as suitable model compared to ordinary regression model for clay activation and adsorption application.

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PROSPECTION AND CHARACTERISATION OF KAOLIN OF MANKON, NORTH-WEST REGION CAMEROON

Nzeukou Nzeugang A. (1)*, Mefire Mounton H. S. (2), Mache J. R (1), Fagel N. (3)

(1) Local Materials Promotion Authority (MIPROMALO), P.O. Box, 2396 Yaoundé, Cameroon, (2) EGEM Meiganga, University of Ngaoundere, P.O. Box, 115 Cameroon, (3) Laboratory of Clays, Geochemistry and sedimentary Environments (AGEs), Allée du six Août, 14 B- 4000 LIEGE (Sart Tilman), Belgium

Geological, mineralogical, physical and ceramic studies were carried out on kaolin occurrences in Mankon in order to determine their industrial applications. Mankon is a locality found in Bamenda, North western Cameroon. 05 samples were selected for investigations. Minerals were identified using X-Ray Diffractometer and Fourier Transform Infrared Spectrometry. Ceramic tests (i.e., linear shrinkage, bulk density, flexural strength and rate of water absorption) were done on pellets fired at 1000-1300 °C. These analyses confirmed the presence of kaolin and quartz as the major constituents. Chemical analysis evidences the presence of a high amount of organic matter (from 4 to 10%). Raw clays show low to moderate plasticity (4 - 12%) and low absorption of methylene blue (0.2 < blue value < 2.5). The grain size analysis show clay content varies from 11% to 39%. The Mankon clays display requested properties for local ceramic application. Moreover the high kaolinite content, associated with its low iron abundance, demonstrates that Mankon clay is a suitable raw material for white burning industrial clay of kaolin.

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APPLICATION OF PURIFIED BENTONITE AND SYNTHETIC SMECTITES

Makoto Ogawa*, Sareeya Bureekaew

School of Energy Science and Engineering, Vidyasirimedhi Institute of Science and Technology (VISTEC), 555 Moo1
Payupnai, Wangchan, Rayong 21210, Thailand
*makoto.ogawa@vistec.ac.th

Due to the increased demands of the high purity smectites for advanced materials applications [1,2,3], synthetic smectites with varied composition and particle size as well as the advanced techniques of the purification of natural bentonites have attracted siginificant interets. In this lecture, the purification of bentonites will be introduced from classical methods to the recently developed processes. In addition, the recent development of application of purified bentonite and a synthetic saponite in advanced functional materials will be introduced.

The characterization, the purification and the application of bentonite from newly developed bentonite mine in Japan, was conducted by the combination of classical methods with modification [4,5]. Organophilic clays were obtained from conventional ion exchange reactions with cationic surfactants and also by the solid-solid reaction between acidic clays and alkylamines at room temperature [4].

Synthetic saponite containing a photosensitizing metal complex, tris(2,2'-bipyridine)ruthenium(II), was complexed with colloidal anatase and used for the visible light photocatalytic reaction of aqueous benzene to phenol. The addition of phenol to the initial aqueous benzene solution was effective to improve the reaction yield and the product selectivity [6]. The hybrid photocatalysts have been fabricated as transparent film. The catalyst film was mounted in a flow reactor device to catalyze such photocatalytic reactions as the decomposition of aqueous acetic acid and N-alkylation of benzylamine with ethanol. The photocatalytic flow reactor is robust, without decomposition and/or leaching of the dye and the catalyst layer was sticked to the poly(ethene-co-tetrafluoroethene) substrate during the reactions. Thanks to the robustness, the reactor can be used repeatedly without loss of catalytic activity. Taking advantage of the flow reactor device, we can change the reaction period by the flow rate and can cycle the flow process to achieve desired reaction yields [7].

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INTARACTION EXPERIMENT USING CEMENT MORTARS AND SULFATE SOLUTIONS

Chiaki T. Oguchi (1)*, Naoaki Taguchi (2)

(1) Department of Science and Technology, Saitama University, Saitama, 338-8570, Japan, (2) Department of Civil Engineering, Saitama University, (present affiliation: Yamato Inc.), Japan
*ogchiaki@mail.saitama-u.ac.jp

To clarify deterioration processes of sulfate attack on cement mortars, dissolution experiment using sulfate solutions was performed. Two kinds of mortars, high-early-strength Portland cement mortar (HESPC) and the alumina cement mortar (HAC), were immersed in different concentration of sodium sulfate and magnesium sulfate solutions. In order to evaluate the total amount of soluble ions dissolved from the mortars, electric conductivity (EC) was monitored until 1440 hours.

The electrical conductivity increased drastically during the initial three days. According to the XRF-EDS results, the CaO contents of the HESPC specimens and the CaO and Al_2O_3 contents of the HAC specimens decreased. Thus, the decrease in the EC values is considered to be due to dissolution of these elements from the mortars. The amount of the dissolved elements increased with the increasing concentration of the solutions. The released elements reacted with some elements in the solution. The dominant mineral in the HESPC is portlandite ($Ca(OH)_2$), which generally reacts with carbon dioxide in solution. Subsequently, calcium carbonate ($CaCO_3$) was precipitated just after the reaction and is considered to promote Ca degradation. Calcium carbonate ($CaCO_3$) would dissolve again within the solution and precipitate as gypsum after interaction with magnesium sulphate. This interaction is considered to continue throughout the experiment; therefore, the EC values decrease gradually. Furthermore, the degree of decrease of the EC values was greater in the magnesium sulphate solution than that in the sodium sulphate solution. This phenomenon implies that the specimens that were immersed in magnesium sulphate solution produced many secondary minerals on the specimen surface. This phenomenon was also observed from the results of the XRD and SEM-EDS.

Reflecting the above reaction, the degradation progresses and Equotip hardness numbers decreased. The HESPC specimens decreased more rapidly than did the HAC specimens. As seen in the SEM results, cracks were propagated in the HESPC specimens. Thus, the solution tended to penetrate into the inside of the specimen and creates pressure when salts, e.g., gypsum, were crystallised. However, the HAC specimens did not exhibit such cracks and did not significantly decrease the hardness during the experiment.

It can be concluded that the specimens that were immersed in sodium sulphate solution tended toward rapid hardness decreases on the specimen surface. Although magnesium sulphate solution tends to produce secondary minerals, the hardness of the specimen surface decreased more severely in sodium sulphate solution than in magnesium sulphate solution. The surface hardness reduction occurs more in deterioration during the recrystallisation of sodium sulphate rather than during the reprecipitation processes of mortar components, such as $CaCO_3$ and gypsum production.

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MIXING ENHANCEMENT EFFECT OF MOLECULAR GELS COMPOSED OF HYDROGELATOR WITH LAPONITE ON THIXOTROPIC BEHAVIOR

Yutaka Ohsedo (1,2)*, Masashi Oono (3), Kowichiro Saruhashi (3), Hisayuki Watanabe (1,3), Nobuyoshi Miyamoto (4)

(1) Global Innovation Center, Kyushu University, 6-1, Kasuga-koen Kasuga-city Fukuoka 816-8580 Japan, (2) Comprehensive Research Organization, Fukuoka Institute of Technology, 3-30-1, Wajiro-Higashi, Higashi-ku, Fukuoka 811-0295, Japan, (3) Nissan Chemical Industries, Ltd., 2-10-1 Tsuboinishi, Funabashi, Chiba 274-8507, Japan, (4) Department of Life, Environment and Materials Science, Fukuoka Institute of Technology, 3-30-1, Wajiro-Higashi, Higashi-ku, Fukuoka 811-0295, Japan
*ohsedo@gic.kyushu-u.ac.jp

Molecular hydrogels composed of low-molecular-weight gelators or polymer gelators have attracted attention not only as alternative materials for polymer gels but also as new types of soft matter capable of responding to multiple external stimuli [1]. In gels, whereas thixotropic gels are expected to be medical materials for its biocompatible and spreadable properties, to add thixotropic properties to gels is not easy issue [2-4]. Here this study demonstrates a simple method to create thixotropic hydrogel by mixing hydrogelators and inorganic nanosheet, Laponite [5].

Palmitoyl-glycine-histidine hydrogelator (PalGH) was provided by Nissan Chemical Industries, Ltd. and used as received. Polymer hydrogelator, poly(3-sodium sulfo-*p*-phenylene terephthalamide) (NaPPDT) was synthesized as shown in the literature [6]. Laponite® XLG (Rockwood Additives Limited) was provided by Wilbur-Ellis Co., (JAPAN) LTD. and used as received. The gelation and thixotropic behavior of mixtures were evaluated using the vial inversion method and then rheometric measurements were conducted for quantitative evaluation.

In the two-component composite hydrogel comprising 1 wt% of PalGH hydrogel and 1 wt% Laponite aqueous solution, thixotropic behavior was observed. The individual components did not exhibit thixotropic behavior at the same concentration. Moreover, a 2 wt% PalGH hydrogel showed thixotropic behavior but required longer time for recovery to the gel state after shaking comparing to the composite. Furthermore, 1 and 2 wt% Laponite aqueous solutions remained in the liquid state. This mixing enhancement for composite may be due to the formation of an improved network of closer and finer fibers compared with that found in one-component systems.

The same type of mixing enhancement was also observed in two-component composite hydrogel comprising NaPPDT and Laponite aqueous solution in lower concentration region.

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AMORPHOUS PHOTONIC CRYSTALS FABRICATED USING THE MONODISPERSE SPHERICAL SILICA PARTICLES COATED WITH A HECTORITE-LIKE LAYERED SILICATE

Tomohiko Okada*, Chisato Takada, Chiharu Ohta

Department of Chemistry and Materials Engineering, Shinshu University, Nagano 380-8553, Japan
*tomohiko@shinshu-u.ac.jp

Change in the periodic array of particles (tissue) by absorption of molecules makes a possible application as sensing in which the structural color of the assemblies responds with chemicals. Lotsch and Ozin have reported that a synthetic smectite is useful as the building blocks to construct a clay Blagg stack film [1] and an all-clay inverse opal superstructure [2]. The smectite part has played an important role in sensing molecules or cations because swelling by the intercalation changes the periodicity, leading to vary the structural color. Here we report an amorphous colloidal array film comprised of monodisperse spherical silica particles and a synthetic hectorite-like layered silicate. We have developed a method to provide monodisperse spherical silica particles coated with swellable layered silicate microcrystals that possess swelling and ion exchange abilities [3]. The structural color of the coated particles supported on a substrate will respond to ion-exchange reactions with an organic cations.

The hydrothermal synthesis of the coated particles was performed based on the previous report [3b]; monodisperse spherical silica particles (200 and 250 nm) were allowed to react hydrothermally (373 K) in a Teflon-lined autoclave with an aqueous solution of LiF and $MgCl_2$ at a molar ratio of Li:Mg:Si=0.84:0.69:8.0 in the presence of urea (equal mole of Si) for 2 d. In some cases, the added amount of Li and Mg was doubled to increase the loading amount of the layered silicate. The precipitate was then collected by centrifugation, followed by being washed with mixture of water and ethanol (50/50=*v*/*v*). After the resulting solid was dispersed in a LiF aqueous solution, the aqueous suspension was cast on a quartz substrate without any surface modification. A cationic surfactant (dimethyl(distearyl) ammonium bromide) was used as the ion-exchange experiment. Diffuse reflectance spectroscopy was used to obtain the reflectance spectra of the cast film.

Fine particles of stacked layers were observed on all monodisperse spherical particle surfaces in the TEM images. The fine particles were ascribable to hectorite-like layered silicate as revealed by the XRD analysis. The particle size distribution of the hybrid silica was recorded using TEM images to be 193±4 nm (Li:Mg=0.84:0.69) and 191±2 nm (Li:Mg=1.68:1.38) when 200 nm in diameter was used as the starting silica. After the reactions with the cationic surfactant, the average diameter increased to be 196±8 nm (Li:Mg=0.84:0.69) and 199±9 nm (Li:Mg=1.68:1.38), reflecting from the thickness of the hectorite stacked layers on the silica. Because the basal spacing of the layered silicate increased to 2.2 nm by the intercalation of the surfactant in both samples, it is strongly suggested that the observed increase in diameter is derived from the interlayer expansion.

The color of the supported films before the reactions was blue and green (angle-independent), when using the starting silica in diameter was 200 and 250 nm, respectively, and position of a peak in the reflection spectrum was 415 and 522 nm. Because the position differed depending on the silica size used, the observed color is possibly due to structural color of opal superstructure. Amorphous array packing was observed in the SEM observations rather than hexagonal close and face centered cubic packing, indicating amorphous photonic crystals with only short-range order [4]. Each peak red-shifted upon the reactions with the cationic surfactant to 425 nm (for 200 nm-silica) and 532 nm (for 250 nm-silica). Hence, we assume that the observed structural color change was induced by increase in diameter of the coated particles accompanied by swelling of the silicate.

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AB INITIO NUMERICAL STUDY OF HALLOYSITE

Masahiko Okumura (1)*, Masahiko Machida (1), Toshihiro Kogure (2)

(1) Center for Computational Science and e-Systems, Japan Atomic Energy Agency, Kashiwa, Chiba 277-0871, Japan, (2) Department of Earth & Planetary Science, Graduate School of Science, The University of Tokyo, Hongo 113-0033, Japan
*okumura.masahiko@jaea.go.jp

Halloysite is a natural nanotube consisting of kaolinite layers. This unique clay mineral is an attractive nanomaterial with a wide range of possible applications [1,2]. For instance, halloysite is a promising candidate of drug deliverer [1,2], because it is ubiquitous, inexpensive and biocompatible.

In spite of the expectations for the applications, detailed structures and the origin of the tubular morphology have not been understood. However, recent advanced experimental techniques are changing the situation. For example, Kogure *et al*. [3] revealed the fundamental structure of halloysite using high-resolution electron microscopy with a computer-assisted minimal-dose system. They showed that the axis of the halloysite tube is perpendicular to the mirror plane [4] in the kaolinite layer. On the other hand, the curving mechanism of the kaolinite layers in halloysite is still unclear [1]. Several origins of the curving have been proposed: mismatch of lateral dimensions between tetrahedral and octahedral sheets, tetrahedral rotation, interlayer hydroxyl groups in octahedrons, and surface tension of water [1].

In this study, we performed first-principles simulations of the curved kaolinite layer using the plane wave density functional theory (Vienna Ab-initio Simulation Package, VASP) [5-9] to examine the axis direction and curvature radius of the tubular halloysite reported by Kogure *et al*. [3]. We considered six models corresponding to the possible axes of the cylinder/scroll structures, considering the symmetry of the kaolinite layer. For each system, a single kaolinite layer, which had infinite length in the axis direction by the periodic boundary condition and two edges of about 30 nm in length in the direction perpendicular to the axis, was prepared. In order to find the optimum curvature radius, we performed geometrical optimizations for these six models and found that every kaolinite layer bended in the direction perpendicular to the axis with a curvature but the energy and curvature radius were different among the models. In addition, we made larger models with 50 nm length to confirm the results in the 30 nm systems and check the finite-size effect. From these calculations, the most energetically stable model and its curvature radius were consistent with the experimental results [3].

Furthermore, we made an artificial model whose hydroxyls in the kaolinite sheet were replaced by fluorines. Our result showed that the fluorine halloysite shows smaller curvature than one of the normal halloysite. This implies that the hydrogen atoms in the halloysite plays a critical role on determining the curvature radius.

Our results showed that halloysite curves spontaneously without thermal effects and external forces. The origin of the curved kaolinite layer is repulsion among silicons in the tetrahedral sheet, which is consistent with a scenario proposed by Singh [10].

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MOLECULAR MODELING OF ADSORPTION SITES IN MICACEOUS CLAY MINERALS

Masahiko Okumura*, Hiroki Nakamura, Masahiko Machida

Center for Computational Science and e-Systems, Japan Atomic Energy Agency, Kashiwa, Chiba 277-0871, Japan
*okumura.masahiko@jaea.go.jp

Large amounts of radiocesium were released into the environment due to the Fukushima Dai-ichi nuclear power plant (FDNPP) accident. A large part of radioactive cesium is adsorbed by soil within 10cm thickness from the surface. To reduce the air dose rate in Fukushima area, the Japanese Government has performed large scale decontamination campaigns mainly using surface soil removal technique. It is efficient to reduce dose of the gamma-ray. But, another serious social issue has raised: designation of disposal sites of the waste soil produced by the decontamination. The amount of waste soils is too much beyond the normal notion of Japanese land use. To solve the serious problem, economical and ecological techniques of volume reduction and safe storage for the waste soil are needed. But development of such techniques has not been realized yet. One of reasons for difficulty of development of these techniques is lack of microscopic knowledge about interaction between radiocesium and soil. It has revealed that micaceous clay minerals are good adsorbents, which have several adsorption sites with different strength of adsorption. But mechanisms of adsorption are still open problems, because the unknown mechanisms are related to microscopic structures of the adsorption sites which are difficult to be approached by recent advanced experimental techniques. In order to reveal adsorption mechanisms of the various sites in micaceous clay minerals, we performed numerical simulation of basal surfaces, edges, frayed edges, and interlayer sites. We used density functional theory (DFT) and classical molecular dynamics (MD) simulation techniques. In this presentation, we show a brief summary of results of our recent studies:

- MD study of cesium adsorption on the basal surface of several micaceous clay minerals [1]

We performed MD simulation of cesium adsorption onto basal surfaces of six clay minerals with different layer charges and structures of the octahedral sheets. Potentials of mean forces of cesium adsorption on each clay mineral were evaluated. It is revealed that layer charge dominates adsorption strength and clay minerals with dioctahedral sheet gives stronger affinity of cesium than ones with trioctahedral sheet due to electrostatic repulsion between adsorbed Cs^+ and the H atom of the OH^- ion in the octahedral sheet.

- MD simulation of edge sites [2]

We made a model of illite particle including edge adsorption sites. Free energies of ion exchange reactions among cesium, potassium, and sodium are evaluated. As a result, high selective adsorption of cesium against sodium on the edge sites was found, which is different from the adsorption on the basal surface.

- DFT study of frayed edge sites [3]

Frayed edge site (FES) is known as an adsorption site which shows strong affinity of cesium, which has a characteristic “wedge” structure. To reveal effects of the wedge structure on the affinity of cesium, we made simple models of FES with several interlayer distances of the wider side of the wedge structures. From the simulation, it was revealed that the interlayer distance plays a critical role on the selective adsorption of cesium, i.e., strong affinity of cesium is caused by matching of the ion radius of cesium with the interlayer distance.

- DFT simulation of interlayer sites [4]

Recent experiment showed that cesium ions can migrate into deep part of interlayer of phlogopite [5]. This is counter intuitive because it is expected that they are adsorbed near edge like another observation on muscovite. To understand this phenomenon, we evaluated adsorption energy of serial adsorption of cesium by muscovite, phlogopite, and annite. It was revealed that this phenomenon is also related to ion radius and interlayer distance: occupation of interlayer by single type of ion gives constant interlayer distance which is energetically stable.

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STRUCTURAL AND MORPHOLOGICAL PROPERTIES OF COPPER-EXCHANGED PHILIPPINE NATURAL ZEOLITES

Eleanor M. Olegario-Sanchez*, Jenichi Clairvaux Felizco, Herman D. Mendoza

Department of Mining, Metallurgical and Materials Engineering, University of the Philippines, 1101 Diliman, Quezon City, Philippines
*eleanor.olegario@gmail.com

Zeolites are highly crystalline hydrated aluminosilicate clays. The superior ion exchange capacity and high internal porosity of zeolites make them ideal for various applications, such as in dye adsorption, cementitious mixtures, slow release filters, heavy metal removal, adjuvant anticancer therapy, and catalysis [1-6]. Copper-exchanged zeolite is starting to gain attention due to its important role as catalysts in industrial processes such as in NOx decomposition, hydrocarbon conversion, and sulfur removal in petroleum products [7]. Moreover, its potential as antibacterial agent in water treatment is already being realized. Copper is a well-known antibacterial agent [8-9], but problems arise such as leaching and oxidation. An answer to this problem is by encapsulating the Cu in cage-like matrices, such as zeolites.

Cu-exchanged Philippine natural zeolites from SAILE Industries, Inc. in Mangatarem, Pangasinan, Philippines were successfully characterized for its physical and chemical properties. Scanning Electron Microscopy (SEM) was employed to investigate the morphology of the sample during each stage of the sample preparation. On the other hand, X-ray diffraction was used to determine the mineral composition, as well as to observe the presence of Cu in the sample and the effect of calcination on the structural properties. To determine the zeolite's chemical composition, X-ray fluorescence was used.

Philippine natural zeolite was ground up to a range of 35 μm >Dp>180 μm size fractions. The ground zeolite was then soaked in HCl, and then washed several times with blue litmus paper until a neutral pH was achieved and no chlorine is detected. Next, the sample was sodium activated. It is then washed thoroughly until no chlorine is present. The sample was further oven-dried at 110 °C for 5 hours. The dried zeolite was dispersed in copper sulfate (CuSO4 5/2H2O), forming a slurry for 24 h. The copper exchanged zeolite is then washed to remove excess copper and air dried for 24 hours. Finally, the samples were calcined at varying temperatures of 600 °C and 800 °C for 5 h.

Morphological analysis revealed the natural zeolites to be of porous and plate-like structures, which suggests the presence of clinoptilolite-heulandite family of zeolites. After Cu-exchange, no change in the structure was observed, but upon annealing at 600 °C, CuO nanowires appeared. The XRD results confirmed the dominance of clinoptilolite and heulandite in the natural zeolite sample. The Cu-treated zeolite annealed at 600 °C also showed clinoptilolite-heulandite peaks, as well as a broad CuO peak. Annealing at a higher temperature of 800 °C led to the amorphization of the zeolite peaks, which suggests that the zeolite structure may have collapsed at this temperature. The CuO peak also became more crystalline, which is expected to occur at high temperatures. Chemical analysis by XRF determined that the sample contained 8.10% CuO after Cu-exchange and annealing, which is desirable for a wide variety of applications.

Keywords: Philippine Natural Zeolite, Cu-Zeolite, Clinoptilolite.

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THE EFFECT OF COFFEE EXTRACT AS A GREEN REDUCING AGENT OF AN ION-EXCHANGED SILVER-ZEOLITE FOR ANTIMICROBIAL APPLICATIONS

Anna Victoria G. Lim**, Eduardo R. Magdaluyo, Jr***, Eleanor M. Olegario-Sanchez*

Department of Mining, Metallurgical, and Materials Engineering, University of Philippines Diliman, Quezon City 1101, Metro Manila, Philippines.
*eleanor.olegario@gmail.com; **avglim3@gmail.com; ***ed.magdaluyojr@coe.upd.edu.ph

The popularity of silver nanoparticles in medicine and health care is attributed to its broad spectrum of antimicrobial activity and low manufacturing costs [1]. Zeolite is an attractive choice as a carrier support due to its properties like ion exchange capacity, specific surface area, chemically inert, non-toxic, and availability. There are many studies incorporating silver nanoparticles into the zeolite super cage; however, the use of toxic reducing agents like sodium borohydride along with a stabilizer is necessary. A study by Bashir and Khan [2], have demonstrated the mechanism by which hydroxyl groups in amylose from starch aids in the reduction of silver ions. Similarly, coffee contains several hydroxyl groups found in its phenol compounds that can reduce silver [3]. Coffee is a safe reducing agent, capping agent and antimicrobial agent [4].

In this study, varying amounts of extracts from Arabica ground coffee (GC) and ground coffee waste (GCW) are used as reducing agents in the ion-exchange of silver in sodium pre-treated zeolite.

The mordenite type zeolite from SAILE Industries, Inc. Mangatarem, Pangasinan, Philippines is sodium activated and was suspended in a silver acetate solution under constant stirring. Varying amounts of coffee extracts were then added to a total volume of 50mL solution. The system was then allowed to age in the dark environment for 24 h. Afterwards the material was filtered, washed and dried at 80C for 8 h. Characterization techniques for the Ag-Zeolite are XRD, AAS, SEM and PSA. The Ag-Zeolite was tested for its antimicrobial properties against *Escherichia coli* and *Staphylococcus aureus*.

The AAS result indicates that with varying coffee extract dosages, the 15ml dosage for both GC and GCW as reducing agents show the highest silver concentration unto the zeolite. The antimicrobial assays indicate that all Ag-Zeolite materials with GC and GCW reducing agents inhibited growth for both bacteria. The Ag-Zeolite with GCW as reducing agent shows higher antimicrobial index results against both bacteria as compared with the Ag-Zeolite with GC.

Keywords: silver zeolite, mordenite, green synthesis, silver nanoparticles, coffee extract.

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THE GEOMECHANICS CLASSIFICATION AND KINEMATIC ANALYSIS FOR THE SLOPE STABILITY INVESTIGATION OF AN INTER-STRATIFIED CLAY MINE PROJECT IN MANGATAREM, PANGASINAN, PHILIPPINES

Apolinario J. Katipunan, Lynn Mitzi C. Sumangil, Merian F. Viena, Eleanor M. Olegario-Sanchez*, Herman D. Mendoza

Department of Mining, Metallurgical and Materials Engineering, University of the Philippines, 1101 Diliman, Quezon City, Philippines
*eleanor.olegario@gmail.com

In any surface excavation involving cut slopes, the minimum requirement for an open pit mine operation is a slope stability analysis. Such study is done to assess the stability of the mine slope after excavation based on the orientation of its geological structures and the rock discontinuities and the rock mass rating in general. This will locate safe zones, critical failure surfaces, and calculate the factors of safety based on the applied numerical methods. This will also determine the vulnerability of the slope to various modes of failure. The use of different methodologies with increasing complexity in analysis will aid in validating the results. It will further help in quantifying clay-soil rock mass behaviour. Mine operations having relatively loose and soft commodities may also benefit from the study to increase mine safety and create more effective designs.

An interstratified clay (zeolite-bentonite) open pit mine project located at Mangatarem, Pangasinan, was geomechanically classified and preliminarily assessed for its slope stability using kinematic analysis. Field investigations were conducted to define rock mass, which were then complimented with laboratory tests of rock samples. The rock mass was classified geomechanically using Rock Quality Designation (RQD), Rock Mass Rating (RMR), and Slope Mass Rating (SMR). Kinematic analyses were conducted using Markland's test for plane and wedge sliding failure, and Goodman's test for toppling failure. The clay minerals were characterized with XRD to determine its mineralogy and XRF for its elemental analysis and composition.

The open pit mine operation encompasses five stratigraphic relations. The Zambales Ophiolite Complex spans from west to southwest, and is overlain by the Aksitero Formation near the claim's western margin. The Moriones Formation extensively occupies the north and northeast. Quarternary Alluvia are found on the southeast and northwest. The Andesitic/Dacitic Plug on southwest is more popularly known as Mount Malabobo.

On the basis of the classification systems, the rock mass of the open pit mine was rated to be fair to good rock. The kinematic analyses indicated low probability of structurally controlled failures in the mine site. It is concluded that current working design and condition of the mine is sufficiently safe, and no stabilization measures are necessary.

Keywords: philippine clay mine, slope stability, rock mass rating.

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THE EFFECT OF Ag-EXCHANGED PHILIPPINE NATURAL ZEOLITES AND PLASMA TREATMENT TO THE THERMAL AND STERILITY PROPERITES OF CHITOSAN COMPOSITES

Kathrina Loi M. Taaca, Eleanor M. Olegario-Sanchez*, Magdaleno R. Vasquez, Jr.

Department of Mining, Metallurgical and Materials Engineering, University of the Philippines, 1101 Diliman, Quezon City, Philippines
*eleanor.olegario@gmail.com

Zeolites are microporous crystalline aluminosilicates with excellent adsorption and cation exchange capabilities. These properties allowed the minerals to be widely used in several drug delivery systems and antimicrobial applications. Studies have shown that zeolites have the ability to control ion release which aids in the prevention of concentration-dependent toxicity. These properties therefore, were shown to be suitable candidates as fillers to polymer matrices for biomedical applications.

In this study, sodium-treated Philippine natural zeolites from SAILE Industries, Inc. in Mangatarem, Pangasinan where modified thru ion exchange method to incorporate silver ion. A ratio of 1g:5mL of natural zeolite and 0.05 M $AgNO_3$ solution was used for the said process. The filtered zeolites were then calcined at a temperature of 400 °C for 5h. The Ag-exchanged zeolites (Ag-Z) were then dispersed in a chitosan polymer matrix (AgZ-Ch) thru solvent casting approach. A 5% (w/v) of Ag-Z suspension was used to produce the chitosan composites with varying Ag-Z contents ranging from 0% to 2.0%. The Ag-Z-Ch samples were also exposed to Argon plasma at 30 Pa for 120 seconds to determine the possible effect of the modification to the composites. The synthesized Ag-Z and Ag-Z-Ch samples were then characterized for its thermal stability, sterility and water absorption capability.

Thermal analyses of Ag-Z and Ag-Z-Ch composites were done using thermogravimetric analysis (TGA) and differential thermogravimetric analysis (DTG). Results showed that the onset of degradation for the Ag-Z sample is 45.45 °C. This is about 59% lower than the onset for water loss of Na-zeolites and this can be due to the introduction of Ag into the structure of zeolite. Moreover, 80.98% of the Ag-Z samples retained after degradation. On the other hand, the thermal analysis of the Ag-Z-Ch composites showed three degradation steps. It was also shown that the increasing Ag-Z content (0 to 2.0 wt%) results to decreasing onset of the first degradation step, from 60.9 to 44.37 °C. Sterility testing was done by transferring the pristine and plasma-treated Ag-Z-Ch composites into a Tryptic Soy Broth (TSB) solution bottles, incubating these samples at 35 °C and streaking on a Nutrient Agar (NA) plates. The test was utilized to determine the presence or potential of the samples for bacterial growth. The results of the test showed no colony form in every unit of the NA plates, indicating that the presence of Ag-Z and plasma treatment could not induce bacterial growth on the surface of the composite samples. Water absorption capacity of the composite is expected to improve due to the presence of Ag-Z as well as via plasma modification.

Overall, the composites have met the initial properties of a biomaterial: 1) thermally stable wherein it will not degrade at normal body temperature (37 °C); 2) the composite will not induce bacterial growth upon entering the human body; and 3) has the capacity to absorb water. These shows the potential of the Ag-Z-Ch composite for biomedical application.

Keywords: Philippine natural zeolite, chitosan, sterility, thermal stability, biomedical application.

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SYNTHESIS OF SOLID FOAMS FOR FLAME RETARDATION FROM BIONANOCOMPOSITES BASED ON PALYGORSKITE AND BIOPOLYMERS

Artur Oliveira (1)*, Jackson Azevedo (1), Ana Alcântara (2), Sibele Pergher (1)

(1) LABPEMOL - Universidade Federal do Rio Grande do Norte, Natal, Brasil, (2) Laboratório de Química de Interfaces e Materiais, UFMA, São Luiz, Brasil

Plastics made from polymers are one of the main elemental material in commercial and home environments [1]. Thus, the incorporation of halogen-based compounds with the aim of retarding the flames without changing the qualities of the product was highlighted [2]. The problem of this incorporation into the polymers was in the environmental impacts caused, where a large amount of toxins, such as dioxins and furans, were released in the combustion process. To avoid these problems, halogen-free flame-retardants such as nanocomposites has been studied [3]. Therefore, the search for materials that present functionality, technological properties, low cost and that are sustainable make the bionanocomposites in materials of great interest [4]. Besides the growing search, there is currently an ecological appeal, which aims to preserve the environment through the lesser use of fossil-based materials.

Bionanocomposites are hybrid materials formed from a continuous phase, usually organic, dispersed in an inorganic phase, which the both materials comes from nature, where at least one of the phases has a nanoscale structure [5]. The biopolymers used in this work were pectin and rice starch. Pectin is a polysaccharide extracted from citrus fruits, where its structure has carboxylic groups conferring a negative character, which consists of residues of uronic acid [6]. Pectin has been widely used in the food industry and as vehicle to controlled drug release [6]. Rice starch is a neutral overall charge polysaccharide which has about 72-82% amylopectin, branched chain structure and 18 to 33% amylose, linear chain structure[7]. The inorganic compound used was a palygorskite clay, which has a 2:1 structure (tetrahedral and octahedral) with fibrous morphology, high porosity and high specific surface area (approximately 200 m^2/g), as well as the presence of silanols (-SiOH) [5].

For the foam synthesis, a solution of palygorskite clay containing between 5% and 25% of the initial polymer mass was kept under stirring with distilled water for 15 to 30 minutes. In parallel, solutions containing 0.12% to 2% (m/v) from pectin or rice starch are prepared under stirring using distilled water until complete dissolution. After dissolution of biopolymer, the solution was added to the clay solution and kept under stirring for predetermined times. Subsequently, the mixture is frozen for 60 h under a temperature of -5 °C and lyophilized for 72 h under vacuum, obtaining the bionanocomposite as foam form. The characterization was analyzed by XRD, FTIR, SEM, TGA and Burner Test by ASTM D4986-03 method.

The flame retardant properties that were evaluated through the burner test allowed to observe that all the synthesized bionanocomposites, as much as the pectin as the rice starch, presented very promising results, where they have resistance to the flame. Besides that, some samples have self-extinguishing behavior.

Thus, the bionanocomposite, which is formed from palygorskite clay, and the pectin or rice starch biopolymers exhibits flame retardant properties and may be used in the composition for the production of anti-flame materials.

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A STUDY ON MINERAL ASSEMBLAGES, TEXTURES AND ZONNING PATTERNS OF HYDROTHERMAL ORIGINATED AHIRÖZÜ KAOLIN DEPOSITS, MIHALIÇÇIK-ESKIŞEHIR, TURKEY

Işil Ömeroğlu, Asuman Günal Türkmenoğlu

Middle East Technical University, Department of Geological Engineering, 06800 Çankaya/Ankara, Turkey

In this study, the influences of hydrothermal fluids on the mineralogy, texture and composition of the rocks associated with the kaolin deposits exposed in the area between Ahırözü-Hamidiye-Üçbaşlı villages at the southeast of Mihallıççık, Eskişehir were investigated by using mineralogical, petrographical and geochemical methods. In the study area, Triassic age blue-green schists and marbles in additon to the serpentinized ultramafic rocks are exposed. The kaolinization occurred at their contact with a Triassic age granitic body as a result of an intense hydrothermal alteration.

Based on the field observations, mineral associations and textures, the original rocks exposed in the study area were identified as basic and felsic igneous varieties and metamorphic rocks having mylonitic textures. Dominantly, five different secondary mineralization products were detected as clay, chlorite, listwanite, carbonate (i.e. dolomite) and amorphous silica. Secondary quartz crystals fill the stockwork type microfractures of the host rocks as a result of the precipitation of excess silica in the system. Therefore, two types of alterations related with these mineralization processes are determined in the study area, namely; argillic and propylitic (Ömeroğlu et al. 2016). The mineral paragenesis of argillic alteration is composed of kaolinite, smectite, illite, natroalunite in addition to the accessory minerals which are identified as dickite and pyrite. This mineral paragenesis corresponds to low-intermediate argillic alteration caused by chemical fluids having neutral to acidic pH with low temperature values less then 200 °C. On the contrary, the mineral paragenesis of propylitic alteration is composed of key mineral epidote and chlorite, illite and pyrite as the main accessory alteration products. The chemistry of the fluids is suggested as having neutral pH with temperatures higher than 250 °C (Ömeroğlu et al. 2016).

The Ishikawa alteration index (AI) and the chlorite-carbonate-pyrite index (CCPI) have been used to study the intensity of alteration occurred in the study area. The AI index has been firstproposed by Ishikawa et al. (1976) to reveal the effect of sericite and chlorite alteration formed in the footwall volcanics around Kuroko deposits (Large et al. 2001). The main point of this index is the breakdown of sodic plagioclase and volcanic glass resulting in the replacement of sericite and chlorite (Large et al. 2001). The index introduces values changing from 20 to 60 for unaltered rocks whereas offering values from 50 to 100 for hydrothermally altered rocks with an AI=100 including total replacement of feldspars and glass by sericite and/or chlorite. However, chlorite-carbonate-pyrite index (CCPI) has also been developed to calculate the increase in the amount of MgO and FeOdue to the occurrence of Mg-Fe chlorite in the system whenit replaces albite, K-feldspar or sericite in the igneous rocks andresulted in the loss of Na_2O and K_2O (Large et al. 2001). This index is also connected with carbonate alteration in addition to the enrichment of pyrite, hematite and magnetite assemblages. According to the alteration trends, it has been observed that the least altered volcanic samples introduceapproximately AI=30. Withan increased carbonate alteration, the samples in which CCPI (>90) values have been increased compared to samples dominantly composed of chlorite alteration.

In this study, based on the AI and CCPI indexes and alteration box plot, the various alteration degrees of the rocks are defined. Petrographic, mineralogical and geochemical data are used to distinguish different alteration zones in the study area.

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EFFECT OF Fe-CONTAINING IMOGOLITE ON OXIDATION OF CYSTINE

Ryohei Mochizuki, Momoko Ishida, Takashi Arai, Masashi Ookawa*, Takanobu Goto

Department of chemistry and biochemistry, National Institute of Technology, Numazu college, Numazu, 410-8501, Japan
*mokawa@numazu-ct.ac.jp

Imogolite is a naturally occurring aluminosilicate clay mineral with a typical chemical composition of $(OH)_3Al_2O_3SiOH$. It forms tubular structure accompanying with an outer diameter of ca. 2 nm and an inner diameter of 1 nm. The tube wall consists of a single continuous gibbsite sheet and orthosilicate anions. Although imogolite is expected to have a shape-selective character similar to zeolites, two investigations have been carried out to use natural imogolite as a catalyst by Imamura [1,2]. Recently we synthesized Fe-containing imogolite and found that the synthetic material played as an oxidative catalyst [3], in which phenol was seemed to be directly produced via oxidation of benzene by hydrogen peroxide (H_2O_2) with this catalyst. However, we could not demonstrate the oxidative pathway of benzene by this catalyst. Hence, further study is needed to answer a question whether various compounds are oxidized by Fe-containing imogolite or not. In this study, we attempted oxidation of sulfur in cystine that is an amino acid with a disulfide bond in its molecule. Cystine is used to produce cysteine sulfinic acid (CSA) which is a precursor of taurine in biosynthetic pathway in animals.

The Fe-containing imogolite was synthesized using the mixture of aqueous solutions of $FeCl_3$ and $AlCl_3$ (atomic ratio of Al / (Fe+Al) = 0.05) and Na_4SiO_4 aqueous solution through a careful examination of preparation conditions. The fibrous morphology was observed in the AFM image of Fe-containing imogolite, which is similar to the synthetic imogolite. The typical oxidation reaction of sulphur amino acid was carried out using 10 mg of L-cystine, 0.2 mL of formic acid, 8.1 μL of H_2O_2 (31 wt.%) and 8 μL of conc. HCl with 20 mg of solid state catalyst such as Fe-containing imogolite, imogolite, silica gel and gibbsite. The reaction was continued for 1.5 hr. at 0 °C. The reaction was terminated by an addition of water, and the formed amino acids were separated and identified by cellulose TLC densitometry using QuantiScan. A mixture of 1-propanol-acetic acid-water was used as a development solvent and 2% ninhydrin solution for visualization.

Without catalyst, L-cystine S,S-dioxide (CSD) was exclusively observed as a main product accompanying with CSA and cysteic acid (CA) at weak levels. This CSD formation did not change when silica gel or gibbsite was used as a catalyst, suggesting that these compounds did not affect the cystine oxidation. However, significant level of CSA was produced when Fe-containing imogolite was added into the reaction mixture, in which CSA formations was increased with an increasing of the catalyst contents (up to 20 mg). The production of these amino acids did not change significantly when cysteine was used for the reaction instead of cystine. Our present data suggest that Fe-imogolite have a potentiality not to oxidize sulfur in cystine but to promote cleavage of CSD which is formed from cystine by oxidation reaction under the condition we employed.

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STUDIES ON FORMATION PROCESS OF Ge-IMOGOLITE CONTAINING Fe BY DLS AND UV-VIS SPECTROSCOPY

Masashi Ookawa*, Eiji Kato, Minami Watanabe, Kaho Osada, Takashi Arai, Setsuko Yamane

Department of chemistry and biochemistry, National Institute of Technology, Numazu college, Numazu, 410-8501, Japan
*mokawa@numazu-ct.ac.jp

Imogolite is a hydrated aluminosilicate with a unique tubular structure. It can be used as a functional material such as a catalyst but it needs to undergo chemical modification. We have discovered that imogolite containing Fe^{3+} has potential as an oxidation catalyst for aromatic hydrocarbons [1] On the other hand, some studies on synthesis, structure or formation process of germanium analog of the aluminosilicate imogolite (Ge-imogolite) also performed, recently. Mukherjee et al. [2] indicated that the particle size estimated by dynamic light scattering (DLS) implies the tube length. We have also synthesized a Ge-imogolite from the starting solution obtained by dissolving GeO_2 [3]. Furthermore we synthesized Ge-imogolite containing Fe and found that it served as a catalyst of oxidation reactions of benzene [4]. We have found that the solution with Fe^{3+} colored at the aging step of precursor solution by heat. Since the tubular structure is formed during this step, it is thought that the coloring is related to the formation. In this study, the formation process of Ge-imogolite with Fe^{3+} ions was investigated using by DLS and UV-VIS spectroscopy.

We synthesized Ge-imogolite containing Fe though a modified synthesis method of Ge-imogolite [3]. $FeCl_3/(AlCl_3 + FeCl_3) = 0$ and 0.10 were used as starting compositions. The aqueous solution of mixture of $AlCl_3$ and $FeCl_3$ and sodium orthogermanate aqueous solution were mixed and stirred for 1.5 h. The precursor was obtained by adding 0.5 M NaOH aqueous solution slowly until pH 5.5. The salt-free precursor was obtained by centrifugal separation and was then dispersed in deionized water. After addition of dilute HCl and stirring for 2 hours, it was aged at 95 °C. The sample solution was collected in glassy bottle by a peristaltic pump at given time during aging step. Their solutions were analyzed by DLS and UV-VIS spectroscopy.

The clear peak was observed from a 5 nm to 60 nm and peak top became big gradually in the particle size distribution obtained by DLS of the aged solution without Fe^{3+} ions ($Fe/(Al+Fe) = 0$). The peak top of particle size distribution obtained is plotted against aging time. In the case of solution without Fe^{3+} ions, the values of particle size were similar to those reported by Mukherjee et al. [2] in spite of different synthesis method. On the other hands, particle size in the solution with Fe^{3+} ions became bigger at the early stage. It is clear that the grown-up rate of tubes was promoted by introducing Fe^{3+} ions.

The absorption band at ca. 260 nm was observed in UV-VIS spectrum of the solution without aging and it was assigned as charge-transfer of Fe^{3+} in precursor of Ge-imogolite containing Fe. The absorption at ca. 260 nm decreased and at the region from 300 nm to 350 nm increased with aging time. These clear changes continued for 48h and the isosbestic point was observed at 276 nm. It means the state of Fe^{3+} species was changed with the formation of tubular structure. The small absorption was observed at 485 nm in the second-derivative spectra of aged solution. The absorption near 481 nm was observed in FeOOH crystal such as goethite or lepidocrocite and it was assigned as an electron-paired transition [5]. It is known that the electron-paired transition caused by the pair of edge shared or faced shared Fe^{3+}-Fe^{3+}. We suggest that the absorption band near 485 nm in aged solution is assigned as an electron paired transition because the absorption position is almost same and there may be opportunities for the iron ions adjacent during aging step. The edge shared Fe^{3+}-Fe^{3+} would form in Ge-imogolite containing Fe^{3+} when Fe^{3+} ions were substituted by Al^{3+} ions during formation of the tube structure.

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USE OF ORGANO-FUNCTIONALISED EXPANDIBLE MICAS OF HIGH LOAD AS DRUG CARRIERS

Santiago Medina (1), Olga R. Lobato (2), Mª del Mar Orta (2)*

(1) X-ray Laboratory, Research, Technology and Innovation Center of the University of Seville, Seville, Spain, (2) Department of Analytical Chemistry, Faculty of Pharmacy, University of Seville, Seville, Spain

Clay minerals in their natural forms, are inorganic cation exchangers and so they can carry out ion exchange with basic drugs in solution. On the other hand, clay minerals are widely used in conventional pharmaceutical dosage [1]. In addition, there are organo-clays with high retention capacity obtained by adsorption processes [2], and the synthesis of this type of tailor-made materials could increase the capacity of adsorption of drugs. The objective of this work is to study the retention capacity of acetylsalicylic acid by an expandable synthetic organo-mica of high load functionalized [3] and to study the structural changes produced in the starting materials after the assays.

An organo-mica functionalized by alkylammonium chains of 18 carbon atoms was synthesized by cation exchange reaction. An acetylsalicylic acid adsorption test was designed for the organo-mica at different concentrations. The materials involved in this study were characterized by X-ray diffraction techniques, transmission electron microscopy, thermal analysis and physisorption. The concentration of acetylsalicylic acid in the supernatant at different times was analyzed by HPLC.

The results show that the adsorption of acetylsalicylic acid on organo-mica occurs very rapidly in the first hours, being irreversible during the test time. There are not changes in the laminar structure of the organo-mica, decreasing the interlaminar space, which could be explained as a decrease in the angle of inclination of the alkylammonium chains.

From the results obtained, it can be concluded that these materials could be used in the retention of organic compounds in two senses, one as a decontamination filter in aquatic environments and another for the transportation of medicines.

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CONTROLLED MOLECULAR THICKNESS IN 2D MICA NANOSHEETS FOR TAILORED SEMICONDUCTORS

Sang Sub Kim (1), Minoru Osada (2)*, Ping Wu (3), Hyoun Woo Kim (4)

(1) Inha University, Incheon, Republic of Korea, (2) National Institute for Materials Science (NIMS), Tsukuba, Japan, (3) University of Technology & Design, Singapore, Singapore, (4) Hanyang University, Seoul 133-791, Republic of Korea

Bandgap engineering of atomically thin 2D crystals is critical for their applications in nanoelectronics, optoelectronics, and photonics. Here we report a simple but rather unexpected approach for band engineering of muscovite-type mica nanosheets ($KAl_3Si_3O_{10}(OH)_2$) *via* controlled molecular thickness. Through an analysis of density functional calculations, we analyze electronic structures in 2D mica nanosheets and develop a general picture for a tunable bandgap narrowing induced by controlled molecular thickness. From photoluminescence, x-ray photoemission spectroscopy, and conducting atomic force microscopy, we observe an abnormal bandgap narrowing in 2D mica nanosheets, contrary to well-known quantum size effects. In mica nanosheets, decreasing the number of layers results in reduced bandgap energy from 7 eV to 2.5 eV, and the bilayer case exhibits a semiconducting nature with ~2.5 eV. Structural modeling by transmission electron microscopy and density functional calculations reveal that this bandgap narrowing can be defined as a consequence of lattice relaxations as well as surface doping effects. These band gap engineered 2D mica nanosheets open up an exciting opportunity for new physical properties in 2D materials and may find diverse applications in 2D electronic/optoelectronic devices.

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PHOTODEGRADATION OF TETRACYCLINES ADSORBED ON CLAY MINERALS UNDER SUNLIGHT

Josy A. Osajima (1)*, Maria G. Fonseca (2), Edson. C. da Silva Filho (1), Ana Sanchéz-Polo (3), Manuel Sanchéz-Polo (3), Esperanza C. Gil (3), Cesar A.Viseras Iborra (3,4)

(1) Department of MaterialsScience, Universidade Federal do Piauí, Teresina, Brazil, (2) Department of Chemistry, Universidade Federal da Paraíba, João Pessoa, 58051-970, Brazil, (3) Department of Pharmacy and Pharmaceutical Technology, University of Granada, Campus of Cartuja, 18071 s/n. (Granada), Spain, (4) Andalusian Institute of Earth Sciences, CSIC-University of Granada, Avda. de Las Palmeras 4, 18100. (Granada), Spain
*josy_osajima@yahoo.com.br

The resistance of some compounds to conventional treatments engenders the search for alternative methods, such as photodegradation. Antibiotics and photoproducts are found in the environment, indicating that these compounds are persistent in the environmental. Commonly, clay minerals are used as adsorbents for the treatment of wastewater containing organic micropollutants, such as dyes or drugs [1,2]. However, adsorption processes do not promote the degradation of the molecules, therefore, they are to provide only one of the polluting compounds phase shift [3]. In this perspective, many studies have been conducted in order to apply the clay on systems that actually cause the degradation of these contaminants [4]. The goal of this work was to investigate the degradation of the tetracyclines adsorbed on clay minerals under sunlight for water treatment. The tetracyclines were tetracycline (TC) (Fagron) and docytetracycline (DC) (Fagron). The selected clay minerals were: sepiolite was provided by Vicalvaro (Spain) (SV); palygorskite (Pharmasorb colloidal©, PHC) was from BASF, and montmorillonite (VeegumHS©, VHS) was kindly donated by Vanderbilt Minerals (USA). All the clays were sieved (90-125 µm) before use. The drugs were used as received, without further purification. The product interaction experiments were performed based on previous study [5]. The used drug concentration was 2.0 gL^{-1} in 20.0 g of the each clay mineral. Microwave extraction was performed by Milestone microwave extraction system equipped with 12 teflon vessels carrousel and internal temperature control. The maximum irradiation power was 400 W. Sample of 0.105 g was transferred in the teflon vessel and 20.0 mL of deionized water was added. After, microwave irradiation (20 min, 80 °C), the extract was transferred in the PP tube and centrifuged for 15 min at 10500 rpm and the solution was filtrated using 0.45 µm filter micropore. The concentration of TCs was determined by Acquity HPLC System (Waters), column (Waters CORTECS™ C18 column 2.1 x 75 mm, 2.7 µm) with a flow rate of 0.4 $mLmin^{-1}$. The mobile phase was a misture of water with acetonitrile. The products of interactionwere irradiated and put in a Petri dish to be collected on pre-determined times. The solar simulator used was model 1500 Solarbox, equipped with a Xenon lamp (irradiance range from 250 to 1100 Wm^{-2}) that supplies radiance energy in spectral range from 290 to 800 nm. The used clay mineral has decreased the efficiency of the photodegradation of these antibiotics. Although, it is important to increase the exposure time of the interaction product in order to investigate possible structural changes of the systems [6].

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WATER INDUCED SOIL EROSION ASSESSMENT AND MONITORING USING REMOTE SENSING AND GIS

Zouhair Ourhzif, Ahmed Algouti, Abdellah Algouti

Laboratoiry Earth Science, Geotourism, Natural Hazard and Remote Sensing, Faculty of sciences Marrakech Morocco
ourhzifz@gmail.com

The average and high mountain country semi-arid such as it appears in the High Atlas, seems a original domain very different from the wet mountain and temperate. The precipitations and the mediocrity of the vegetable cover are brutal and powerful there: it is a mountain dissected by the streaming at all elevation, even if in High Mountain the mark of the gelifraction which starts the mass movement of material, such as rock, earth or debris, down the slope of a hill or cliff.

The Imini plateau is a capable area for occurrence various kinds of erosion because of its mountainous feature, geological and climatologic variety. The main objective of this research is to produce adetailed water erosion susceptibility map for the Imini and Ounilla basin in the south front of the high Atlas of Marrakech. Erosion susceptibility zoning involves a degree of interpretation and spatial distribution rate of the terrain units according to their propensity to produce erosion which is that dependent on topography, geology, geotechnical properties, climate, vegetation and anthropogenic factors such as development and clearing of vegetation.

The province of Ouarzazate is characterized by its oasis landscapes. Agriculture is the main activity in this region. The geographical distribution of population, shows a high concentration along the main roads and the banks of the main wadis.

The area has a semi-arid to arid desert climate. The average annual rainfall averages generally up to 120 mm . The distribution of rainfall in the year shows two seasons, dry from April to September and wet from November to March.

This study was conducted using a Geographic Information System (GIS), in order to prioritize the different areas of the sub-watershed, producing a synthetic map for the distribution of degrees of sensitivity to erosion.

In effect, three classes of multifactorial vulnerability to water erosion have been distinguished areas with low vulnerability 40,18%; the areas to medium vulnerability 24.93% and areas highly vulnerable 34,88%. As well, in the sub-basin, the classes at medium and high multifactor vulnerability represent 60% of the area.

Keyword: water erosion, vulnerability, GIS, semiarid climate.

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GEOCHEMICAL CHARACTERISATION OF THE <2 µm FRACTION OF CRETACEOUS-TERTIARY KAOLINS FROM EASTERN DAHOMEY AND NIGER DELTA BASINS, NIGERIA: IMPLICATIONS ON PALEOENVIRONMENT, PROVENANCE, AND TECTONIC SETTINGS

Olaonipekun Oyebanjo (1)*, George-Ivo Ekosse (2), And John Odiyo (1)

(1) School of Environmental Sciences, University of Venda, P/Bag X5050, Thohoyandou, 0950, South Africa, (2) Directorate of Research and Innovation, University of Venda, P/Bag X5050, Thohoyandou, 0950, South Africa
*oladayo2004@yahoo.com

The geochemistry of the <2 µm fraction of Cretaceous-Tertiary Kaolins from Eastern Dahomey and Niger Delta Basins, Nigeria was conducted to infer their paleoenvironment, provenance, and tectonic settings using major, trace, and rare earth elements (REE). A total of twenty-eight (28) samples comprising of fifteen (15) Cretaceous and thirteen (13) Tertiary kaolins, respectively, were collected. Weathering indices such as chemical index of alteration (CIA, 96.98-99.39) and chemical index of weathering (CIW, 98.76-99.89) suggested intense chemical weathering under a wet tropical climatic condition [1,2]. V/Cr ratio and bivariate plots of V versus Ni and Ni versus Co indicated that they were deposited under marine anoxic environment which is consistent with the horst and graben structural framework model of the Eastern Dahomey and Niger Delta Basins [3,4]. The major, trace and REE data suggest that these deposits were derived from a mixture of mafic, intermediate, and felsic source rocks. The mafic source rock contribution was inferred based on the geochemical discriminant plot [5], relatively high TiO_2, and Ni contents which could not be directly related to a granitic source [6]. Bivariate plots of TiO_2 versus Al_2O_3 indicated intermediate-mafic source whereas Th/Co versus La/Sc, and trivariate plot of La-Th-Sc plotted on the fields of intermediate-granitic source [7]. Based on the REE ratios, chondrite-normalized REE patterns showing light REE enrichment relative to heavy REE, and negative Eu anomaly, the felsic source rock was inferred [8]. The geochemical discrimination and trivariate plots showed that the Cretaceous and Tertiary kaolins have been deposited in passive margin tectonic settings [9,10,11].

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CLAY MINERALS AND IONIC LIQUIDS COMPOSITES AS SORBENTS FOR EMERGING MICRO-POLLUTANTS REMOVAL

Ruta Ozola (1)*, Maris Klavins (1), Andris Zicmanis (2), Elina Aboltina (2), Juris Burlakovs (1,3)

(1) Faculty of Geography and Earth Sciences, University of Latvia, Riga, LV-1004, Latvia, (2) Faculty of Chemistry, University of Latvia, Riga, LV-1004, Latvia, (3) Faculty of Health and Life Sciences, Linnaeus University, Kalmar, SE-391 82, Sweden
*ozola.ruuta@gmail.com

Ionic liquids intercalation into the galleries of clay materials have attracted a great interest due to their ability to provide hydrophobic properties to modified clay materials [1]. Therefore, newly obtained composites can be used as sorbents of emerging micro-pollutants such as pharmaceutically active compounds. The presence of pharmaceutical products at significant concentrations in numerous water compartments is an important environmental issue [2].

The research aims to prepare organically modified clays using various ionic liquids and evaluate the removal efficiency of pharmaceutically active compounds from aqueous solutions.

In this study, synthesized different chain length ionic liquids namely, 1,3-dimethylimidazolium dimethylphosphate, 1-tetradecyl-3-dimethylimidazolium dimethylphosphate, 1,2,3-trimethylimidazolium dimethylphosphate, 1-tetradecyl l-3-methylimidazolium chloride, 1-dodecyl-3-methylimidazolium chloride and 1-octyl-3-methylimidazolium chloride were intercalated in the galleries of synthetic bentonite and natural smectite dominated clays.

To verify the intercalation of ionic liquid cations, X-ray diffraction (XRD), thermogravimetric analysis (TGA) and Fourier transform infrared spectroscopy (FTIR) were used. The modification experiments were investigated under various environmental conditions - e.g., pH, sorbent dosage, contact time and temperature. Further the sorption capacity of obtained sorbents in respect to model pharmaceutical substances were studied.

Obtained results offer a new approach and potential applications of ionic liquid modified clays, especially for water treatment.

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PERIODICALLY WRINKLED GRAPHENE FOR DESIGN OF ORGANIZED CLAY STRUCTURES

Barbara Pacakova (1,2)*, Tim Verhagen (2), Milan Bousa (3), Uwe Hübner (4), Anton Repko (5), Alice Mantlikova (2), Jana Vejpravova (2,6), Martin Kalbac (3), Otakar Frank (3)

(1) Norwegian University of Science and Technology, Trondheim, Norway, (2) Institute of Physics of the CAS, v.v.i., Prague, Czech Republic, (3) J. Heyrovsky Institute of Physical Chemistry of the CAS, v.v.i., Prague, Czech Republic, (4) Leibniz Institute of Photonic Technology, Jena, Germany, (5) Faculty of Science, Charles University in Prague, Prague, Czech Republic, (6) Faculty of Mathematics and Physics, Charles University in Prague, Prague, Czech Republic

Layered material-carbon nanocomposites are very promising for ‘green’ applications in the energy storage or chemical (gas) sensing. One of the very interesting nanocomposites could be the clay-graphene system [1], with the graphene working as an electrode. Fabrication of ordered clay structures on graphene can be done using the self-assembly of clay particles. To increase the efficiency of the fabrication process targeting the defined design of clay structures on graphene, wrinkled graphene can be used rather than standard flat graphene transferred over the flat substrate.

We are showing two types of wrinkled graphene structures: homogeneously wrinkled graphene [2,3] and graphene with large arrays of parallel equidistantly separated long wrinkles [4]. Both types of graphene wrinkle networks were made using the pre-patterned substrates; the Si/SiO_2 (300 nm) substrate decorated with the superparamagnetic nanoparticles [2,3], and hexagonal array of the SiO_2 nanopillars [4].

The wrinkle hierarchy can be well controlled for both sample types. Area covered by wrinkles on the nanoparticle-supported graphene increases linearly with the nanoparticle density, forming typical wrinkle shapes with the wrinkles propagating in all directions [2,3]. On the contrary, the networks of parallel equidistantly separated long wrinkles (Fig. 1) found on the nanopillars-supported graphene are formed on the line defects in graphene (grain boundaries). If no line defect is present, the wrinkles on nanopillar-supported graphene form networks qualitatively comparable with the wrinkles on nanoparticle-supported graphene [4].

Both wrinkle network types are promising candidates for the smart substrates allowing formation of the clay structures with predictable and defined geometry, such as the well-separated clay islands or long parallel lamellas.

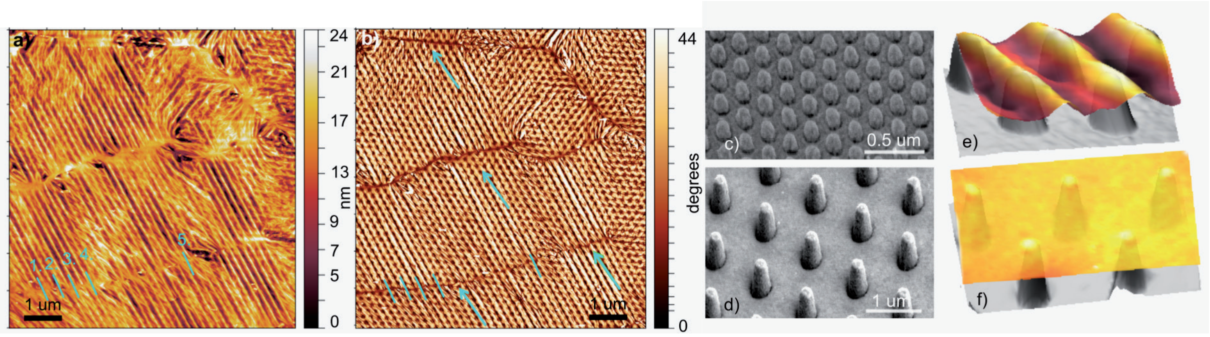

Fig.1. Formation of the aligned wrinkle networks induced by the graphene line interfaces (marked with green arrows); a) AFM topography and b) phase images. As seen, the graphene line interface is barely observable in the AFM topography (a) and the position of the interface cannot be determined from the cross-sections of the topography. (c, d) HRSEM images of the nanopillar arrays. (e, f) 3D AFM topography visualization of the wrinkled graphene on the top of the nanopillar arrays.

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VEGF-ASSOCIATED CLAY GELS PROMOTES ANGIOGENESIS IN AN *IN VITRO* AND A MURINE-BASED MODEL: POSSIBLE TREATMENT FOR CHRONIC DIABETIC ULCERS

Daniel Page (1,2)*, Raj Mani (4), Claire Clarkin (3), Jon Dawson (2), Nicolas Evans (1,2)

(1) Department of Bioengineering, Faculty of Engineering and the Environment, University of Southampton, UK, City, (2) Centre for Human Development and Health, Stem Cells & Regeneration, Faculty of Medicine, University of Southampton, U.K., (3) Centre for Biological Sciences, Faculty of Natural and Environmental Sciences, University of Southampton, UK., (4) Medical Physics & Bioengineering, University Hospital Southampton NHS Foundation Trust, U.K.

People that suffer with diabetes have a high risk of developing diabetic foot ulcers, a type of chronic wound associated with hyperglycaemia. Biological agents, including vascular endothelial growth factor (VEGF), have been investigated as agents that improve wound healing [1], yet delivery in an active economical form remains a significant clinical challenge [2]. The affinity of clays for biological molecules is well established [3]. We tested the hypothesis that gels formed from Laponite, a synthetic smectite clay biomaterial, can retain VEGF in an active form, both in an *in vitro* and an *in vivo* model.

In vitro model: 3% Laponite hydrogels containing fibronectin was premixed with (0.04-5.00 µg/ml) and without rhVEGF$_{165}$ (incorporated and control) and used to coat the surfaces of a 48-well plate. Plain growth medium was added to all Laponite-VEGF surfaces and to half of the control surfaces (negative control); all remaining control surfaces were treated with growth medium mixed with rhVEGF$_{165}$ (0.04 µg/ml) (positive control). Human umbilical vein endothelial cells (HUVECs) were seeded at 2.5 x 10^4 cells/well on all Laponite surfaces. After incubating at 37 °C for 18 hours, tubule networks were quantified by image analysis. *In vivo* model: rhVEGF$_{165}$ was pre-mixed within 3% Laponite gels and subcutaneously injected on the dorsum of healthy mice at three different doses (0.1, 1.0 and 4.0 µg total VEGF). A control hydrogel biomaterial (1.1% alginate) was also tested using the same doses. Contralateral vehicle controls containing no VEGF were always tested for both Laponite and alginate groups. Laponite/alginate biomaterials were recovered after 21 days and the degree of blood vessel formation determined by macroscopic image analysis.

VEGF-mediated stimulation of HUVEC tubules was successfully established and identified on Laponite hydrogel surfaces. It was shown that HUVEC tubule formation was significantly increased when cultured on Laponite hydrogels containing 1.00-5.00 µg/ml VEGF (p = <0.01 to <0.0001). In the *in vivo* murine model, Laponite and alginate hydrogels were both retained subcutaneously after 21 days; there was evidence of dose-dependent vessel ingrowth of Laponite biomaterial when compared to the vehicle control group. In contrast, there was no evidence of any blood vessel ingrowth within alginate gels at any VEGF dose.

We have shown the potential for Laponite hydrogels in retaining biologically active VEGF to promote angiogenesis *in vitro* and when applied *in vivo*. The use of these clays could have significant clinical potential to localise proangiogenic VEGF to chronic wounds and improve the rate of recovery. This would require further study using a wound healing model in healthy and diabetic mice.

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THERMO-IR SPECTROSCOPY IN THE STUDY OF MONTMORILLONITE MODIFIED WITH TETRABUTYL-AMMONIUM AND PHOSPHONIUM CATIONS

Helena Palkova (1)*, Malgorzata Zimowska (2), Lubos Jankovic (1), Ewa. M. Serwicka (2), Jana Madejova (1)

(1) Institute of Inorganic Chemistry, Slovak Academy of Sciences, Bratislava, SK-845 36, Slovak Republic, (2) Jerzy Haber Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences, 30-239 Krakow, Poland
*helena.palkova@savba.sk

Various IR spectroscopy techniques have found application in the investigation of clay minerals modified with organoclays. In this study the IR spectroscopy in both, middle (MIR) and near (NIR) region was used to investigate thermal behaviour of organic cations loaded to montmorillonite and the influence of organic cation type and its loading amount on the changes in the spectra were evaluated.

The organoclays were prepared from Na-montmorillonite SAz-1 (Na-S) and tetrabutylphosphonium (Bu_4P-) and ammonium (Bu_4N-) salts. Thereafter the samples were exposed to treatment in 6 M HCl for 12 h to investigate their chemical stability. The reflectance methods, i.e. ATR in the MIR (4000 - 400 cm^{-1}) and DRIFT in the NIR (8000 - 4000 cm^{-1}) regions, were used to analyse the changes in the spectra of solid samples. Upon cation loading, the C-H vibrational modes of methyl and methylene groups appeared in the spectra: stretching νC-H between 2970-2860 cm^{-1} and bending δC-H within 1480-1380 cm^{-1}. Spectra of Bu_4P-S and Bu_4N-S differed in the shape and position of C-H bands. In accordance with carbon elemental analysis showing lower content of carbon in the samples after 12 h acid treatment, the reduced intensities of the ν and δ C-H bands also confirmed the leaching of organic cations. Complementary information to MIR region provided NIR spectra. Besides the first overtones 2ν and combination (ν+δ) bands of the structural OH groups (around 7100 cm^{-1} and 4515 cm^{-1}) and water (near 6800 and 5250 cm^{-1}), the 2νC-H and (ν+δ)C-H bands were present in the spectra. Heating of the samples in a chamber designed for *in-situ* measurement evoked gradual decrease in the intensity of the $(\nu+\delta)_{H2O}$ band and it was not observable anymore in the spectra taken at 170 °C. Higher temperatures affected also the C-H bands for both samples and due to the organic cations release the 2νC-H and (ν+δ)C-H bands dropped in the intensities. This change was detected at higher temperature for Bu_4P-S (above 500 °C) than for Bu_4N-S (above 380 °C) confirming higher thermal resistance of phosphonium modified sample. The spectra of acid treated samples showed also the first overtone of the Si-OH units confirming degradation of the montmorillonite structure. The intensity of this band increased significantly with increasing temperature and remained present in the structure even after heating at 500 °C.

Infrared module coupled to the thermal analyser was applied to follow the vapour phase release from the organoclay samples. The TG/DTG profiles of both samples showed pronounced mass loss due to the decomposition of organic cations within temperature 200-800 °C. While Bu_4P-S showed onset temperature near 300 °C, significantly lower temperature, around 200 °C, was found for Bu_4N-S. Upon organic phase evolution the absorption bands related to the C-H vibrations of gaseous products (aliphatic hydrocarbons) appeared in the transmission MIR spectra. The intensities of the absorption bands reached maxima at 460 °C and 277 °C and for Bu_4P-S and Bu_4N-S, respectively. The mass loss attributed to the organic cation decomposition for the acid-treated samples dropped down below 50% of its initial value due to the leaching of organic phase. Moreover, the onset temperature of organic phase release was shifted to higher temperature indicating that only more strongly held cations withstand the harsh condition of acid treatment and remained attached to the partially perturbed layered structure. The comparison of the changes in the spectra acquired using various infrared methods the higher thermal stability of alkyl-phosphonium over alkyl-ammonium cations was confirmed.

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SHAPING OF POROUS GEOPOLYMER SPHERES

Elettra Papa*, Riccardo Bendoni, Valentina Medri, Elena Landi

ISTEC-CNR, Institute of Science and Technology for Ceramics, 48018 Faenza, Ravenna, Italy

This preliminary study reports a simple process for the production of geopolymer porous spheres through an injection and solidification method using liquid nitrogen.

Metakaolin-based geopolymer slurries were prepared in advance, using a potassium-based disilicate as alkaline activating solution, and left at room temperature for several hours (maturation step) in order to trigger the geopolymerization without reaching a complete chemical consolidation.

The mixture was injected as it is or mixed with water or an organic template in order to modulate the porosity developed in the final spheres.

Indeed, the production process of geopolymers in aqueous medium allows the tailoring of the porosity by tuning the water content in the starting mixture, which affects the intrinsic mesoporosity of the geopolymer matrix, being water a pore former during the polycondensation stage [1,2]. The porosity of the spheres can be further tailored adding organic polymers in the mixture that act as templates of the material skeleton.

The spheres, formed after the injection, were then freeze dried in a lyophilizer to remove the solidified water and complete the chemical consolidation of the geopolymer. The polymeric template can be later removed by thermal treatment.

The goal of this study was to synthetize geopolymer spheres with hierarchical porous structures differing in term of intrinsic mesoporosity and architecture, which means distribution of voids/material within the sphere.

The developed materials find potential applications in fields as catalysis, filtration, adsorption, etc.

Geopolymer slurries composition and maturation steps were deeply investigated in order to optimize the consolidation process and to design the porosity in the final spheres. For the same reason, the timing of the organic template addition to the geopolymer mixture was also studied.

The selected geopolymer spheres were characterized in term of size, morphology, macro- and microstructure, composition-stoichiometry, porosity distribution and specific surface area.

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USE OF PALYGORSKITE FIBRES AND HALLOYSITE NANOTUBES TO REDUCE IRON CONCENTRATION IN WATER AND WASTE WATERS

Christina Lazaratou (1)*, Dimitrios Papoulis (1), Dionysios Panagiotaras (2),
Georgios Panagopoulos (2)

(1) Department of Geology, University of Patras, Rio 26 504, Patras, Greece, (2) Department of Mechanical Engineering, Technological Educational Institute of Western Greece, 1 M. Alexandrou 26 334, Patras, Greece

Palygorskite fibres and halloysite nanotubes were used for the reduction of iron cations (Fe^{+2}) in aqueous solutions under various experimental conditions. Palygorskite sample was taken from Ventzia basin deposit in Grevena (Western Macedonia, Greece), and halloysite from the Dragon mine (Utah, USA). Both clay minerals were characterized using XRD, FTIR, SEM and CEC and then were saturated by cations by exchanging NaCl and $CaCl_2$ (1M). The Na-treated samples Na-Palygorskite (Na-Pal) and Na-Halloysite (Na-Hal) as well as the Ca-treated samples Ca-Palygorskite (Ca-Pal) and Ca-Halloysite (Ca-Hal) show enhanced CEC. Depending on the mass/volume ratio of the initial concentration of the cations and aqueous solution, pH, temperature, and contact time, the iron adsorption efficiency was different. It was shown that the Ca-treated clay minerals were more effective than the Na-treated materials, and especially palygorskite for high ratios (0,4g/20ml, 0,4g/50ml) and for initial concentrations of the cations 1 mg/L and 5 mg/L (99,8% adsorption efficiency). However, Ca-Hal seems to be a better choice for neutral or basic pH 7-9, instead of Ca-Pal which is a better adsorbent at acid pH 4-6, and at higher temperatures (>45 ^{o}C) too. Moreover, both clay minerals present similarities to their effectiveness on contact time with cations, and can be characterised as efficient low cost adsorbents. Comparing the two clay minerals tested palygorskite is more effective than halloysite as it was expected due to its higher CEC.

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WASTEWATER REMEDIATION BY SIMULTANEOUS REMOVAL OF DIFFERENT POLLUTANTS THROUGH MONTMORILLONITE CLAY

Filippo Parisi (1)*, Luciana Sciascia (2), Giuseppe Lazzara (1), Marcello Merli (2),
Stefana Milioto (1), Alessandro Pavese (3)

(1) Dipartimento di Fisica e Chimica, Palermo, Italy, (2) Dipartimento di Scienze della Terra e del Mare, Palermo, Italy, (3) Dipartimento di Scienze della Terra, Torino, Italy

Industrial wastewaters often contain different class of pollutants, such as dyes and metals. The simultaneous presence of both type of pollutants, makes it difficult to dispose of them properly and efficiently.

The main objective of this work was to use montmorillonite, Mt, readily and inexpensively available in most places, for the simultaneous adsorption (and removal) of two type of pollutants. The attention was focusedon two “models” pollutants: CeIII and crystal violet. The choice was based on their widespread presence in industrial wastewaters of various origin and their effects on human (and animal and plant) health. Moreover, after separationfrom the industrial wastewater, the contaminantscan be individually recycled in industrial production without or a simple treatment.

Adsorption isotherms of the two pollutants onto Mt clay were first gathered separately under different pH conditions. It was observed that the affinity of the two contaminants toward the clay is strongly affected by the solution pH.

The obtained information was employed to propose two efficient protocols for the removal and separation of the two contaminants from an aqueous solution mimicking an industrial wastewater.

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MINERALOGY AND GEOCHEMISTRY OF THE 5TH CENTURY SOIL LAYERS ON KOREAN EARTHEN FORTRESS WALL IN GONGSANSEONG RAMPART

Jun Hyoung Park, Chang Uk Park, Young Hoon Jo, Chan Hee Lee*

Dept. of Cultural Heritage Conservation Sciences, Kongju National University, Gongu, 32588, Republic of Korea
*chanlee@kongju.ac.kr

The Gongsanseong is the fortress wall which located in Gongju City, Republic of Korea. The Gongsanseong Fortress that protected Gongju, the capital of Baekje Kingdom for 64 years from AD 475 ~ 538, was a representative cultural remain of Ungjin Baekje Period. A variety material like rock and soil was used to construct the ramparts. Emergency excavation was conducted while part of rampart on the Gongsanseong was collapsed in September 14, 2013. As a result of excavation, Panchuk part was found at the bottom of rampart that attracted much attention from academic circle (J. H. Park *et al*., 2016). This study analyzed material features of soil used in panchuk part, construction methods of rampart and causes of collapsibility.

By selecting experimental soil sample per layer of Panchuk area and controlled soil sample in surrounding rampart, quantitative color and magnetic susceptibility analysis was performed. These samples were categorized brown or white layer that showed slightly different magnetic susceptibility. As a result of precision observation based on microscope, brown layer is an output of weathering of gneiss and white layer was an output of weathering of felsic igneous rock. To figure out soil distribution and soil property between layers, particle analysis was performed. In result, particles over 1mm grain size had the largest rate. Also, as a result of checking effective grain size, uniformity factor and coefficient of curvature, most soil samples showed heterogeneous characteristics except only one layer. Therefore, most Panchuk part seemed to be built layers by adding gravel with uneven quantity.

At X-ray diffraction analysis, quartz, plagioclase and alkali feldspar were observed as major mineral composition. Also, most layers had montmorillonite on reduction conditions in the cause of poor drain and index horizon of the bottom had vermiculite on oxidation condition. As a result of chemical analysis, the soil sample showed similar SiO_2 and Al_2O_3 composition regardless of per layer. The difference in color is closely related to the Fe_2O_3 content. The same color layer represents similar geochemical behaviour characteristics. As a result of analysing the gneiss and felsic igneous rock exposed near the rampart, the brown layer was similar to gneiss, and the white layer was similar to felsic igneous rock. So, the used soil for construction is estimated to have been supplied near the rampart.

To estimate the construction process through analysis results, Panchuk part which settled in exposed body rock as ‘L’ shape directly had constructed using soils weathered by gneiss or felsic granite alternately. It seems that these soils did not go through sieving process and some gravels were added for construction. After construction, the rampart of Gongsanseong has physical and chemical damaged. To analysis clay mineral composition of soils from rampart, rainfall caused lubrication between inside rampart and bottom stone. In this process, soils inside rampart were swept away and biased load became excessive, so structural modification was occurred. Therefore, the Gongsanseong rampart was collapsed because lubricated side way appeared between stones and foundation part that cause sliding. Based on these resources, the cause of collapse and mechanism of rampart could be analyzed quantitatively that may be used as important materials for conservation and management system of the Gongsanseong.

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A NEW LOOK AT BIO-KAOLINITE FORMATION AT ROOM TEMPERATURE

Vincenzo Pasquale (1), Stefano Dumontet (1), F. Javier Huertas (2), Antonio Lettino (3), Saverio Fiore (3)*

(1) Department of Sciences and Technology, Parthenope University of Naples, Italy, (2) Instituto Andaluz de Ciencias de Tierra (CSIC-University of Granada), Armilla (Granada), Spain, (3) Institute of Methodologies for Environmental Analysis, National Research Council, Tito Scalo - Potenza, Italy

Interactions between microorganisms and minerals in low energy systems have a long history, as they are incessantly occurring for at least 3 billion years [1]. Minerals of different origin, chemistry, structure and chemical reactivity are continuously interacting with an undefined number of microorganisms displaying a host of phenotypic, genotypic, biochemical and surface properties.

The biogenic clay formation is a matter of great interest from both geological and pedologic standpoints and three main hypotheses were formulated to explain the clay formation at low temperature: a) the process is completely driven by abiotic mechanisms (e.g., [2]); b) the process is a phenomenon under both microbial and inorganic control [3]; c) the process is mainly biologically driven [4].

Kaolinite, a very common clay mineral, plays a relevant role in both soil ecosystem and in the industrial sector. Even though the kaolinite formation in high energy environments is a well-known phenomenon [5], its crystallization at room temperature was obtained only by Linares and Huertas [6] and Fiore et al. [4]. Linares and Huertas focused their work on the abiotic synthesis of kaolinite thanks to humic acids as complexing agents able to get Al in octahedral coordination. Fiore et al. speculated on the microbially induced precipitation of this mineral and documented the formation of few crystals of kaolinite in Si-Al gels precipitated from solution and microflora extracted from a peat soil. An axenic solution, containing the same concentrations of Al and Si, failed to produce the same result.

Extending the incubation over 5 years produced some crystals of low crystallinity kaolinite and highly mineralized bacterial cells. The use of complexing agents, as oxalic acid, alpha-ketoglutaric acid, EDTA and humic acids failed to precipitate kaolinite in axenic solutions containing silicium (as $Na_2SiO_3{\bullet}5H_2O$) and aluminium ($Al(NO_3)_3{\bullet}9H_2O$).

In the present work we report an experiment aimed at obtaining kaolinite from Al and Si solution in presence of fungi. Solutions containing Si, Al and a selected fungal species produced single crystals and packets of kaolinite from few nm up to 2 microns.

This surprising result casts a new light on the process of kaolinite formation in low energy environments. Maybe the role of bacteria has been overestimated compared to the fungal action.

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A PROPOSAL FOR BAUXITE QUALITY CONTROL USING THE COMBINED RIETVELD - LE BAIL - INTERNAL STANDARD XRPD METHOD WITH AN HKL MODEL DEVELOPED FOR KAOLINITE

Simone Paz (1,2)*, Rômulo Angélica (2), Henrique Kahn (1)

(1) Programa de Pós-Graduação em Engenharia Mineral, Universidade de São Paulo, São Paulo-SP, 05508-900, Brasil, (2) Programa de Pós-Graduação em Geologia e Geoquímica, Universidade Federal do Pará, Belém-PA, 66075-110, Brasil
*paz@ufpa.br

In the bauxite industry - exploration, beneficiation and refinery - two main chemical parameters are used for the quality control: available alumina ($AvAl_2O_3$) and reactive silica ($RxSiO_2$). Both are determined using a procedure that simulates the Bayer process at the lab scale [1]. For gibbsitic bauxites, subject of this study, the available alumina is associated with gibbsite, and the reactive silica is associated with kaolinite. For this reason, they are also referred to as gibbsitic alumina and kaolinitic silica. High-grade bauxites contain >41 wt.% $AvAl_2O_3$ and <5 wt.% $RxSiO_2$, while low-grade bauxites contain <41 wt.% $AvAl_2O_3$ and 5-20 wt.% $RxSiO_2$. Gibbsitic bauxites are most valuable in terms of operational cost; the refining process of these bauxites consumes less energy because gibbsite digestion occurs at low temperatures (130-160 ºC). However, significant quantities of kaolinite increase the operational costs because under the conventional conditions of the Bayer process, kaolinite reacts with NaOH (leaching agent) to form a sodalite-type desilication product, which results in irreversible NaOH losses [2-4]. In Northern Brazil (Pará State) are located the three largest bauxite mines in the country (>90% of Brazilian production) and the largest metallurgical alumina refinery in the world (Hydro Alunorte). The loss of caustic soda due to sodalite formation in the Hydro Alunorte refinery has been reported to be much higher than the estimated value based on the amount of reactive silica that has been measured by quality control. It happens mainly in the bauxites from Paragominas (region of Miltônia, Pará State), which typically exhibit high reactive silica contents prior to washing. However, the estimated experimental errors are almost always within the deviations expected by the certified values, which has prevented obtaining a clear answer to this problem. A great innovation for this industry would be to make this control by mineralogical parameters, i.e., the % of gibbsite and % of kaolinite via X-ray Powder Diffraction Analysis (XRPD). Even with the fast increase in the last years of studies related to mineralogical phase quantification using XRPD analysis, there are still some challenges related to bauxite quantification. For instance, the lack of crystal structure information related to kaolinite, which has been underestimated when trying to apply the Rietveld method with available Crystallographic Information File (CFI). In this work, a combination of the Rietveld, Le Bail and Internal standard methods was tested, and the results were very promising for a Brazilian gibbsitic bauxite. This combination not only improved the quality of gibbsite and kaolinite quantification, as decreased computer processing time, making it a more convenient and fast procedure, requirements for an industrial control method.

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SURVIVAL AND ACTIVITY OF SULPHIDE-PRODUCING BACTERIA IN COMPACTED CLAYS IN LABORATORY AND FULL SCALE EXPERIMENTS

Karsten Pedersen, Andreas Bengtsson, Anders Blom, Trevor Taborowski

Micans AB, Mölnlycke, Sweden

Bentonites rich in swelling montmorillonite clay are used to construct engineered barriers in geological repositories for low- intermediate- and high-level radioactive wastes. While there are several low- and intermediate-level repositories in operation around the world, high-level repositories are still in planning or under construction. Various types of metal containers, made of iron or copper, are, or will be used to encapsulate the wastes, often together with concrete or bitumen. Sulphide is in general very corrosive to these metals and safety cases for radioactive waste disposal must, therefore, evaluate the risks involved with sulphide corrosion. The main source of sulphide in geological repository environments is past and present bacterial reduction of sulphate, sulphur and thiosulphate to sulphide. Sulphide-producing bacteria (SPB) have been found in most commercially available bentonites [5,6].

Bacterial sulphide-producing activity in compacted clays was recently investigated as a function of clay type, saturated wet density and geomechanical stress [1,2]. The modelling of sulphide transport in the clays as a non-reactive anion showed a discrepancy between observed corrosion of copper and the amounts of reduced sulphate. It appeared as if sulphide was immobilised by the clays. Therefore, experiments were preformed to study the reactivity of sulphide with bentonite clays. Sulphide was found to reduce ferric iron in montmorillonite type bentonites under the formation of elemental sulphur, ferrous iron and iron sulphide. The immobilisation capacity of the clays was 40 µmole sulphide (g clay)$^{-1}$ or more, depending on the load of sulphide and type of clay. This immobilisation effect can reduce the mass of sulphide that reacts with metal canisters over repository life times, but the concomitant reduction of ferric iron may be problematic due to the destabilizing effect of ferrous iron on dioctahedral smectites such as montmorillonites [3].

Various bentonite clays have small but significant amounts of natural and introduced (during mining) organic matter (OM) than may be utilized by SPB. Such OM may also decrease or increase the mobility of radionuclides. There is a need in the long-term safety case for geological disposal of radioactive wastes to explore if OM in bentonites can promote activity of SPB and influence radionuclide migration [4]. A new high-resolution analysis method for OM speciation in bentonite clays was, therefore developed. All investigated clays had a high diversity of OM and each clay had an uniqe speciation signature of the OM. Laboratory experiments indicated that SPB can utilise some of these organic compounds.

Sulphide-producing activity and survival of SPB generally decrease with increasing geomechanical stress and density of compacted clays. The understanding of the influencing features behind this decrease is still obscure. The wet density of compacted, water saturated clays relates to swelling pressure, water activity and pore space. Further, bentonite clays vary in content and diversity of inherent bacteria and OM. There can be irregularities in the micrometre scale of bacterial life in the compacted clays that allow local, heterogeneous growth. Bacteria may propagate as colonies at such positions in the engineered barriers. These features will be discussed. The full understanding of how bacterial sulphide-producing activity can be mitigated may assist the selection of safe clay types and procedures to construct safe engineered barriers.

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CLIMATIC AND PALAEOCEANOGRAPHIC CHANGES DURING THE PLIENSBACHIAN (EARLY JURASSIC) INFERRED FROM CLAY MINERALOGY AND STABLE ISOTOPE (C-O) GEOCHEMISTRY (NW EUROPE)

Cédric Bougeault (1), Pierre Pellenard (1)*, Jean-François Deconinck (1), Stephen P. Hesselbo (2), Emilia Huret (3), Nicolas Thibault (4)

(1) UMR CNRS 6282 Biogéosciences, Univ. Bourgogne Franche-Comté, 6 Bd Gabriel, 21000 Dijon, France, (2) Camborne School of Mines, and Environment and Sustainability Institute, University of Exeter, Penryn Campus, Penryn, TR10 9EZ, UK, (3) ANDRA, Parc de la Croix-Blanche, 1-7 rue Jean Monnet, 92298 Châtenay-Malabry, France, (4) Department of Geosciences and Natural Resource Management, University of Copenhagen, Øster Voldgade 10, DK-1350 København K., Denmark

The Early Jurassic was broadly a greenhouse climate period that was punctuated by short warm and cold climatic events, positive and negative excursions of carbon isotopes, and episodes of enhanced organic matter burial. Clay minerals from Pliensbachian sediments recovered from two boreholes in the Paris Basin, are used here as proxies of detrital supplies, runoff conditions, and palaeoceanographic changes. The combined use of these minerals with stable isotope data (C-O) from bulk carbonates and organic matter allows palaeoclimatic reconstructions to be refined for the Pliensbachian. Kaolinite/illite ratio is discussed as a reliable proxy of the hydrological cycle and runoff from landmasses.

Three periods of enhanced runoff are recognised within the Pliensbachian: (1) at the Sinemurian-Pliensbachian transition with a significant increase of kaolinite concomitant with the negative carbon isotope excursion at the Sinemurian Pliensbachian Boundary Event (SPBE); (2) the Early/Late Pliensbachian transition associated with more humid conditions and a major change in oceanic circulation during the Davoei Zone, likely triggered by sea-level rise [2]; the newly created palaeogeography, notably the flooding of the London-Brabant Massif, allowed boreal detrital supplies, including kaolinite and chlorite, to be exported to the Paris Basin; and (3) an enhanced runoff episode occurred during the late Pliensbachian (Subdonosus Subzone of the Margaritatus Zone), associated to warm conditions, favouring organic matter production and preservation.

Our study highlights the major role of the London Brabant Massif in influencing oceanic circulation of the NW European area, as a topographic barrier (emerged lands) during periods of lowstand sea-level and its flooding during period of high sea-level. This massif was the unique source of smectite in the Paris Basin [1]. Two episodes of smectite-rich sedimentation coincide with regressive intervals, indicating emersion of the London Brabant Massif and thus suggesting that an amplitude of sea-level change high enough to be linked to glacio-eustasy. This mechanism is consistent with sedimentological and geochemical evidences of continental ice growth notably during the Latest Pliensbachian (Spinatum Zone), and possibly during the Early Pliensbachian (late Jamesoni/early Ibex Zones).

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STRATEGIES FOR IMPROVED DETECTION AND QUANTIFICATION OF TIO_2 POLYMORPHS IN CLAY MATERIALS BY X-RAY DIFFRACTION

Helen Pendlowski (1)*, Stephen Hillier (1,2), Ian Phillips (1)

(1) The James Hutton Institute, Aberdeen, AB15 8QH, United Kingdom, (2) Department of Soil and Environment, Swedish University of Agricultural Sciences, Box7014, Uppsala SE-750 07, Sweden
*helen.pendlowski@hutton.ac.uk

The minerals anatase (CAS no 1317-70-0), rutile (CAS no 1317-80-2) and brookite (CAS no 12188-41-9), common polymorphs of TiO_2, are not uncommon minor/trace components of many clay materials such as bentonites and kaolins. Following the proposal by the French Agency for Food, Environmental and Occupational Health & Safety (ANSES) on behalf of the French Member State Competent Authority (MSCA) to the European Chemicals Agency (ECHA) for titanium dioxide to be classified as a Category 1B carcinogen by inhalation [1], there has been increased interest in accurate quantification of anatase, rutile and brookite in industrial clay materials. All three minerals are relatively good diffractors with nominal reference intensity ratios (RIRs) of 3.8, 2.8 and 1.6 respectively. With appropriate sample preparation and good counting statistics analysis by X-ray diffraction can obtain lower limits of detection that are routinely in the sub-percent range, with anatase being the most readily detectable mineral. In a practical sense, however, detection and quantification of these minerals in clay materials is often affected by line overlap with other minerals. Several strategies designed to alter the main clay mineral components of such clay materials to improve detection and quantification of these minor minerals have been tested including selective dissolutions and dehydroxylation. The details of these procedures and their use in improving detection and quantification of the TiO_2 polymorphs in clay materials will be presented.

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CUSTOMIZING SPECTRAL LIBRARIES FOR EFFECTIVE MINERAL EXPLORATION

Jeanne B. Percival (1)*, Sean A. Bosman (2), Eric G. Potter (1), Jan Peter (1), Alexandra B. Laudadio (3), Ashley C. Abraham (3), Daniel A. Shiley (4), Chris Sherry (4)

(1) Geological Survey of Canada, Ottawa, Canada K1A 0E8, (2) Saskatchewan Geological Survey, Regina, CanadaS4P 3Z8, (3) Department of Earth Sciences, Carleton University, Ottawa, Canada K1S 5B6, (4) ASD Inc.- PANalytical, Boulder, U.S.A.80301

Explorationists require rapid analytical results to make cost-effective decisions during drilling operations. Progress over the last few decades in field instrumentation has facilitated acquisition of*in situ*, non-destructive, rapid, semi-quantitative to quantitative chemical analyses, provided that calibration, interferences and matrix effects are well considered. Handheld X-ray fluorescence spectroscopy (XRF)has become more precisein detecting elements of interest in exploration programs and Laser-Induced Breakdown Spectroscopy (LIBS) is now capable of being used in the field. However, forcertain deposit types, alteration mineralogy may be a stronger indicator of proximity to mineralization. This is especially important in volcanogenic massive sulfide (VMS), epithermal gold (high or low sulphidation), Iron Oxide-Copper-Gold (IOCG), sedimentary exhalative (SEDEX), Mississippi Valley-type (MVT) and unconformity uranium deposits. Changes in clay mineralogyprovide information on genetic and/or alteration history, and may reflect different source rocks, fluids, or depths of formation. In epithermal gold deposits, the high sulphidation processes give rise to alunite, a characteristic indicator mineral. In the uranium-rich Athabasca Basin (AB), Canada, clay mineral alteration can guide the location of more detailed geophysical surveys, surface sampling and ultimately, drilling operations, as a project advances. Clay mineralogical changes from diagenetic dickite to hydrothermal illite are commonly observed associated with uranium deposits in the eastern part of the AB. In contrast, mineralogical changes are less extensive and more subtlein deposits in the western part of the AB and deposits hosted in basement rocks.

For rapid mineral identification, both portable X-ray diffractometry (XRD) and infrared (IR) spectrometry are effective techniques. However, XRD requires some sample preparation whereas IR does not, other than ensuring a dry surface. Today, handheldIR spectrometers are equipped with on-board spectral libraries which enable rapid qualitative analysis of major minerals, and this permitsthe facile recognition of key alteration minerals. Spectral libraries can be general or customized for specificmineral deposit environments. To create a library, careful collection of spectra in a controlled environment on pure specimensof key alteration minerals is required. The spectrometer system is validated prior to use using a wavelength standard to ensure consistency across all reference samples. In this study, spectra were collected using a Spectralon® white reference puck as a relative reference and then were mathematically transformed to absolute reflectance format to account for the reflectance characteristics of the Spectralon® panel. The spectrum of each new example is then compared to other examples of this mineral ensuring that only the most representative spectra are added to the library. This comparison process requires many examples of each mineral to characterize that species. To this end, we participated in collecting spectra on a variety of standards using the "Kodama clay collection" (a suite of carefully analysed samplesdonated to the GSC following Dr. H. Kodama's retirement) that were incorporated into the National Mineral Collection [1]. The spectra collected were evaluated using a variety of spectral plotting software and after validating each new example they were incorporated into the on-board library of the handheld ASD-HALOnear-infrared mineral identification instrument. Currently, collection of spectra is underway for rare earth element-bearing minerals, typical of carbonatite and alkali intrusive deposits, housed in the National Mineral Collection. This talk will examine the utility of alteration minerals in exploration programs and how field portable instruments can provide essential rapid, non-destructive, qualitative to quantitative information.

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CLAY MINERALOGY COMPOSITION OF MIDDLE MIOCENE LEITHA LIMESTONE FORMATION FROM CORES OF A WATER WELL IN THE SOUTHERN VIENNA BASIN (AUSTRIA)

Mandana Peresson*, Stepan Ćorić, Christian Rupp, Beatrix Moshammer, Gerhard Bieber, Alexander Römer

Geological Survey of Austria, 1030 Vienna, Austria

The Leitha Mountains are located 30 km southeast of Vienna. They separate the Vienna Basin from the Pannonian Basin. The Vienna Basin is a thin-skinned pull-apart basin on top of the Alpine-Carpathian fold-thrust belt (Decker & Peresson, 1996). The basement of the Leitha Mountains is formed by Lower East Alpine crystalline units and covered by Badenian and Sarmatian (Langhian and Serravallian) sediments, which embodied a shallow carbonate platform (Schmid et al., 2001). Fully marine deposition started at the beginning of Early Badenian. During the Middle Miocene the Leitha Mountains formed a topographic high with extensive carbonate production. The succession is well known for coralline algal limestones (Leitha Limestone), but also comprises a variety of different facies types, which are topic of intensive research work (Wiedl et al., 2012). A 40 m deep water well was drilled in the northern part of the Leitha Mountains in February 2016. The Geological Survey of Austria was in charge for lithological and mineralogical data sampling and interpretation.

The well can be divided into 3 different stratigraphic and lithological zones with a transition from siliciclastic to carbonate depositional environment: 1) The cores from the first 8m comprise grayish to reddish sandy and gravel sediments. The sand fraction is characterized by a very high amount of shell fragments. The faunas were classified as Sarmatian siliciclastic sediments in a shallow marin environment. 2) Between 8 and 13 meters lithology is changing completely. There is a predominance of dark gray marls and clays with high rate of bioturbation. Diverse bentonic foraminifera and nannoplancton give evidence to a deep neritic to bathyal habitat of Upper Badenian age (NN6). 3) Until the final depth of 40.4 meters there is an intercalation of dark grey clay marls with Leitha limestone enriched in corallinacea and foraminifers. The faunal elements including nannoplancton data indicate Middle Badenian age (NN5) in a shallow middle neritic depositional environment.

For representative grain size analysis, wet sieving and X-Ray sedigraph techniques have been applied. The bulk rock and clay mineralogy of 8 samples was determined by XRD. The sample from the Sarmatian section is composed of 41% quartz, 6% phyllosilicates, 9% feldspar and 44% carbonate, mainly calcite. The bulk rock mineralogy of the underlying Upper Badenian samples show a dominance of phyllosilicates up to 57%, followed by quartz with a maximum of 30%, carbonate content varies between 10-30%. The samples of the Middle Badenian succession consist almost completely of carbonate (75-88% calcite). There is evidence of tectonic and climatic control in the clay mineral assemblages. Clay mineralogy of all samples is dominated by smectite and illite, there is significant difference in the amount of kaolinite, chlorite and vermiculite. The siliciclastic influence of the Sarmatian cores is demonstrated by the highest amount of vermiculite and chlorite and little amount of kaolinite. Upper Badenian samples show lesser amount of vermiculite, chlorite and kaolinite and the highest quantity of smectite, which correspond with a period of sea level highstand. High content of kaolinite (18-37%) and complete absence of chlorite was detected only in the Middle Badenian samples, which indicates strong tropical weathering conditions and less tectonic influence in the source area.

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MULTIDISCIPLINARY STUDY OF THE LOW-GRADE METAMORPHISM IN THE PULO DO LOBO METASEDIMENTARY BELT (SW IBERIAN VARISCIDES): X-RAY DIFFRACTION, RSCM AND CHLORITE THERMOMETRY FROM COMPOSITIONAL MAPS

Irene Pérez-Cáceres (1), David Martínez Poyatos (1), Olivier Vidal (2), Olivier Beyssac (3), Fernando Nieto (4), Fernando Simancas (1), Antonio Azor (1)

(1) Departamento de Geodinámica, Facultad de Ciencias, Universidad de Granada, Campus de Fuentenueva s/n, 18071 Granada, Spain, (2) Institut de Sciences de la Terre (ISTerre), CNRS-Université Grenoble Alpes, 1381 rue de la Piscine, 38041 Grenoble, France., 3) Institut de Minéralogie et de Physique des Milieux Condensés (IMPMC), CNRS-Université Pierre et Marie Curie, Case Courrier 115, 4 place Jussieu, 75005 Paris, France, (4) Departamento de Mineralogía y Petrología, Facultad de Ciencias, Universidad de Granada, Campus de Fuentenueva s/n, 18071 Granada, Spain

The Pulo do Lobo belt (SW Iberian Variscides) is a low-grade metasedimentary unit considered as a subduction-related accretionary prism formed in relation to the suture contact between the Ossa-Morena and South Portuguese zones. The classical interpretation of this contact has been challenged with the dating of the metabasites of both Beja-Acebuches unit and those imbricated within the Pulo do Lobo metasediments. The early Carboniferous ages allow attributing these rocks to a thermal transtensional event of that age that interrupted the ongoing Variscan collision.

The metamorphic evolution of the polydeformed Pulo do Lobo rocks is poorly known, therefore we have applied three methodologies to eighteen samples of metapelites in order to provide with new data on this evolution. X-Ray diffraction (XRD) was used to characterize the mineralogy and to measure crystallographic parameters. Compositional maps derived from electron probe microanalysis and processed with Xmap Tools were used to obtain mineralogical maps and chlorite thermometric data through thermodynamic modeling. Raman spectrometry of carbonaceous matter (RSCM) was used to stablish peak temperatures. The results can be summarized as follows:

1. The obtained data, combined with microstructural analysis, allow the characterization of two low-grade metamorphic events (M1 and M2) related to the Devonian D1 and middle-upper Carboniferous D2 deformation phases in the Pulo do Lobo belt.
2. M1 corresponds to the epizone. The temperatures obtained by RSCM (≈400-500 °C) are higher than those obtained with the other methods, the discrepancy being interpreted in terms of the higher sensibility of the carbonaceous matter to quickly reequilibrate during a short-lived thermal event (e.g., during the early Carboniferous transtensional event).
3. Relic high-temperature cores in the compositional maps of S1 chlorites, chlorite/smectite mixed layers, and the variable, though very-low, temperatures calculated with chlorite geothermometers, evidence clorite retrogression after M1 metamorphic climax.
4. M2 do not exceed the anchizone/epizone boundary (≈300-330 °C). The metamorphic gap between M1 and M2 corroborates the existence of an unconformity between the Devonian and Carboniferous successions of the Pulo do Lobo belt.
5. The very low celadonite content in white mica and low values of *b*-cell dimension indicate low-pressure conditions, which are incompatible with the high-pressure gradient that would be expected in a subduction-related accretionary prism.

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EXPERIMENTAL INVESTIGATION OF MINERAL CONTROL ON THE MICROBIAL MODE OF ATTACK ON MINERAL SURFACES FOR THE OBTENTION OF INORGANIC NUTRIENTS

Araceli Perez-Sanz (1)*, Javier Cuadros (1), Silvia Pressel (2), Anne Jungblut (2)

(1) Department of Earth Sciences, Natural History Museum, Cromwell Road, London SW7 5BD UK, (2) Department of Life Sciences, Natural History Museum, Cromwell Road, London SW7 5BD UK

Microorganisms interact with mineral surfaces in different ways through microbially mediated formation and dissolution of minerals, the formation of mineral-organic associations through the deposition of microbial products, or the acquisition and utilization of organic material from the mineral-organic associations for microbial metabolism [1]. The production of microbial substances, with the subsequent biofilm formation, is assumed to be the major mechanism by which bacteria and fungus contribute to mineral alteration, and it is especially important when microorganisms grow in environments with limited nutrient concentrations [2]. Scanning Electron Microscopy (SEM) techniques can provide important information about the way in which extracellular polymers substances coat minerals and about the chemical changes taking place on the mineral surfaces.

The objective of this work was to determine the changing strategies followed by microorganisms to obtain inorganic nutrients from silicate minerals of different composition, some of them with nutrient deficiency. Batch experiments were performed in petri dishes. Three phyllosilicates (kaolinite, vermiculite and biotite) and volcanic lava were incubated with a bacterium (*Bacillus subtilis*) and a fungus (*Aspergillus niger*). Organic nutrients were added but inorganic nutrients were only those in the mineral substrates. The experiments were maintained at 25 °C in the dark for four months. After the experiments, some replicates of the minerals were investigated coated with the microbial colonies in order to see the spatial relation between biofilm and minerals. These samples were washed with Millipore water, freeze-dried and analysed by SEM-EDX. In other replicates, the biofilms were removed to investigate the alteration footprint of the microorganisms on the mineral surfaces.

The attack of the two microorganisms on the several minerals was very different. The fungus was more aggressive than the bacterium. Vermiculite and biotite were mainly attacked at the edges of the chips (layer edges) where the fungus produced a severe loss of all cations except Si and the bacterium produced a variable depletion of Si, Mg and K. The fungus produced differential dissolution of the several minerals in the lava (glass, plagioclase, pyroxene, amphibole). Kaolinite showed slight differences in the Si/Al ratios. These results indicate the large control of mineral composition and crystal structure on the mode and intensity of microbial attack.

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REVISITING THE NONTRONITE MÖSSBAUER SPECTRA USING A SERIES OF SYNTHETIC NONTRONITES

Petit Sabine (1)*, Baron Fabien (1), Pentrak Martin (2), Stucki Joseph W. (2)

(1) Institut de Chimie des Milieux et Matériaux de Poitiers (IC2MP), UMR CNRS 7285 Université de Poitiers, Poitiers, France, (2) Department of Natural Resources and Environmental Sciences, University of Illinois at Urbana-Champaign, Urbana, Ilinois, USA
*sabine.petit@univ-poitiers.fr

Mössbauer spectroscopy has often been used to determine the Fe(III)/Fe(II) ratio and the distribution of Fe(III) between the octahedral and the tetrahedral sheets of smectites and other clay minerals. The Mössbauer spectra are generally fitted with a sum of doublets, but the empirical attribution of each doublet has failed to yield a uniform interpretation of the spectra of natural reference Fe(III)-rich smectites, especially with regard to [4]Fe(III), because little consensus exists as to the [4]Fe(III) content of natural samples. The originality of this work was to use a series of synthetic nontronites. These synthetic nontronites were well characterized and have a wide range of [4]Fe(III) contents and a simple chemical composition following the $[Si_{4-x}\,[4]Fe(III)_x]\,[6]Fe(III)_2O_{10}(OH)_2Na_x$ structural formula with x ranging from 0.43 to 1.3 (Baron et al., 2016).

Mössbauer spectra were obtained at 298, 77, and 4 K. The deconvolution of Mössbauer spectra of synthetic samples was done by fixing the area of doublets for each cationic environment calculated from a structural model. This fundamental step allowed a more proper interpretation of the Mössbauer spectra and a complete and coherent representation of the distribution of Fe(III) between the octahedral and tetrahedral crystallographic sites of the nontronite structure.

Although the use of a simple model from the sum of Lorentzian line-shape has been considered to be less theoretically correct than a Voigt-based model (Rancourt 1994), the self-consistent results obtained with the synthetic nontronites provided evidence of the important role of the local environment around a [6]Fe(III) cation as well as the role of crystallinity (i.e., the long distance lattice defects) in determining the Mössbauer parameter values, particularly the value for Δ. As previously mentioned by Rancourt (1994), the deconvolution of Mössbauer spectra did not tend to a unique solution. However, in the present paper, the use of six synthetic nontronite samples in which Mössbauer parameters at both 77 K and 298 K tended toward similar and coherent δ and Δ values thus giving confidence in the methodology. This approach was then applied to spectra of natural Fe(III)-rich smectites. Results revealed the necessity of taking into account the distribution of tetrahedral cations ([4]R(III)) around [6]Fe(III) cations in order to deconvolute the Mössbauer spectra, and also highlighted the influence of sample crystallinity on Mössbauer parameters. These results are to be published by Baron et al. (2017).

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HEAVY METALS CATIONS REMOVAL BY MECHANOCHEMICALLY ACTIVATED SAPONITE

Lukáš Petra (1)*, Peter Billik (2), Peter Komadel (1)

(1) Institute of Inorganic Chemistry, Slovak Academy of Sciences, Dúbravská cesta 9, SK-845 36 Bratislava, Slovakia, (2) Department of Inorganic Chemistry, Faculty of Natural Sciences, Comenius University in Bratislava, Ilkovičova 6, SK-841 04 Bratislava, Slovakia
*lukas.petra@savba.sk

The use of smectites for heavy metal cations removal has been extensively studied for years. The inconvenience of their application is the possibility to outflow adsorbed metal cations. Mechanochemical activation is a way to change the physical properties of smectites towards effective fixation of heavy metal cations. This can be achieved effectively in a planetary ball mill, where the impact energy is transferred to the powder resulting from the ball to ball and ball to wall collisions. Mechanochemical activation of smectites by high-energy grinding (HEG) results in substantial changes of their structure and produces fresh and active surfaces and therefore they can be used for heavy metals removal and immobilisation. Moreover, the removal of metal cations by mechanochemically activated smectites has not been extensively analysed yet.

Hence, the aim of this work was to prepare modified materials suitable for metal cations removal based on saponite Sumecton using HEG for 2, 4, and 6 minutes. The corresponding structural changes were tracked by scanning electron microscopy, X-ray diffraction, FTIR spectroscopy, the determination of cation exchange capacity and specific surface area, and thermal analysis. The removal of Cu^{2+} and Ni^{2+} by parent and treated samples was further investigated. Batch adsorption experiments were run in aqueous solutions to study the influence of initial metal cations concentration and pH on the amount of removed metal cations. The concentrations of Cu^{2+} and Ni^{2+} ions in supernatants before and after adsorption were determined by atomic adsorption spectrometry. The amount of removed metals ions per mass unit of the adsorbent at equilibrium q_r (mg/g) was calculated using equation (1).

$$q_r = \frac{(c_0 - c_f) \cdot V}{m} \tag{1}$$

Where c_0 (mg/L) is the initial concentration of the metal ion, c_f (mg/L) is its final concentration, V (L) is the volume of adsorbate solution, and m (g) is the mass of the adsorbent.

Mechanical stress during high-energy grinding of saponite smectite sample changed the structure considerably and active Mg-OH surface with high acid neutralization capacity appeared. For Cu^{2+} removal, the formation of insoluble $Cu(OH)_2$ was confirmed by X-ray diffraction and SEM analysis, whereas for $Ni^{2+,}$ the formation of $Ni(OH)_2$ was confirmed by SEM. The removal of Cu^{2+} in the $Cu(OH)_2$ form by activated saponite was more efficient than Ni^{2+} removal. Mechanical activation increased Cu^{2+} removal or adsorption from 33.2 mg/g to 287 mg/g and Ni^{2+} from 46.0 mg/g to 124 mg/g. The removed metal cations form insoluble hydroxides on the surface of ground saponite, so the ions are fixed and unavailable for further ion exchange. This study provides a promising option of smectite modification to prepare efficient adsorbents for treating wastewater containing heavy metals, such as Cu^{2+} and Ni^{2+}. The removal performances are significantly better than those of smectite based adsorbents reported previously. The results reveal that the mechanochemical activation is a low-cost, effective, and available method of smectite structure modification and can be considered a potential candidate for feasible application.

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VALORIZATION OF FIRED BRICK CLAY IN LIGHTWEIGHT WASTES BASED GEOPOLYMER AGGREGATES

Julie Peyne (1,2)*, Jérôme Gautron (2), Julie Doudeau (3), Emmanuel Joussein (4),
Sylvie Rossignol (1)

(1) Laboratoire SPCTS, Limoges, France, (2) Bouyer Leroux, La Séguinière, France, (3) Bouyer Leroux, Colomiers, France, (4) Laboratoire GREASE, Limoges France

From the late 1970's, a new class of materials, also known as geopolymer materials have demonstrated an increasing interest in various industrial applications, due to their outstanding properties, such as mechanical, thermal and chemical properties, constant within the time. Recent researches have investigated the use of low quality clay, by-products sourced from various industries instead of a pure metakaolin, which is one the most aluminosilicate materials used for geopolymer. The raw clay materials in geopolymer materials are of great interest for building applications, where the demands of reducing the energy consumption is high. Furthermore, the valorization of waste production such as construction demolition waste (which represent 25 - 30 wt% of all waste in the EU), for example bricks, is an important challenge for the future.

The aim of this work is the synthesizing of new lightweight waste based geopolymer aggregates from fired brick clay, in order to replace the natural lightweight aggregates. This study mainly focuses of lightweight geopolymer aggregates made from fired brick clay and silica fume (another waste from metallurgy industry) with various alkaline solutions. Indeed, several lightweight based geopolymer aggregates were synthesized. Then, the consolidated samples were physically and chemically characterized (such as density, water resistance properties and pore size distribution). Then, mechanical tests were performed. To finish, composite materials made from cement, geopolymer and brick clay were synthesized to observe the interactions between the lightweight wastes based geopolymer and the matrix. The results evidenced a great interest in the use of fired brick clay in the production of lightweight wastes based geopolymer, with for example a mechanical behavior similar to natural lightweight aggregates. Plus they also exhibit a density within the range 0.4 to 0.7 g/cm^3.

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INFLUENCE OF SILICATE SOLUTION PREPARATION ON GEOPOLYMERS BASED ON BRICK CLAY MATERIALS

Julie Peyne (1,2)*, Jérôme Gautron (2), JulieDoudeau (3), Emmanuel Joussein (4),
Sylvie Rossignol (1)

(1) Laboratoire SPCTS, Limoges, France, (2) Bouyer Leroux, La Séguinière, France, (3) Bouyer Leroux, Colomiers, France,
(4) Laboratoire GREASE, Limoges France

From the late 1970's, a new class of materials, also known as geopolymer materials have demonstrated an increasing interest in various industrial applications, due to their outstanding properties, such as mechanical, thermal and chemical properties, constant within the time. The main parameter to control the formation of the geopolymer is the aluminosilicate source. Indeed, numerous studies are conducted on the use of alternative low quality clay, by products from various industries as an aluminosilicate source. Still, recent research have also investigated the effect of the alkaline solution on the polycondensation reaction.

Thus, this study concerns the effect of mixed alkali cation solutions on the polycondensation reactions of geomaterials based on brick clay mixtures. To achieve this objective, various alkaline silicate solution (Na, K and Na-K) with different Si/M molar ratio was used with a calcined brick clay materials, previously described as potential raw material in the case of geomaterials. To evidence mainly the effect of the alkali cation in presence of such an aluminosilicate source, FTIR and Raman spectroscopy, thermal analyses and compressive tests were performed to reveal the performance of the alkaline solution and aluminosilicate source. Nonetheless, the alkaline solutions features were intensively investigated by spectroscopy techniques. The various solutions contained different siliceous species (rings, chains) that modified the polycondensation reactions and the Si-O-Ca bond formation. The effect of the polarizability of the alkaline and earth alkaline solutions must be controlled to enhance the final properties. Better mechanical properties were obtained with a blow water content.

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HYBRID IMOGOLITE FOR TRAPPING PERSISTANT ORGANIC POLLUTANTS

Pierre Picot (1)*, Thibaud Coradin (2), Antoine Thill (1)

(1) LIONS, NIMBE, CEA, CNRS, Université Paris-Saclay, Gif-sur-Yvette 91191, France, (2) Sorbonne Universités, UPMC Univ. Paris 06, CNRS, Collège de France, Paris 75005, France
*pierre.picot@cea.fr

In 2013 the European Union modified the Water Framework Directive adding 12 new substances to the 33 previous ones establishing a list of 45 priority substances in the field of water in order to define norms for "good status" for water. Among these substances are the so-called persistent organic pollutants (POP) which are small molecules slightly soluble in water and poorly biodegradable and therefore tending to accumulate in living organisms. They belong to three main families: polycyclic aromatic hydrocarbons, halogenated and polychlorinated biphenyl compounds.

Imogolite is a natural aluminosilicate nanotube discovered in 1962 by Yoshinaga and Aomine in volcanic Japanese soils [1]. This nanotube has a monodisperse diameter ranging from 2 and 2.8 nm (depending on its formation and composition) and a polydisperse length (from a few tens of nanometers to several microns) [2]. In recent years, it has been realised that many structural and chemical modifications of imogolite-like structures can be achieved [3,4]. In 2010, Bottero et al. succeeded in modifying the tube internal surface by substituting the usual silicon precursor, tetraethoxysilane, with amethyltriethoxysilane [5]. This allows for the formation of a hybrid Janus nanotube with a hydrophilic external surface and ahydrophobic internal surface.

In 2013, Amara et al. showed that such Janus nanotubes can capture small hydrophobic molecules in water [6]. Later on, we showed that these hybrid nanotubes can stabilise oil-in-water Pickering emulsionand extract a dye from an organic phase [7]. These properties were attributed to the ability of methyl-imogolites cavities to accommodate oil or oil/dye mixtures.

In this presentation, we will first present some modifications of the synthesis of hybrid imogolite aiming at improving their dispersion in water and reducing the presence of side products, such as proto-imogolite and aluminium hydroxides. In a second part, the trapping of some POP compounds by hybrid imogolites will be described. An original set-up involving dialysis bags was developed. The amount of pollutants trapped were measured by various techniques (UV-vis spectroscopy, ICP-MS, microcalorimetry…). The POP removal efficiency of the hybrid imogolite and its potential use for water remediation or monitoring will be finally discussed.

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CLAYS IN 19th CENTURY BOOKS AND PRINTS

Flavia Pinzari (1,2)*, Marina Bicchieri (3)

(1) Consiglio per la ricerca in agricoltura e l'analisi dell'economia agraria (CREA), Rome, Italy, (2) Natural History Museum, London, UK, (3) TEA s.a.s. di Elena Console & C.

Paper is a discontinuous and heterogeneous artificial system composed of cellulose fibres and other components that vary according to the papermaking process, fibre type, and the historical period in which it was produced [1]. Modern and ancient paper can contain large amounts of clay as filling material [1,2].

Kaolin, a hydrated Al-phyllosilicate mineral, is the most common clay added to paper as a filler, followed by montmorillonite clay. The first documented use of clay as a filler in European papermaking is reported by Hunter D. [3], in England in 1807. Currently about 40 percent of the kaolin produced is used in the filling and coating of paper. In filling, the kaolin is mixed with the cellulose fibre and becomes part of the paper sheet giving to it opacity and printability. In coating, the kaolin is distributed with an adhesive on the paper's surface with the aim of conferring gloss, colour and improving the printability. Kaolin applied in coating is currently prepared in order to use particles that are less than two micrometres in diameter.

According to the locations where clay is extracted the quality can vary considerably. When the kaolin is extracted it is likely to contain impurities. Processing steps can include sieving, magnetic removal of iron and bleaching.

While coating is intended to make paper more suitable for printing, when impurities, in particular iron compounds, are not carefully removed, the paper becomes less durable inducing problems in the preservation of printed documents.

In fact, deterioration of paper can be caused by chemical factors. One aspect of deterioration found on paper artefacts are characteristics spots known as "foxing". The damage phenomenon consists in the formation of small and isolated rusty red spots which are often not directly linked to structural degradation of the substratum. Foxing stains show intensive luminescence in UV light at the initial phase of formation, when they are still undetectable at the visible light. Research on the nature and origin of foxing dates back to the 1930's [4]. Since the first studies, foxed spots were controversially attributed to biological agents (fungi and bacteria) or to chemical factors (iron oxidation, organic and inorganic dust particles, etc.).

The presence of metal impurities associated to some defacing staining on old and ancient paper can derive from the use of clays containing impurities. Ferruginous and titano-ferrous minerals are the common impurities found in kaolin and iron can be present in clays used in papermaking as oxides, hydroxides, oxy hydroxides, sulphides and carbonates. The relationship between the total iron content in the kaolin, the structural order of the iron species and the surface reactivity of kaolin can represent important variables that determine the potential damage to paper.

Actually, when archival and library material of paper is stored under unfavourable conditions, it may be deteriorated by factors triggered from the reaction of the metals present in clays and other factors such as light, temperature, oxygen, humidity changes, air pollutants and microorganisms.

Here we show some examples of 19th-20th century heritage objects made of paper (books, prints and archival documents) containing clay minerals. The co-occurrence of some clay impurities with cellulose oxidation phenomena are also documented by means of scanning electron microscopy (SEM), microanalysis (EDS), μ-RAMAN spectroscopy [5], atomic force spectroscopy (AFM) and multispectral imaging.

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A FUNGAL POINT OF VIEW: MICROSCALE FACTS IN FUNGI-CLAY MINERALS INTERACTIONS IN SOIL

Flavia Pinzari (1)*, Javier Cuadros (2)

(1) Consiglio per la ricerca in agricoltura e l'analisi dell'economia agraria, Rome, Italy, (2) Department of Earth Sciences, Natural History Museum, London, UK

In this talk the "intrigues" between fungi and clays will be discussed and some indications of possible new perspectives in this field will be outlined. The interaction between clay minerals and fungi have been discontinuously investigated in the last fifty years, and in all the published results a strong reciprocal interaction has always been highlighted. Stotzky and Rem [1] showed that the respiration of 27 fungal species was markedly inhibited by montmorillonite. The inhibition was greater as the metabolic activity of the mycelium increased but according to the authors it was not caused by a limitation in carbon substrate. Their conclusion was that inhibition of fungal respiration was related to the viscosity of the systems, which, in turn, influenced the rate of O_2 diffusion. Clay minerals can form different complexes with fungal polysaccharides as Chenu [2] pointed out. The micro organization of structures formed between clay minerals and the fungal glucans was different for Ca-kaolinite and Ca-montmorillonite, both with enhanced porosities. Fungal polysaccharides showed a strong water-stabilizing effect with the formation of stable organo-clay networks. The interaction between clays and fungi in soil proved to influence also the ecology of other groups of microorganisms, impacting for example on the antagonism between fungi and bacteria. Campbell and Ephgrave [3] found that the effectiveness of the bacteria that control the spread of the plant pathogen *Gaeumannomyces graminis* varied between field sites according to clay contents in soil and demonstrated that clay absorption to both hyphae and bacteria clearly influenced the interaction between the two. The absorption of fine clays to fungal mat can also induce a change in fungal behaviour. Fomina and Gadd [4] showed that the inclusion of clay minerals (bentonite rock, palygorskite and kaolinite) in the liquid medium influenced size, shape and structure of the mycelial pellets produced. It has emerged from many studies that the properties of clay-fungus aggregates are different from those of clays and fungi separately.

Fungi, however, not only interact with clays but generate them. In fact, fungi play an important role in the dissolution of silicates and therefore in the genesis of clay minerals. Actually the presence of clay minerals is a marker of rocks bioweathering. Fungi dissolve silicates by acidifying their microenvironments, exuding chelating molecules, and by mechanical disruption of the crystal lattice.

Several authors have shown that fungi, especially ectomycorrhizal species, are able to actively weather silicate minerals to extract nutrients like P, K, Ca, Mg and Fe, especially under conditions of nutrient limitation. However, not all the fungi dissolve minerals in the same way. Pinzari et al [5] showed that fungal phlogopite weathering features were irregular and variable according to the fungal species. The authors compared the weathering action of three fungi and showed a different ability in cation rearrangement in the mica.

A very intriguing hypothesis is that fungi can modulate their weathering efficiency towards clays, according to their nutritional needs and the mineral environment in which they grow. Some evidence in this direction come from studies like the one by Xiao et al. [6] who analysed the mechanisms at molecular level by which fungi weather potassium-bearing minerals. They prepared differential expression cDNA libraries of *Aspergillus fumigatus* using suppression subtractive hybridization (SSH) technology. The model fungus was cultured with and without potassium-bearing minerals. They discovered that during mineral weathering the fungus changed its metabolism, regulating ion absorption and promoting acid production. This discovery suggests that, amazingly, some genes are activated in fungi by the presence of specific minerals.

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ALTERNATIVE METHODS FOR DETERMINING THE SWELLING POTENTIAL OF CLAYS

Plötze Michael*, Herzog Ralf

ETH Zurich, Institute for Geotechnical Engineering, 8093 Zurich, Switzerland

The swelling of clays, a time-dependent volumetric increase, which is based on a physicochemical reaction with water, is one of the most important phenomena in the soil-mechanical behaviour of cohesive soils. The clay minerals are responsible for the swelling. However, not all clay minerals are swelling due to the same mechanism. Clay minerals, such as illite and kaolinite, only show an osmotic swelling. Smectite, however, exhibits additionally an innercrystalline swelling which causes the greatest swelling strain and pressure. The measurement of the volume change can be lengthy and very complex. In practical geotechnical work often a fast assessment of the swelling potential of cohesive soils is necessary. The aim of this work was therefore to explore alternative, simple and fast methods for determining the swelling behaviour of cohesive soils.

Four clays (two different illites and two bentonites) and two soil samples (lacustrine clays) from Switzerland are used for this purpose. Uniaxial swelling tests in oedometer cells are performed serving as the standard experiment and giving the comparative value for the alternative methods. These swelling tests reveal that the soil samples have the lowest swelling strain (0-10%). The Illite has a swelling strain between 10 and 20%. The two bentonites show, as expected, much higher swelling potentials strongly dependent from cationic form (Ca-bentonite Calcigel: 50%, Na-bentonite Volclay: appr. 400%). Various alternative experiments with respect to the potential water absorption of clay-containing soils were carried out. These experiments include the Enslin-Neff measurement (maximum water uptake under free swelling conditions acc. DIN 18122-2), the measurement of the swell index acc. to ASTM D5890-11, and the shrink-swell indices acc. to Briaud et al. (2003) and Thomas et al. (2000). Other parameters like the cation exchange capacity (terraGIS UNSW, 2007) and the mineralogical composition, particularly the clay mineral content were related to the swelling potential.

None of the alternative methods could completely represent the results from the “classical” uniaxial swelling strain measurements. The ASTM experiment delivers only for bentonites suitable results. The Enslin-Neff experiment can indicate the relationships of the swelling strain best. On the basis of this experiment an estimate could be elaborated, which can be used to assess the swelling potential of the clays and soils despite the still existing deviations from the measured swelling strain. The other shrink-swell indices use results from the Enslin-Neff measurement with some additionally determined parameters but have not brought any improvement in the correlation with the swelling strain. The CEC and the mineralogical composition do not take into account the influence of the cationic form on the swelling potential. As a result, the pure smectite content does not show a good correlation with the swelling strain. Therefore, a second model was developed, involving weighted clay mineral components.

The two alternative methods, Enslin-Neff experiment and weighted clay mineral contents, allow a classification of the swelling potential. These two approaches are recommended to deepen in further investigations to improve the quality of the predictions.

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NEW DOPED PHYLLOSILICATES FOR INDUSTRIAL APPLICATIONS

Mathilde Poirier (1)*, Christophe Le Roux (1), Suzanne Fery-Forgues (2), Pierre Micoud (1), Francois Martin (1)

(1) Laboratoire GET, CNRS UMR 5563, 14 avenue Edouard Belin, 31400 Toulouse, France, (2) Laboratoire SPCMIB, CNRS UMR 5068 Université Toulouse III - Paul Sabatier, 118 route de Narbonne, 31062 Toulouse, France
*mathilde.poirier@get.omp.eu

Synthetic clay minerals are a new generation of layered solids that offer unique control over the chemical structure, cation exchange capacity and physical aspect [1]. They can be tailored to promote specific properties in view of a wide range of applications in the field of materials.

Since 2006, the «ERT Géomatériaux» team of the GET laboratory of Toulouse (France) has elaborated several non-swelling synthetic phyllosilicates such as talc, mica, kaolinite under hydrothermal conditions [2-6]. These new minerals present notable similarities with their natural analogs such as the lamellar TOT structure. They also have a number of distinctive features such as their submicronic size, their hydrophilic behaviour and their chemical purity that is guaranteed by the hydrothermal synthesis procedure.

Combining the favorable features of the synthetic minerals with an organic molecule that displays specific properties gave access to new organic-inorganic hybrids. In particular, many studies undertaken in the laboratory have led to the preparation of doped hybrids thanks to the strong and unexpected adsorption potential of the synthetic phyllosilicates towards specific organic molecules [7]. The elaboration of such nanocomposites is easy, cost-effective and versatile. The hybrids have been analyzed by several analytical tools (XRD, NMR, DLS, fluorescence microscopy and spectroscopy) and the interaction between the organic and mineral phases was thoroughly analyzed. The adsorption process was much more efficient in synthetic minerals than in natural minerals. To conclude, the elaboration of such organic-inorganic hybrids is very promising and opens a new route towards optical brighteners, cosmetics, polymers, as well as in the field of paper milling, inks and biological markers.

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STRUCTURE OF HALLOYSITE NANOTUBES INTERCALATED WITH IRINOTECAN SOLVED BY MOLECULAR SIMULATION METHODS

Eleni Gianni (1), Dimitrios Papoulis (1), Milan Pšenička (2), Miroslav Pospíšil (2)*

(1) Geology Department, University of Patras, 26504, Patras, Greece, (2) Faculty of Mathematics and Physics, Charles University, Prague, Czech Republic

In our recent work, we used molecular simulation methods to describe tubular structure of hydrated and dehydrated halloysites intercalated with irinotecan. Halloysites are very interesting matrices to be explored as drug nanocarriers due to their biocompatibility and stability. The bioactive drugs can be intercalated into the inner spheres of the tubes and then can be transported to the right place in the human body and released [1].

Preparation and construction of the model of halloysite nanotubes for subsequent calculations was based on published paper, where the atomic coordinates for spiral shape of nanotube were introduced [2]. Unhydrated tube of halloysite was built and modified for using it for optimization with irinotecan molecules. Conformational analysis of irinotecan was done and its final and energetically preferable geometrical conformation was used for testing with various amounts of irinotecan related to experimental data. Also various positions on inner sphere of halloysite were tested. Optimized intercalated structure of halloysite with irinotecan and water molecules was used for molecular dynamics calculations to study mutual interactions between drug molecules, water and halloysite tube. Similar calculations were done for hydrated halloysite tube with irinotecan molecules.

We will present models of both unhydrated and hydrated halloysite tubes with the most probable arrangement of adjacent irinotecan molecules on inner spheres and description of mutual interactions calculated by molecular simulation methods in Material Studio modelling environment.

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ILLITE INDICES UNDER LOW-TEMPERATURE CONDITIONS TO DECIPHER COMPLEX GEODYNAMIC EVOLUTION, A REVIEW

Sébastien Potel (1)*, Tatiana Maison (1), Michael Patrick Doublier (2), Rafael Ferreiro Mählmann (3)

(1) Basins-Reservoirs-Resources (B2R), Institut Polytechnique LaSalle Beauvais, Geosciences Department, F-60026 Beauvais, France, (2) Geoscience Australia, Resources Division, Cnr Jerrabomberra Avenue and Hindmarsh Drive, Symonston 2609, ACT, Australia, (3) Technische Universität Darmstadt, Technical and Low Temperature Petrology, Institut für Angewandte Geowissenschaften, D-64287 Darmstadt, Germany

In very low- and low-grade metapelites and metaclastites, the fundamental methods used to decipher the metamorphic conditions are based on clay mineral evolution and coal petrology [1].

Since the illite "crystallinity" (IC) method [2] is used to monitor gradual changes with increasing metamorphic grade from diagenesis to incipient metamorphism, expressed as a sharpening of the 10 Å illite X-ray diffraction peak. The IC is used as a parameter, empirically related to the aggradation [1] of illite. In addition, and often applied complementary, K white mica *b*-cell dimension [3] has been used to determine the nature of the pressure gradient in the studied samples. This method is based on the fact that (i) with increasing pressure, K-white mica shows an increasing celadonite content at constant temperature; and (ii) K-white mica *b*-cell dimension show a positive correlation with celadonite content [4]. This method was further refined with the construction of an empirical P-T diagram contoured for different K-white mica *b*-cell dimensions [5], and more recent work also demonstrates a excellent correlation with spectral parameters [6].

Combined together, illite "crystallinity" and K-white mica *b*-cell dimension help to gain insight into the tectonic evolution of low-grade metamorphic terranes. For example, nappes with different tectono-thermal histories can be recognized by using both methods. In fact, differences in K-white micas *b*-cell dimension in samples from different nappes with similar KI values will indicate a different metamorphic history [7].

Recent studies combining both methods have shown their reliability under different metamorphic regime and the possibility to decipher complex geological history [8]. However, these two parameters are responding differently in terms of kinetic to the variation of pressure and temperature. In the Vosges, the use of the K-white mica *b*-cell dimension helped to constrain the overprint due to granitic intrusion in a sedimentary basin and to reveal the poly-metamorphic history [9]. In that case, the K-white mica *b*-cell dimension is re-equilibrated by the thermal heating and indicate low-pressure gradient. This is not the case in New Caledonia, where the K-white mica *b*-cell dimension conserve the clue of the high-pressure metamorphic event and is not affected by late re-equilibration during the exhumation (outlined by fluid inclusion and organic matter reflectance) [10]. One main difference between those two cases is the duration of metamorphism, the enthalpy of the system and heat flow.

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ELABORATION AND CHARACTERISATION OF ALUNINOSILICATE REFRACTORY BRICKS FROM TWO CLAYS OF FOUMBAN REGION (WEST CAMEROON)

A. Pountouenchi (1), D. Njoya (1), A. Njoya (2), D. Rabibisao (3), J. R. Mache (4), R. Yongue (5), D. Njopwouo (1), N. Fagel (6), P. Pilate (7), L. Van Parys (8)

(1) Département de Chimie Inorganique Appliquée, Université de Yaoundé I, Cameroun, (2) Département Arts, Technologie et Patrimoine, Institut des Beaux-Arts de Foumban, Université de Dschang, Cameroun, (3) Département Matériaux, Ecole Supérieure Polytechnique, Antananarivo, Madagascar, (4) MIPROMALO, Yaoundé, Cameroun, (5) Département des Sciences de la Terre, Université de Yaoundé I, Cameroun, (6) AGEs, Département de Géologie, Université de Liège, Belgique, (7) Belgian Ceramic Research Centre, Avenue gouverneur Cornez, 7000 Mons, Belgique, (8) Materials Research Institute, Université de Mons, Belgique
*apount@yahoo.fr

The region of Foumban (west Cameroon) contains several clay deposits whose exploitation is limited to the manufacture of pottery and other decorative uses. The use of those clay deposits may be optimized by the manufacture of high added value products.

In this context, the formulation and firing tests were carried out on two clays (KK and MY3) of the Foumban region over a range of temperature from 1300 to 1550 °C. Since KK clay presents a more refractory appearance than clay MY3, KK sample was compacted and fired at 1550 °C to produce chamotte. This chamotte was then mixed with 14, 20 and 30% of each crude raw material as binder phase, humidified with 4 to 6% distilled water, then pressed at 100 and 120 MPa, dried at 110% and sintered at 1400, 1450 and 1500 °C to produce refractory bricks. The technological properties of elaborated bricks (firing shrinkage, bulk density, water absorption, open porosity and compressive strength) have been determined.

The mixture made by 80% of chamotte KK and 20% of MY3 pressed at 120 MPa and sintered at 1450 °C has no firing shrinkage (0%), a bulk density of 2.06 g/cm^3, a water absorption 8.0% and an open porosity of 16.7%. These characteristics are similar to commercialised aluminosilicate refractory bricks. Moreover its compressive strength of 26.5 MPa is comparable to the high alumina content refractory bricks.

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FORCE FIELD PARAMETERIZATION FOR ACCURATE MOLECULAR MODELING OF CLAY EDGES IN CLASSICAL MD SIMULATIONS

Maxime Pouvreau*, Andrey G. Kalinichev

Laboratoire SUBATECH, Institut Mines-Télécom Atlantique, Nantes, France

The ClayFF force field [1] is widely used to model clay minerals, related layered materials, and their interfaces with aqueous solutions. In such simulations, clay particles are typically represented by semi-infinite layers, i.e., they do not have any edges. This simplification is acceptable to a certain extent, but real clay particles always have a finite size and should be terminated by lateral surfaces or edge surfaces. These surfaces can not only exhibit adsorption sites highly different from the ones on the basal surfaces of clay minerals, but are also subject to proton exchange reactions: all physico-chemical processes related to the aqueous phase acidity predominantly occur at the clay particle edges.

The original ClayFF parameterization leads to overly disordered hydroxylated surfaces, limiting its reliability for the modeling of the edge surfaces. This issue can be addressed by adding to the original ClayFF an explicit angle bending term for the Metal-O-H groups, as it has been recently done for Mg-O-H [2]. In the present work we have generalized this approach to develop a new set of parameters for the Mg-O-H, Al-O-H, and Si-O-H terms applicable to clay structures based on a series of systematic DFT calculations for structural models of the bulk crystals, their basal surfaces, and edge surfaces. Gibbsite $Al(OH)_3$ and brucite $Mg(OH)_2$ crystal structures were used in this parameterization, because their layers can be considered as the octahedral backbones of many clay minerals. In addition, the Si-O-H term was parameterized applying the same approach to an edge model of kaolinite $Al_2Si_2O_5(OH)_4$.

Classical molecular dynamics simulations (CMD) using ClayFF with and without the new Metal-O-H term (called, respectively, ClayFF-orig and ClayFF-MOH) were performed to quantitatively analyze the structural and dynamical effects of the new term on the simulated properties by comparing them with the results of *ab initio* molecular dynamics simulations (AIMD). The Metal-O-H angular distributions and spatial orientations of structural O-H groups for the ClayFF-MOH model are in good agreement with the AIMD results and demonstrate a great improvement over the ClayFF-orig models. The dynamical properties were compared by calculating the power spectra of O-H librational motions from the velocity autocorrelation functions of the hydrogen atoms. When transitioning from ClayFF-orig to ClayFF-MOH the whole group of librational bands becomes significantly narrower and is shifted by up to 600 cm^{-1} towards higher frequencies, and the main bands become more pronounced, bringing the results in a much better agreement with similar spectra calculated from AIMD calculations. An important indirect effect of the new ClyFF term is a significant improvement of the quantitative description of the interfacial hydrogen bonding structure and dynamics, observed for the gibbsite basal and edge surfaces as well as for the kaolinite edge surface.

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EFFECT OF ACETATE ON COMPACTED BENTONITE: BACTERIAL DIVERSITY AND MINERALOGICAL CHARACTERIZATION

Cristina Povedano-Priego (1)*, Fadwa Jroundi (1), Inés Martín-Sánchez (1),
Ramiro Vílchez-Vargas (2), F. Javier Huertas (3), Mohamed L. Merroun (1)

(1) Department of Microbiology, University of Granada, 18071 Granada, Spain, (2) Helmholtz Center for Infection Research, 38124 Braunschweig, Germany, (3) Instituto Andaluz de Ciencias de la Tierra, CSIC - Universidad de Granada, 18100 Granada, Spain
*ppriego@ugr.es

Long-term deep geological repositories (DGR) are the preferred option for the treatment and management of radioactive wastes in nuclear power-producing countries. In this concept, nuclear wastes are encapsulated in metal containers that are surrounded by bentonite-engineered barrier and emplaced in the host rock formation. An in-depth understanding of host rock processes relevant to safety is thus required, including the impact of microorganisms under repository relevant conditions. Several studies have been carried out for the selection and characterization of clays that could act properly as backfill and sealing material in the DGR [1].

In Spain, bentonite formation located in "El Cortijo de Archidona" (Cabo de Gata, Almería), was selected as a reference material for bentonite-engineered barriers for the future Spanish repository. These clay formations have been well characterized from mineralogical, geochemical and technological points of view [2]. Studying the potential effects of microbial activity on the various engineered barriers is also of high importance. These studies must cover, among other topics, the presence of indigenous microorganisms and their survival and mobility in compacted clay-based buffer materials under relevant conditions. The study of microbial diversity of the Spanish bentonite is the key point to determine whether the indigenous microbes are able to produce metal corrosion, transformation of the Fe-containing minerals and/or to affect the mobility and migration of radionuclides from repositories to the biosphere [3]. In this study, samples of Spanish bentonite (control and acetate-treated samples) were compacted at two different densities (1.5 and 1.7 g/cm^3), and incubated for six months under anaerobic conditions at room temperature. Acetate was used as an electron donor at the concentration of 30 mM to stimulate the growth of iron-reducing bacteria. Next generation sequencing based on Illumina technology was used to determine the structure and composition of bacterial community of these samples before and after the anaerobic incubation. Using this technique, the bacterial diversity analysis of both samples before the incubation revealed similar results, showing the presence of bacterial phyla such as *Actinobacteria*, *Proteobacteria*, *Bacteroidetes*, *Chloroflexi*, *Firmicutes*, *Acidobacteria*, *Verrucomicrobia* and *Planctomycetes*, among others. These groups have been classified in 560 different genera which include bacteria described for their role in biogeochemical cycle of Fe such as *Acidiferrobacter*, *Ferrimicrobium*, *Ferrithrix* and *Aciditerrimona*. Some bacteria are nitrite-oxidizing organisms such as *Nitrospira*, nitrate reducing bacteria such as *Conexibacter* and *Ramlibacter*, and sulfur-oxidizing bacteria such as *Thiobacillus* and *Thioalbus*. Finally, some of the bacteria are being used for metal/radionuclide bioremediation purposes such as *Variovorax*, *Sphingomonas*, *Stenotrophomonas*, among others. The evolution of the bacterial diversity after six months of anaerobic incubation will be discussed. In addition, the data obtained from mineralogical (X-Ray Diffraction) and microscopic (Scanning Electron Microscopy) studies will be linked to the microbial diversity results to highlight the effects of the compaction and the acetate addition on the bentonite mineralogy and on the indigenous microbiota. The outputs of this study would help to understand the effect of biogeochemical processes within the bentonite barrier under repository relevant conditions as well as in developing appropriate waste treatment, remediation and long-term management strategies.

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MICROWAVE ASSISTED ACID TREATMENT OF KEROLITIC CLAYS FROM THE NEOGENE MADRID BASIN, SPAIN

Francisco Franco (1), Juan Antonio Cecilia (1), Manuel Pozo (2)*, Laura Pardo (1), Eva Bellido (3)

(1) Departamento de Química Inorgánica, Cristalografía y Mineralogía, Facultad de Ciencias Universidad de Málaga, Campus de Teatinos s/n 29071, Málaga, Spain, (2) Departamento de Geología y Geoquímica, Facultad de Ciencias, Universidad Autónoma de Madrid, Cantoblanco, 28049 Madrid, Spain, (3) Instituto Geológico y Minero de España (IGME). 28760, Madrid, Spain
*manuel.pozo@uam.es

The effect of the microwave assisted acid treatment on 5 kerolitic clay samples (K1 to K5) from the Madrid basin was studied. The scope was to assess if the structural characteristics and composition of samples control the effectiveness of treatment. The XRD data showed that the starting samples consist of kerolite-Mg-smectite mixed layers showing variable stevensite content with percentages ranging between 10 and 50%. Minor discrete saponite is present in samples K1, K3 and K4.

The microwave assisted acid treatment of samples with lower amounts of kerolite caused a general decrease of the diffraction peaks, including the 0k0 (020 and 060) reflections. The decrease in intensity is more pronounced in the basal reflections. In addition, the decrease in intensity of the basal reflections is lower in the kerolite-rich mixed layer clays, suggesting a much higher resistance to microwave assisted acid treatment.

X-ray fluorescence (XRF) data showed that Mg^{2+} is the dominant cation in the octahedral sheets, with Al^{3+} and Fe being minor cations. The isomorphic substitutions of Mg^{2+} by Al and Fe are significantly lower in the case of samples with higher kerolite content. The XRF data data showed that microwave assisted acid treatment of kerolitic samples caused partial dissolution of Mg from octahedral sheet and consequent segregation of amorphous silica, being the dissolutions of the octahedral sheets less intense in the samples with higher proportion of kerolite. After the first minutes of treatment the amount of interlayer Ca^{2+} strongly decreases whereas K^+ remained constant. This result suggests that H^+ replaces Ca^{2+} in interlayer positions through ion exchange mechanism during the acid treatment.

SEM micrographs showed that microwave assisted acid treatment reduced the size of the aggregates of laminar particles. These changes are more pronounced in samples K1, K5 and K3 and lower in samples K2 and K4. Moreover, these textural modifications, obtained after few minutes of treatment, are accompanied by a remarkable increase in the BET specific surface area of the kerolite samples, which reach exceptionally high values (up to 435 m^2/g). In the case of samples with higher stevensite contents, the increase in the BET specific surface area is mainly due to increases in micropores, whereas in the sample with higher kerolite contents, it is mainly due to increase in the external surface area of the particles.

This study showed that despite the similar octahedral sheet chemical composition, the structural characteristic governs the properties and effectiveness of the microwave assisted acid treatments of Mg-rich clay minerals. Thus, magnesian clay minerals with interlayer cations, such as stevensite, are more labile than kerolite, which does not have interlayer cations. It is suggested that acid digestion of stevensite occurs simultaneously at the edges of particles and within the interlayer space, whereas in the case of kerolite, it occurs exclusively at the particle edges.

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SMECTITE IN THAI SOILS

Orathai Sukreeyapongse (1), Nattaporn Prakongkep (1)*, Robert Gilkes (2), Hathairat Pichainarong (1), Wassana Pramnoy (1), Ladawan Nakforn (3), Bhannapitch Samrit (4)

(1) Office of Science for Land Development, Land Development Department, Bangkok, 10900 THAILAND, (2) School of Agriculture and Environment, University of Western Australia, 6009 AUSTRALIA, (3) Soil Quality and Productivity Interpretations Group, Land Development Department, Bangkok, 10900 THAILAND, (4) Soil Science Division, Department of Agriculture, Bangkok, 10900 THAILAND
*asoil@hotmail.com

Smectite is commonly a dominant clay mineral in base rich lowland areas throughout the world but there has been no systematic study on this aspect of Thai lowland soils [1]. In many natural smectites, the charge is distributed over both tetrahedral and octahedral sheets. Soil smectites with high amounts of tetrahedral substitution (e.g. beidellite) are believed to fix K^+ and NH_4^+ more strongly than does montmorillonite and thus affect soil fertility [2]. The primary objective of this study was to develop criteria to characterize the smectite present in Thai soils. This research is a component of a survey of the clay mineralogy of Thai soils which is intended to improve our knowledge of soil properties and to help with the development of optimum land management practices.

Topsoil samples from ten lowland soils from the Thai Central Plain were used for this investigation. The sedimentary basin occupying the Thai central plain has been filled with Quaternary fluvial and swamp sediments reaching a thickness of almost 2000 m [3]. The parent materials of some of these soil are associated with limestone derived alluvium and a deltaic environment. These areas have a high water table where ions leached from adjacent upland have accumulated resulting in the authigenesis of smectite and calcite in soils. The dioctahedral smectite in these smectite-rich soils was investigated in detail. The swelling behaviour of heated Li-saturated smectites demonstrated that the smectites are beidellitic in character [4].

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BIOHYBRID BACTERIA@LDH MATERIALS FOR ENVIRONMENTAL REMEDIATION

F. Bruna (1), M. Halma (1), C. Mousty (1), C.Forano (1), T. Alekseeva (2), M. Sancelme (1), P. Besse-Hoggan (1), I. Batisson (3), V. Prévot (1)*

(1) Université Clermont Auvergne, CNRS, SIGMA Clermont, Institut Chimie Clermont-Ferrand, ICCF, F-63000 Clermont-Ferrand, France, (2) Institute of Physical Chemical and Biological Problems of Soil Science. Russian Academy of Sciences, Institutskayaul., 2, 142290 Pushchino, Russia, (3) Université Clermont Auvergne, CNRS, Laboratoire Microorganismes: Génome et Environnement, F-63000 Clermont-Ferrand, France

Biohybrid materials, based on immobilisation of bacteria in organic or inorganic matrices, are crucial for biotechnology uses. These “living materials” present several applications such as catalysts for environmental bioremediation, optical and electrochemical sensors. Among the various supports described for bacteria immobilization, Layered Double Hydroxides also called anionic clays present several advantages including a positively charge surface, a 2D open framework and hydroxylated surface in favor of enhanced interactions with cell membranes [1].

In this study, the immobilisation of bacteria such as *Pseudomonas sp.* strain ADP (ADP) in Layered Double Hydroxides (LDH) was investigated in using various approaches such as adsorption, direct co-precipitation or layer- by- layer process. The efficiency of the resulting bionanocomposites was also studied for applications in biodegradation process or biosensor development. ADP is a well-characterized bacterium able to mineralize the herbicide atrazine, a broad-leaf weed control herbicide which due to its high persistence and mobility in soil has often been detected in surface and groundwater at levels higher than authorized. Several ADP@Mg_2Al-NO_3 LDH bionanocomposites were obtained using ADP suspensions and LDH nanoparticles or by conducting the LDH synthesis from $Al(NO_3)_3$ /$Mg(NO_3)_2$ aqueous solution directly in presence of cells. Systematically, the as-prepared bionanocomposites were deeply characterized by XRD, FT-IR spectroscopy, Zeta-potential, thermo gravimetric analyses (TGA) and transmission electron microscopy (TEM) to get better insight on the biohybrid structure and the interaction involved between the biological and inorganic components .Biodegradation of atrazine using ADP@ LDH biohybrids was then studied and compared to ADP free cells stored under the same conditions. Atrazine biodegradation was followed by HPLC analyses of the supernatants at different times. Strikingly, biodegradation activity of ADP cells can be strongly improved after immobilisation on LDH according to the immobilization strategy and the LDH composition. Moreover, excellent cell viability was highlighted for the ADP immobilized into the bionanocomposites thanks to the soft chemistry conditions used during the processes. Such bacterial cells@LDH bionanocomposites offer interesting advantages such as stability, protection of cells and enhance the activity. This study was extended to the design of thin bacteria/Layered Double Hydroxides (LDH) films in which bacterial cells of ADP were assembled alternatively with Mg_2Al-NO_3 LDH nanosheets by a layer-by-layer deposition method [4]. The metabolic activity of immobilized bacteria was further determined using chronoamperometry by measuring the biochemical oxygen demand in presence of glucose using an artificial electron acceptor.

Following similar strategies, an *Escherichia coli* strain expressing a mesotrione-transforming nitroreductase[5] was also immobilized on LDH and its bioremediation efficiency tested.

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LDH NANOCOMPOSITE FILMS MADE FROM LDH HYBRID LATEX SUSPENSIONS: AN EFFICIENT WAY TO TAILOR THE FILMS PROPERTIES

Florent Dalmas (1), Samuel Pearson (2), Baptiste Gary (1), Elodie Bourgeat-Lami (2), Laurent Chazeau (1), Vanessa Prévot (3)*

(1) Université de Lyon, INSA-Lyon, MATEIS CNRS UMR5510, 7 av J. Capelle, F-69621 Villeurbanne, France, (2) Université de Lyon, Université. Claude Bernard Lyon 1, CPE Lyon, C2P2 CNRS, UMR 5265, Chemistry, Catalysis, Polymers and Processes (C2P2), 43 Bvd. du 11 Novembre 1918, F-69616 Villeurbanne, France, (3) Université Clermont Auvergne, CNRS, ICCF - Institut de Chimie de Clermont-Ferrand, F-63000 Clermont-Ferrand, France

Since the report on the improvements of the mechanical properties in polyamides containing exfoliated clay platelets, clay based nanocomposites have attracted considerable interest [1]. In this context, Layered double hydroxides (LDH) platelets displaying unique anion exchange capacities, and high water content appear as attractive alternative to cationic clays [2].

In this study, LDH nanoplatelets were investigated as efficient fillers in waterborne nanocomposite film materials. In a first approach, nanocomposite films were simply prepared by casting physical mixtures of surfactant-free poly(methyl methacrylate-co-butyl acrylate) [P(MA-co-BA)] film-forming latexes and aqueous LDH suspensions [3]. Electrostatic interaction between positively charged LDH nanoparticles and negatively charged poly(methyl methacrylate-co-butylacrylate) (P(MMA-BA) latex promote the adhesion of the LDH platelets on the latex surface [4]. Because the P(MMA-BA) Tg is close to room temperature, film formation was performed at room temperature as currently reported in coatings applications.

To go further, new latex microstructures were also synthesized by using the RAFT-mediated encapsulating emulsion polymerization (REEP) process from a [P(MA-co-BA)] matrix and similar LDH filler and subsequently involved in film formation. In such approach, negatively-charged macroRAFT agents can be electrostatically adsorbed onto the surface of the positively-charged LDH particles, providing both colloidal stability [5] and a re-activatable group (the RAFT function) from which polymerization could be recommenced during the subsequent REEP [6]. The nature of the adsorbed polymer proved critical to the morphology of the resulting latex particles, formed by starve-feed emulsion polymerization of a methylacrylate (MA)/BA monomer mixture (80:20 w/w) in the presence of the stabilized LDH particles. Various latex morphologies such as encapsulating LDH latex, dumbbell-like and armoured LDH latexes were obtained and used to form films. The multiscale microstructure of the obtained nanocomposites was investigated by WAXS, FIB/SEM and TEM. The viscoelastic behavior was then discussed through Dynamic Mechanical Analysis (DMA) experiments evidencing that a fine tuning of the nanocomposite film morphology can be achieved targeting specific properties (barrier, mechanical…).

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HETEROGENOUS FENTON LIKE DECOLORIZATION OF METHYLENE BLUE OVER GREEN CLAY FROM VELAY

Alcina Johnson Sudagar (1), Christine Mouty (1), Mustapha Abdelmoula (2), Vanessa Prevot (1)*

(1) Université Clermont Auvergne, CNRS, SIGMA Clermont, Institut de Chimie de Clermont-Ferrand, F-63000 Clermont-Ferrand, France, (2) Laboratoire de Chimie Physique et Microbiologie pour l'Environnement (LCPME) CNRS, UMR7564 - Université de Lorraine - 54000 Nancy

Advanced oxidation processes (AOPs) leading to the oxidation of organic and inorganic contaminants appear as an interesting alternative technology to treat wastewaters. Various types of APOs such as UV based, ozone based, hydroxyl based and Fenton and Fenton-like oxidation have been developed for the generation of active hydroxyl radical [1,2]. To overcome the homogenous Fenton process drawbacks (e.g. pH control, sludge formation, cost), iron based materials were investigated to develop heterogenous Fenton reaction. Clay minerals have been extensively investigated in Fenton related oxidation processes because of their ability to reduce the amount of Fe required for mineralization of contaminants, their low cost and high surface area [3]. Pillaring technique can be used to prepare heterogeneous clay based catalysts by incorporating compounds such as Fe (III)/ TiO_2, Fe_2O_3, Al, Al-Fe and Al-Ce-Fe between the layers of natural or synthetic clays. However, the major disadvantage of pillaring intercalation of Fe in clays concerns the reproducibility of the composite materials as Fe is known to form different polycations depending on the preparation conditions. An alternative way is to use clays containing iron in their structural layers.

In this study, pure clay mineral fractions (<500 nm) were obtained from Velay Green clay by decarbonation and subsequent size fractionation using centrifugation with the aim of understanding the intrinsic properties of these extracts from rich volcanic earth containing iron. It was confirmed that the Velay Green clay was mainly composed of illite and kaolinite. Several complementary solid state characterization techniques were used to determine structure and textural properties of the clay minerals. Mössbauer spectroscopy revealed the presence of Fe (III) in the lattice sites of both clay minerals. In parallel, electrochemical characterization was performed by cyclic voltametry in the presence of methylene blue and methyl viologen acting as redox mediators to evidence the accessibility of Fe (III) in the clay structure.

Further, the clay material was tested as heterogeneous catalyst for the Fenton like rection. Methylene blue (MB) decolorization was investigated in the presence of the clay fraction and H_2O_2 for evidencing the catalytic activity of iron (III) in the clay fraction.

The influence of different parameters such as initial pH, temperature, H_2O_2 concentration, time of reaction and clay amount on the MB degradation was studied.

Fig. 1 Methylene blue formula

The results obtained demonstrate the efficiency of clay mineral fractions from Velay Green clay to degradate MB. The influence of hte different parameters will be detailled in our presentation.

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MOLECULAR SIMULATIONS OF THE GRADUAL RELEASE PROCESS OF MEFENAMIC ACID INTERCALATED INTO LAYERED DOUBLE HYDROXIDES

Milan Pšenička (1)*, Miroslav Pospíšil (1), Jakub Škoda (1), Kamila Riedlová (2)

(1) Charles University, Faculty of Mathematics and Physics, Prague, Czech Republic, (2) Charles University, Faculty of Natural Sciences Prague, Czech Republic
*milan.psenicka@matfyz.cz

Due to the continually increasing demand for new multifunctional nanomaterials suitable for using in biomedicine, it is necessary to combine actual medical knowledge and new approaches to the preparation of materials with desired physical and chemical properties. One of these unique materials are LDHs that exhibit desired properties, which allows them to be suitable nanocarriers of synthetic or natural organic compounds. It was found that LDHs are able to increase the chemical stability of the resulting intercalated material and allow its subsequent slow release in the body, or can restrict and eliminate undesirable side effects. We investigated LDHs intercalated by mefenamic acid in water environment using molecular mechanics and classical molecular dynamics methods.

Mefenamic acid is used as non-steroidal drug for its anti-inflammatory effects as well as an analgesic for the treatment of rheumatoid arthritis, menstrual symptoms and headaches. However, due to its low solubility and because of certain side effects, especially gastrointestinal (including bleeding, ulceration and perforation of the stomach or intestines), it is necessary to find a suitable sorbent, which helps to prevent these side effects by its stabilization and its controlled gradual release. Some suitable materials for this purpose appear to be from LDHs group of layered materials.

Mefenamic acid intercalation into various types of LDHs was already performed in [1]. Based on the experimentally obtained results we created initial models for molecular modelling. Geometry of intercalated structures was optimized and calculated in Materials Studio2 and LAMMPS modelling environment. Resultant calculated structures with the best agreement with experimental data and interaction energies will be presented. Also, the analysis of dynamical properties as diffusion coefficients and mean square displacements will be compared with experimental results and also with our previous theoretical studies of LDHs intercalated by statin drugs.

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SELF-REGENERATING BIO-CLAYS FOR CHEMICAL AND BIOLOGICAL REMEDIATION OF FORMALDEHYDE

Yael Zvulunov (1), Ayelet Fishman (2) Adi Radian (1)*

(1) Civil and Environmental Engineering, Technion, Haifa, Israel, 3200003, (2) Biotechnology and Food Engineering, Technion, Haifa, Israel, 3200003
*aradian@technion.ac.il

Formaldehyde (FA) is a common organic chemical used in the production of resins, adhesives, paints, and preservatives. It is toxic to most organisms including humans, and has been listed as a probable carcinogen. Although FA remediation technologies have advanced over the past decades, there are still significant problems that prevent high remediation efficiency; chemical adsorption for example, only concentrates FA on a solid matrix requiring further handling of the spent sorbent. Bioremediation, on the other hand, degrades FA completely, yet is difficult to implement due to bacterial sensitivity to unfavourable environmental conditions and high FA concentrations in industrial effluents. In this study, we aim to design an improved FA remediation strategy by synergistically combining the biological and chemical approaches. To that end, a bio-reactive clay-polymer-bacteria composite is designed to both rapidly adsorbs and degrade FA. The polymer, polyetheleneimine (PEI) was selected due to its high affinity to clay minerals, [1] the ability to covalently yet reversibly bind FA, [2-4] and because of its use as a bacterial adhesion agent [5]. Initially, a PEI-montmorillonite (MMT) clay composite was designed and characterized. PEI adsorption to MMT was rapid and reached high loadings (>0.755 g/g MMT). Charge reversal was apparent at 33% CEC coverage, suggesting the extension of the polycation into the bulk liquid. Furthermore, experiments showed that the adsorption was governed by electrostatic interaction that were strongly pH dependent. FA binding to the clay composite at circumneutral pH was found to be challenging due to the reversibility of the reaction. Therefore, fine tuning of PEI loading, polymer MW, pH and thermal conditions coupled with characterization by zeta potential, FTIR and XRD measurements were used. These experiments allow the stoichiometric binding and release of FA as a function of pH and available amine groups to be established and controlled. *Pseudomonas sp.* that have shown the ability to assimilate and degrade FA under a wide range of pH values were chosen to be incorporated in the PEI-MMT composite. Bacterial adsorption and spatial organization on the composite as well as the FA degrading activity under various conditions was established. This unique configuration, where the bacteria are incorporated in the sorbent, can allow self-regeneration of the sorbent binding sites enabling long term continuous use. This concept of combining adsorption and biodegradation is promising for the removal of FA and can also serve as a model platform for the one-step removal of a wide range of pollutants.

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APPLICATION OF DIFFERENTLY TREATED ILLITE AND ILLITE CLAY FOR DEVELOPMENT OF CERAMICS

Gaida Sedmale (1)*, Martins Randers (1), Maris Rundans (1), Valdis Seglins (2)

(1) Riga Technical University, Institute of Silicate Materials, Paula Valdena Str. 3, Riga, LV1048, Latvia, (2) Latvian University, Faculty of Geography and Earth Sciences, Jelgavas Str. 1, Riga, LV1004, Latvia

In recent years clay minerals as natural nanoparticles can be used to produce high-performance products such as modified cellulose with the improved thermal properties, to promote sintering process for high - temperature ceramics densification, as well as to obtain low-temperature ceramic materials - geopolymers, and etc. Often there is used different ways to change the structure of clay minerals - 1:1 layer lattice alumosilicate mineral, kaolinite, as well 2:1 alumosilicates, illite.

This study shows the results of possibility to destroy or change of 2:1 layer silicate, illite, structure by using of different kinds of treatment (alkaline solution, mechanical, thermal and hydrothermal) and its influence on structure and properties of treated illite and consecutively impact of treated illite on low temperature ceramic products development. These results are compared with the corresponding treated clay and products from it.

In this study quaternary clays form Apriki-Laza pit located in western part of Latvia were used as source of illite. Separation of illite from clay was performed using chemical and sedimentation methods. For chemical treatment there are used 1M, 4M, 6M and 8M NaOH- water solutions. Mechanical treatment was carried out by using planetary mill Retsch 100 for 24 h at 280 rev./min., thermal - at 580 °C for 1h by using Nabertherm furnace and hydrothermal - at 175 °C and p~1 MPa for 24 h and 72 h. There was used also $Al(OH)_3$ for compositions with treated illite. These compositions, as well treated corresponding clay were pressed into cylindrical samples (h = 25 - 28 mm and Ø = 20 mm) and sintered at different temperatures 1000 - 1100 °C for illite compositions with $Al(OH)_3$ and at up to 600^oC for chemically treated clay to obtain ceramic products.

Phase transitions both of treated illite and corresponding clay was analysed by differential thermal analysis (Setsys Evolution 1750) in temperature range 20 °C to 1000 °C at heating rate of 10 °C/min. Phase composition of treated illite and clay was analysed by XRD (model D8 Advance Bruker and model Rigaku, Japan with CuKα radiation at 2θ scanning interval from 10° to 60° and speed 4°/min.) and SEM (model Nova-Nano SEM 650, Netherlands).

It is shown that the destruction of clay mineral illite structure during the different treatment is reached partly. Noticeable treatment effect of illite was observed by use of thermal processing at temperature up to 550 - 580 °C which led to release adsorbed and structural water, i.e., complete dehydration, whereas chemical, with 8M NaOH solution, led to formation of zeolite group mineral - sodium aluminium silicate hydrate $Na_6(AlSiO_4)_6 \cdot 4H_2O$. Hydrothermal treatment of illite led to small swelling, obviously indicated by muscovite formation.

The main difference of treatment of both illite and respective clay on development of ceramic products is that the more active form of illite is reached by thermal treatment, but for respective clay - chemical treatment, impacted mainly by carbonate and quartz phases.

By use of thermal treated illite as an active component in compositions with $Al(OH)_3$ by sintering at temperature 1100 °C there is obtained dense ceramic with main crystalline phase - corundum (α-Al_2O_3) and accompanying - hematite (Fe_2O_3) phase and is characterized by compressive strength up to 170 MPa. Main tendency there is that in compositions illite - 40… 50% $Al(OH)_3$ the sintering temperature is remarkably lowered what is required for formation of traditionally developed corundum ceramics.

It is also shown that despite the fact that impact of chemical treatment on corresponding clay structure changes is small, however there is observed effects on lowering of sintering temperatures together with pressure strength and bulk density what is typical for building ceramics.

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CLAY-BASED FORMULATIONS FOR METFORMIN CONTROLLED RELEASE

Ediana P. Rebitski (1)*, Pilar Aranda (1), Margarita Darder (1), Rafaelle Carraro (2), Eduardo Ruiz-Hitzky (1)

(1) Materials Science Institute of Madrid, CSIC, 28049 Madrid, Spain, (2) Hospital Universitario de la Princesa, 28006, Madrid, Spain
*edianapr@icmm.csic.es

Currently, metformin hydrochloride is the reference drug used for the treatment of type 2 diabetes [1,2], which as it is well known, is a widespread chronic metabolic disease, characterized by elevated blood glucose (hyperglycemia) [3,4]. Metformin is able to decrease blood glucose concentration by mechanisms other than insulin or sulphonylureas [2,3]. It also decreases plasma insulin concentrations, contributing to increase peripheral glucose uptake and decreasing hepatic glucose production [5]. In this way, the glycemic index is improved without gaining weight by the patient. For optimal therapeutic effect, a metformin dosage of 250-500 mg 3-4 times daily, is required to reach a maximum of 2.5 g/day. The absolute bioavailability of metformin hydrochloride is 50-60% in which it has a biological half-life of 6.2 hours. However, the use of therapy with metformin results in a high incidence of gastrointestinal side effects [6], and therefore, it is of great relevance to produce formulations that allow a controlled release of the drug.

In this context, clay minerals have proved to be efficient substrates to produce systems for controlled drug delivery [7]. Thus, here is evaluated the possibility of using montmorillonite to stabilize metformin, allowing its further incorporation in a formulation that may increase its biological half-life, decreasing the daily dosage and presumably, other side effects associated with the regular use of metformin. The selected clay mineral is a commercial sodium montmorillonite (MMT) known as Cloisite®-Nathat presents a cation exchange capacity *ca.* 93 mEq/100 g, and acceptable characteristics for uses in pharmacology [7]. As a first step, metformin has been intercalated in that clay by a cation-exchange reaction carried out in water under agitation during 24 h at room temperature. The resulting hybrid material has been characterized by diverse physicochemical techniques showing a drug content of 190 mEq/100g entrapped in the intracrystalline space of the silicate. The intercalation compound was also combined with pectin and chitosan to produce bionanocomposite materials, in which the presence of chitosan may have additional advantages related to its mucoadhesive properties in view to increase its permanence in the intestinal tract[8,9]. The prepared materials montmorillonite-metformin (MMT-MET) pectin-chitosan/metformin (PEC-CHT/MET) and pectin-chitosan/montmorillonite-metformin (PEC-CHT/MMT-MET) were *in vitro* tested in release experiments in which their passage through the gastro-intestinal tractis simulated by switching the pH conditions and the elapsed time in the different media. Based on obtained preliminary results, the PEC-CHT/MMT-MET system considerably provides a good controlled release compared to the other two systems (MMT-MET and PEC-CHT/MET). Thus, pectin-chitosan/MMT-metformin formulation seems a promising candidate for the oral administration of metformin for the control of type 2 diabetes.

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RECYCLING OF CLAYS-RICH BUILDING RESIDUES AND PAPER-INDUSTRY FLY ASH AS ALTERNATIVERAW MATERIALS IN THE GEOPOLYMERIZATION PROCESS

A. De Rossi (1), M. J. Ribeiro (2)*, J. A. Labrincha (3), R. M. Novais (3), D. Hotza (1), R. F. P. M. Moreira (1)

(1) Department of Chemical Engineering (EQA), Federal University of Santa Catarina (UFSC), PO Box 476, 88040-900 Florianópolis (SC), Brazil, (2) UIDM-ESTG, Polytechnique Institute of Viana do Castelo, 4900-348 Viana do Castelo, Portugal, (3) Department of Materials and Ceramic Engineering / CICECO- Aveiro Institute of Materials, University of Aveiro, Campus Universitário de Santiago, 3810-193 Aveiro, Portugal

The geopolymerization is a hardening and stabilization process of basic aluminosilicate structures, which has been proved as an alternative or complementary technique to common binder systems that use Portland cement or lime. Many industrial solid wastes have chemical composition potentially suitable for the geopolymerization process, enabling reaction of the components leading to materials with distinct properties that may be applied in a wide range of applications. Many studies have been carried out using industrial wastes demonstrating the feasibility of this strategy [1-4]. It is also important to note that the European Commission identified the construction and demolition wastes (CDW) as a priority waste flow for reuse, highlighting the obvious environmental benefits from their recuperation (Directive 2008/98/EC) [5,6]. These benefits include the consumption reducing of natural resources, minimizing the volume of wastes that will ultimately be landfilled and reducing greenhouse gas emissions [7-9]. Thus, this study seeks to evaluate fly ash produced by the paper industry (from energy production) as a source of aluminosilicates and the CDW as light aggregates, for sand replacement, in the development of geopolymeric mortars. The studied variables were different CDW grain sizes, as sand alternative material, curing methods and alkaline activator concentrations. For thegeopolymer mortar characterization chemical, morphological and mechanical analyzes were performed (XRF, SEM, XRD, EDS and compressive strength). The preliminary results show that the wastes may be used in the preparation of geopolymeric mortars, exhibiting interesting mechanical properties (around 15MPa for compressive strength for samples cured at ambient conditions).

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COVALENTLY MODIFIED HALLOYSITE CLAY NANOTUBES: SMART NANOMATERIALS FOR DRUG DELIVERY APPLICATIONS

Serena Riela*, Marina Massaro

(1) Department of Biological, Chemical and Pharmaceutical Sciences and Technology (STEBICEF), University of Palermo, Palermo, Italy

Halloysite nanoclays (HNTs) are promising nanomaterials because of their versatile properties, such as hollow tubular morphology and tunable surface chemistry. HNTs are biocompatible, no toxic and abundantly available at low cost. Due to these characteristics HNTs are suitable for development of hybrid sustainable materials, which are perspective for polymeric matrices reinforcement, active food packaging and drug delivery. HNTs are quite polydisperse in size with a length of ca. 1 mm, while the external diameter and the lumen range between 50-80 nm and 10-15 nm, respectively. Chemically, halloysite is composed of gibbsite octahedral sheet (Al-OH) groups on the inner surface and siloxane (Si−O−Si) groups on the external surface. This different chemistry allows the selective modification of HNTs surfaces. We performed several chemical functionalization of HNTs materials to confer properties valuable in specific applications.

The introduction of chemical modification of both surfaces (inner lumen and outer surface) is a relevant strategy to tune the nanotube properties. Namely, chemical modification of HNT surfaces allows to obtain nanoarchitecture with targeted affinity through outer surface functionalization and drug cargo ability from the nanotube lumen.

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LENNARD-JONES CORRECTION FOR CONCENTRATION PROFILE CALCULATION IN POISSON-BOLTZMANN PROBLEMS

Jari Rinta-Aho, Anniina Seppälä, Markus Olin

VTT Technical Research Centre of Finland Ltd, Espoo, PB 1000, 02044 VTT, Finland

The smectite group minerals are applied as buffer material in KBS-3 method for spent fuel final disposal, and therefore the behaviour of them must be predicted far into future. The formation of surface charge distribution and corresponding potential is among the most important properties of smectites, and has been much studied by different methods. In our study molecular dynamics results are tried to upscale.

There is a huge difference in concentration profiles at spatial range of ångströms near charged surfaces between two different computational approaches: molecular dynamics simulations and solving Poisson-Boltzmann equation for charged surface [1]. Using molecular dynamics the concentration profiles have local maximum values near the charged surfaces and is zero at the surface. In the solutions of Poisson-Boltzmann the local maximum values are at the surfaces. The main reason behind this phenomenon is that during derivation of Poisson-Boltzmann the radii of ions are assumed to be zero [2].

It is well-known that there are strong but short-range repulsive and attractive forces between atoms [3]. The cause of repulsive force is overlapping electron clouds of atoms. The cause of attractive part is induced dipoles. These forces can be combined into one potential function called Lennard-Jones potential [3]. These effects are not included into Poisson-Boltzmann equation.

Basic concept of Lennard-Jones corrected Poisson-Boltzmann equation is first to solve electrostatic potential from boundary value problem of Poisson-Boltzmann equation using e.g. FEM. Calculate Lennard-Jones potential for atom near system boundaries. Lennard-Jones potential and electrostatic potential form solution of Poisson-Boltzmann problem can be added into new potential function. This function can be used to calculate concentration profiles form Boltzmann distribution.

The results of Lennard-Jones corrected Poisson-Boltzmann equation show same kind of results than previous molecular dynamics simulations for slits between montmorillonite plates [1,4,5]. Using both methods there is one sharp pike in cation concentration profile in the middle of plates when width of the slit is small (<10 Å). When the width of the slit increases the pike splits into two. In the both solutions there is practically no anions inside the slid.

Main advantage of this new computational approach is its efficiency compared to molecular dynamics. The model is based on numerical solutions of boundary value problem of partial differential equation. There are plenty of efficient algorithms for these kind of problems available. Total computational time for solution is matter of minutes using normal laptop.

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CLAY MODEL FOR DRUG ADSORPTION: STUDY OF THE INTERACTION OF CIPROFLOXACIN WITH LI-FLUORHECTORITE

Anabel Lam (1), Aramis Rivera (1)*, Claudio M. Zicovich-Wilson (2), Luis Javier Alvarez (3), Jon Otto Fossum (3)

(1) Zeolites Engineering Laboratory, Institute of Materials Science and Technology (IMRE), University of Havana, 10400 Havana, Cuba, (2) Centro de Investigación en Ciencias-IICBA, Universidad Autónoma del Estado de Morelos, Av. Universidad 1001, Col. Chamilpa, 62209 Cuernavaca, Morelos, México, (3) Laboratorio de Simulación. Instituto de Matemáticas, Unidad Cuernavaca, Universidad Nacional Autónoma de México, Av. Universidad s/n, Col. Lomas de Chamilpa 62210 Cuernavaca, Morelos, México, (4) Norwegian University of Science and Technology (NTNU), NO-7491Trondheim, Norway

Clays are common ingredients in pharmaceutical products both as excipients and as active substances. The drug-clay interactions could also be used to achieve technological and biopharmaceutical benefits, being the starting point to use these materials as drug delivery systems. Recently our research group has reported the possibility to intercalate ciprofloxacine into smectite clays [1]. The development of appropriate clay models allowing to simulate the interaction and intercalation of drugs into the clay interlayer spaces is a challenge nowadays. Here we focus on creating a model of Lithium-fluorhectorite clay (Li-FH) that could be used to simulate the intercalation process of ciprofloxacin and then, investigating the interactions associated to the system.

In this work, the structure of fluorohectorite (FH) was constructed starting from relevant crystallographic coordinates [2]. Also, twelve water molecules were added in the interlayer space. After that, the interaction of an aqueous ciprofloxacin solution with the Li-FH model was studied. The results show that a strong interaction is established between the drug molecule and the clay, especially with the surface, although some molecules can penetrate in the interlayer region of the framework. The adsorption energy is around -30 kcal/mol. Importantly, we conclude that the interactions are established between the oxygen of the carboxilic group of the drug and the Li^+ cation of the clay, and also between hydrogen from the drug and the oxygen of the Li-FH framework.

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CUBAN ATTAPULGITE FOR THE DEVELOPMENT OF COSMETICS

Pérez Irela (1), Valdés Leslie (1)*, Simón Gastón (1), Ibañez Gabriela (1), Oquendo Merlyn (1), Velázquez Martha (2), de Ménorval Louis Charles (3), Rivera Aramis (4)

(1) Department of Pharmacy, Institute of Pharmacy and Food (IFAL), University of Havana, 10400 Havana, Cuba, (2) Research Center for Mining and Metallurgy Industry (CIPIMM), Boyeros 8067, Havana, Cuba, (3) Institut Charles Gerhardt Montpellier, Equipe Agrégats, Interface, et Materiaux pour l'Energie (AIME), Université Montpellier, 34095 Montpellier CEDEX 5, France, (4) Zeolites Engineering Laboratory, Institute of Materials Science and Technology (IMRE), University of Havana, 10400 Havana, Cuba

Since ancient times, clays have been used in cosmetic treatments due to the well-known benefits they provide to the skin [1]. Their low toxicity and many of their properties make these materials excellent candidates for the formulation of cosmetics [2,3]. Recently, in Cuba it has been discovered a new deposit of attapulgite, a rigid structure clay. Taking into account the properties of that clay and its current availability in the country, a study of its physical-chemical properties and technological characterization have been carried out. The results have shown the similarity of this mineral to its equivalents used in other countries, as follows from the specialized literature. Acute ophthalmic and dermatological tests were also performed, which indicated that the Cuban attapulgite has very low (or almost no) toxicity -an important asset for cosmetic preparations. In a preliminary study, a facial mask and a gel based on that clay material were formulated for cosmetic purposes. The outcome shows the appropriate technological properties and an exfoliation effect. The sensorial evaluation of both formulations was also carried out, with great acceptance by the consumers surveyed.

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BENTONITE AND VERMICULITE CLAYS AS PHOTOCATALYST FOR INDIVIDUAL AND SIMULTANEOUS PHOTOCATALYTIC DEGRADATION OF SULFAMETHOXAZOLE AND TRIMETHOPRIM IN AQUEOUS PHASE

Iván Martínez-Costa (1), Roberto Leyva-Ramos (1), José Rivera-Utrilla (2)*, Manuel Sánchez-Polo (2), Inmaculada Velo-Gala (2)

(1) Centro de Investigación y Estudios de Posgrado, Facultad de Ciencias Químicas, Universidad Autónoma de San Luis Potosí, Av. Dr. M. Nava No.6, San Luis Potosí, SLP 78210, México, (2) Inorganic Chemistry Department, Science Faculty, Granada University, 18071-Granada, Spain
*jrivera@ugr.es

This study was aimed at evaluating bentonite and vermiculite clays as photoactive materials to degrade two antibiotics widely prescribed: sulfamethoxazole (SMX) and trimethoprim (TMP), in the presence of UV and simulated solar light radiation. Antibiotics are the most commonly used drugs for the treatment of infectious diseases. Sulfamethoxazole (SMX) and trimethoprim (TMP) have been identified as emerging contaminants, and both have been found in underground and superficial water resources, and in effluents of municipal wastewater treatment plants [1,2]. The use of clays as catalysts for the photo-Fenton process is a promising alternative for the treatment of aqueous effluents, because these minerals are abundant, cheap, stable, and friendly to the environment [3]. Additionally, the structures of clays are very stable during the degradation process of pharmaceutics by oxidation that is an outstanding advantage for the AOPs. However, there are limited studies of the application of the chemical activity of the iron naturally contained in clays [4] and the photocatalytic characteristics of clays for the degradation of pollutants in aqueous solutions [5,6].

The physical and chemical properties of the clays were determined to comprehend better the photocatalytic properties of clays. The use of clays as photocatalysts can be a feasible alternative because they are non-toxic and show very good mechanical, thermal and chemical stability [6]. In this work, clays were characterized by various analytical techniques such as N_2 physisorption, XRD, atomic absorption spectrometry, wavelength dispersive X-ray fluorescence (WDXRF) and diffuse reflectance spectroscopy. The band gap (Eg) of clays was determined and all values of Eg were <4 eV, revealing that clays could behave as semiconductor materials and, therefore, as photoactive materials in the presence of UV radiation. This electronic characteristic was maintained over UV and UV/H_2O_2 treatments. The addition of clay strongly increased the degradation rate of the antibiotics SMX and TMP in the systems UV/clay and UV/clay/H_2O_2. The most significant results were observed when vermiculite was added to the UV/H_2O_2 system, increasing 3.5 and 4.6 times the degradation rate constants for SMX and TMP, respectively. Besides, the percentage of degradation of TMP was increased 32.8% in the same system. This behaviour can be attributed to the percentage of doping elements in the vermiculite. The activity of original clay was maintained throughout the photodegradation.

A reaction mechanism was proposed for the photocatalytic degradation of SMX and TMP in the presence of clays. The photodegradation takes place on the surface of the clay, either by the action of the species of iron, or doping elements, promoting a Fenton reaction. Additionally, the doping ions in the clay can promote the generation of e^-/h^+ pairs, which results in the oxidation/reduction of the species present in water and increasing the production of $HO^\bullet$ radicals in the medium. Thus, the clays are promising materials for the photodegradation of antibiotics.

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ARGILLIZATION AS PROXY TO Pb-Ag MINERALIZATION (BRAÇAL MINES, PORTUGAL)

Fernando Rocha*, Fernando Almeida, Cristiana Costa, Cristina Sequeira, Denise Terroso

GeoBioTec, Department of Geosciences, University of Aveiro, Portugal

Mineralized fault-veins containing sulphides rich in Pb and Ag occur at Braçal (Sever do Vouga, Aveiro, NW Portugal) site where mining activities had taken place intermittently since the Roman periods up to the seventies of last century. Since then, mining activities have halted.

Schist is the dominant regional rock and belongs to the Proterozoic "Schist-Greywacke" complex. Ore is composed of calcite, pyrite and galena, dispersed in a clayey dark and plastic matrix. Mineralized veins occur in discontinuous structures, tectonically controlled and hydrothermally affected. Mining reports show that ores higher concentrations occur generally on the intersection of veins, namely on those less affect by faults showing more developed argillization.

Mineralogy and geochemistry of this clayey matrix was characterized by X-ray Diffraction (XRD) and Fluorescence Spectroscopy (XRF); crystallochemistry of some selected samples was also studied by Scanning Electron Microscopy (SEM-EDAX).

Clay minerals associations are dominated by illite; however, in some places, a smectitic component is present in significant contents, and responsible for the high plasticity and absorbent capacity of the clayey material. Along mineralized veins, argillization shows peculiar mineralogical and geochemical features which are related both to the rate of hydrothermal and meteoric fluids circulation and to their activity. Close to the intersection of veins, namely on those more affected by faults showing more developed argillization due to fluids circulation, clay minerals association show an increase in expandable clay minerals, not only smectite (mainly montmorillonite-nontronite) but also illite-smectite, kaolinite-smectite and chorite-smectite. Geochemical data show that argillization development implies increase on Fe_2O_3, Na_2O and loss on ignition. On these same sites, Ag, Pb, Zn, Cu and Ni show a generalized decrease in concentration.

The degree of argillization and, in particular, the increase on expandable clay minerals, can be considered as a negative proxy to the Pb-Ag mineralization.

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STRUCTURAL CHARACTERIZATION OF THE REACTIVITY OF SMECTITE FROM BENTONITE ROCKS OF PORTUGAL

Vanessa Guimarães (1,2), Fernando Rocha (2)*, Iuliu Bobos (1)

(1) Instituto de Ciências da Terra - Porto, DGAOT, Faculdade de Ciências, Universidade do Porto. Rua do Campo Alegre 687. 4169-007 Porto, Portugal, (2) Geobiotec. Departamento de Geociências da Universidade de Aveiro, Campo Universitário de Santiago, 3810-193 Aveiro, Portugal
*tavares.rocha@ua.pt

Reactivity of the <2 μm smectite fractions (PS2, PS3 and BA1) collected from Porto Santo Island (Madeira Arch.) and Benavila (Portugal) was studied by X-ray diffraction (XRD) and infrared spectroscopy (IR) in extreme pH conditions using acid and alkalies at pH well defined. Previously, the structural behaviour of smectite was tested by samples solvation with K^+, Na^+, Ca^{2+} and Li^+ (Green-Kelly test). The layer charge and charge distribution were also evaluated through the solvation properties of the expandable Li- and K-smectite samples in glycerol (GLY) and ethylene glycol (EG), respectively. Smectite BA1 is characterized by the presence of tetrahedral charge between 0.23 and $0.38/O_{10}(OH)_2$, with higher proportion of expanded layers, whereas smectite PS2 has a tetrahedral charge $>0.38/O_{10}(OH)_2$ with lower proportion of expanded layers to 16.5 Å. Smectite PS3 has a tetrahedral charges lower than $0.23/O_{10}(OH)_2$. Two-water (2W) smectite (Ca-montmorillonite) interstratified with 1-water (1W) smectite (Na-montmorillonite) characterize the sample BA1. The Green-Kelly test confirms the presence of a beidellitic component (16.80 Å = beidellite) interstratified with 2W/1W-smectite (9.60 Å = 2W smectite) for sample BA1. The sample PS2 seems to have the same smectite layers as sample BA1, exception doing the presence of K-illite layers randomly interstratified with 2W/1W-smectite with beidellitic character. The smectite layers are of beidellitic character with net layer charge in tetrahedral sheet as indicated by Greene-Kelly test. Sample PS 3 corresponds to a randomly interstratified structure of K-I/1W/2W-smectite (R=0; 80%S), where no beidellitic layers did occur. The <2 μm fractions of sample BA1 were chemical treated in acid and alkaline solution and then XRD run. The intensity of the 001 peak decreased and expanded few Å in both acid (pH = 3.5) and alkaline (pH = 11) environment.

Structural changes observed were well evidenced by IR by changes of the Si-O stretching band and -OH -bending band.

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ADVANCED DIAGENESIS - VERY LOW GRADE METAMORPHISM ON PROTEROZOIC SUPERGROUP DÚRICO-BEIRÃO, PORTUGAL

Fernando Rocha*, Jorge Medina, Cristiana Costa, Rita Bernardino, Denise Terroso

GeoBioTec, Department of Geosciences, University of Aveiro, Portugal

Schist and Greywacke Complex known as "Complexo Xisto-Grauváquico" (and more recently as Supergroup Dúrico-Beirão) occupies a big area of the Central Iberian Zone in Portugal and includes the Beira and Douro Groups with Neoproterozoic to early Cambrian metasedimentary rocks.

In the study area, from where samples come from, situated at Caramulo-Buçaco region (central Portugal), on the basis of lithostratigraphic and structural criteria it is possible to identify four main units: a lower unit that comprises a succession of grey and black mudstones with sandstone intercalations (estimated thickness of 1000 m); second unit has an estimated thickness of around 1500 m and is predominantly composed by muddy material; third unit is less than 2000 m thick and is characterized by the presence of decametric sandstone layers with kilometric lateral extension separated by grey and black mudstones; upper unit has more than 500 m thick and is predominantly composed of muddy material interbedded with rare sandstone layers.

The sedimentary rocks (mudstones and sandstones) were affected by low grade regional metamorphism (greenschist facies). The overall structure of the region was mainly produced during the Variscan Orogeny.

Mineralogy and geochemistry of the studied samples was characterized by X-ray Diffraction (XRD) and Fluorescence Spectroscopy (XRF); crystallochemistry of some selected samples was also studied by Scanning Electron Microscopy (SEM-EDX). Several parameters were assessed, namely: kaolinite illite 'crystallinity' Kubler Index, and b cell parameters of micas and chlorites; in this work, we have also made a simple qualitative estimate of the existence of illite polytypes by comparing the 1Md (112) and 2M1 (025) reflections.

Following the XRD and XRF studies, representative samples were selected for electron microscopy study on the basis of the KI values and the mineral assemblages. Carbon-coated slices were examined by SEM, using BSE imaging and energy-dispersive X-ray (EDX) analysis in order to obtain textural and chemical data.

Studied samples show evidences of Advanced Diagenesis, a few reaching the Very Low Grade Metamorphism. Greywackes in general show minor evolution than shales and slates.

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CATALYTIC ACTIVITY OF GREEN SYNTHESIZED β-FeOOH/KAOLINITE

S. M. Miron (1), A. Beda (1), R. C. Pullar (2), W. Hajjaji (1), J. A. Labrincha (2), F. Rocha (1)*

(1) Geobiotec, Geosciences Dept, University of Aveiro,3810-193 Aveiro, Aveiro 3910-193, Portugal, (2) Department of Materials and Ceramic Engineering & CICECO - Aveiro Institute of Materials, University of Aveiro, Aveiro, Aveiro 3810-193, Portugal

The textile industry has gained more attention in the past few years as the demand on the market for clothes having a long-lasting colour increased, meaning that the used dyes need stronger oxidants agents in order to deteriorate the dye structure. This need is related to the molecular structure that contains complex aromatic amide groups with alkyl, halogen, nitro, hydroxyl, sulfonic acid, substituent(s), and inorganic sodium salts. By discharging the wastewater containing untreated dye there will be major environmental problems as the effluent contains non-biodegradable compounds, such as toxic substances, soaps and detergents, oil and grease and sulfide. In these conditions the treatment is necessary before the release into the environment.

This study focused on the efficiency of the clay combined with green synthesized iron compounds used as catalyst in advanced oxidation process (Fenton and photo-Fenton) for removing organic pollutants from textile wastewater. Extracted antioxidants from coffee were used in order to obtain iron nanoparticles. The key active agents in synthesis are polyphenols. Coffee is known to contain polyphenols such as chlorogenic acids and melanoidins that act both as reducing and capping agent and have antioxidant properties. Also, the antioxidant capacity of coffee is related to the presence of both natural and formed compounds during the processing. In this case, the antioxidant inhibited the oxidation of iron cations, stop the loss of electrons and will make free radicals that will start the chain reaction. The antioxidants were extracted from coffee, mixed with $FeCl_3$ solution and kaolinite in order to obtain stable β-FeOOH/kaolinite.

The removal of methylene blue from aqueous solution was implemented by using photo-Fenton process involving two characteristic parameters: peroxide H_2O_2 and UV light. A series of batch experiments were conducted in order to determine the discoloration rate. The concentration of the dye in water was monitored using ultraviolet-visible (UV-VIS) spectroscopy.

The first experiment of removal of methylene blue from an aqueous solution was carried out using β-FeOOH catalyst alone. Varying the catalyst amount and maintaining the same concentration of the dye (10 ppm), an increase on removal rate was observed, achieving 100% removal with 0.005 g catalyst after 300 minutes. The second trial was performed using the same amount of β-FeOOH/kaolinite and the results illustrated that at a lower concentrations (below 10 ppm) better removal values were obtained (95% after 300 min).

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CLAY MINERAL ASSEMBLAGES AS PROXIES FOR RECONSTRUCTING PALEOCLIMATE, PROVENANCE AND SEDIMENT TRANSPORT PATTERN IN THE ALBORAN SEA BASIN

Marta Rodrigo-Gámiz (1)*, Francisca Martínez-Ruiz (1), Daniel Ariztegui (2), Miguel Ortega-Huertas (3)

(1) Instituto Andaluz de Ciencias de la Tierra (IACT), CSIC-University of Granada, 18100 Armilla, Granada, Spain, (2) Department of Earth Sciences, University of Geneva, Geneva, Switzerland, (3) Departamento de Mineralogía y Petrología, Universidad de Granada, Granada, Spain

The study of clay mineral composition in marine sediments records from the Alboran Sea basin (westernmost Mediterranean) has provided a detailed evolution of the paleoclimate and paleoenvironmental conditions since the Last Glacial Maximum (LGM). Detrital clays derive from the southern Iberian riverine input and eolian dust pulses from the North African margin. Variations over this time period, the last 20 kyr, in clay mineral assemblages reflect climate conditions in the source area as well as fluctuations in provenance and transport mechanisms. In the western Mediterranean detrital mica, chlorite and smectite are mainly fluvial-derived minerals, whereas the major kaolinite input results from reworked wind-blown particles from western Morocco and northern Algeria.

A representative sediment record recovered in the East Alboran basin during the TTR-12 cruise (36’10.414N, 2’45.280W, 1,840 mbsl) has been analyzed. The pelagic sediment record is composed by homogeneous green-brownish mud-clay with some shell fragments and foraminifera. The entire record of 402 cm length was sampled at very high-resolution, each 1.5 cm, obtaining a total of 267 samples. Clay mineral composition was obtained by X-ray diffraction (XRD), developing internal standard patterns for obtaining a precise quantitative analysis. Quantitative analysis was adjusted using the least squares method between each experimental diffractogram and the best-weighted combination of the standard pattern, giving values <4% for clay mineral assemblages. Quantitative geochemical microanalysis of clay minerals was also determined by transmission electron microscopy (TEM).

Detrital clays in the analyzed record represent about 50-60% of the bulk mineral composition. Particularly, clay mineral assemblages are mostly composed of illite (42-56%) and lower proportions of smectites (18-31%), kaolinite and chlorite (both 8-14%), and minor amounts of palygorskite (4-7%). The occurrence and abundance of fibrous eolian-derived clay minerals was also observed by TEM, showing maximum proportions during arid and cold periods like from the end of the LGM to the Oldest Dryas (18.0-14.7 kyr cal. BP), and at the onset of the Younger Dryas (YD, 12.9 kyr cal. BP), as result of the intensification of Saharan dust export across the western Mediterranean. Subsequently, high abundances of palygorskite were observed during the early Holocene (11.6-10.0 kyr cal. BP), mid-Holocene between 9.0-8.0 kyr cal. BP to increase again at 4.6 kyr cal. BP. In contrast, reduced contents of palygorskite and kaolinite clay mineral associations and major quantities of fluvial detrital clays represented by the illite + chlorite/kaolinite ratio are observed during warm and humid periods, involving higher rainfall and freshwater runoff such as at the Bölling-Alleröd period (B-A, 14.7-12.9 kyr cal. BP). In addition, the radiogenic isotopic signature in this marine record has mainly shown a dominant provenance of the detrital material from present-day Morocco, Mali, Mauritania, Niger, and Algeria, mixed with material from southern Iberia, except during the last Heinrich event and the early-middle Holocene transition (ca. 8.9 kyr cal. BP) that showed a contribution of an older terrigenous component, likely Archaean material from the present Senegal region. Thus, variations in the abundance and presence of the clay mineral associations were mainly driven by fluctuations in wind intensity and fluvial discharges. These fluctuations have been associated with variations of the Westerlies and the North Atlantic Oscillation index as well as with northward/southward migrations of the Inter-Tropical Convergence Zone over North Africa that influences western Mediterranean climate conditions.

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EVALUATION OF FIBROUS CLAY MINERALS FOR CO_2 CAPTURE

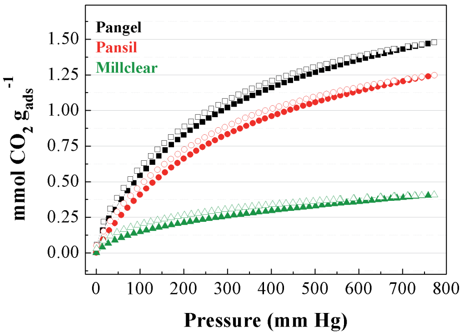
Cecilia J. A. (1), Vilarrasa-García E. (2), Cavalcante C. L. Jr (2), Azevedo D. C. S. (2), Franco F. (1), Rodríguez-Castellón E. (1)*

(1) Universidad de Málaga, Departamento de Química Inorgánica, Cristalografía y Mineralogía, Facultad de Ciencias, 29071 Málaga, Spain, (2) Universidade Federal do Ceará, Departamento de Engenharia Química, GPSA-Grupo de Pesquisa em Separaçoes por Adsorçao, Campus do Pici, 60455-760 Fortaleza, Brazil
*castellon@uma.es

Global warming resulting from the emission of greenhouse gases has become a widespread concern in the last decades. This fact has led to the governments are regulating stringent legislations to diminish the anthropogenic CO_2 emissions. The most sustainable strategy to limit the CO_2 emissions is the CO_2 capture, storage or sequestration (CCS) [1]. Among all technologies for the CO_2 capture, chemical absorption and adsorption are the most suitable ones for post-combustion power plants.

In CCS processes, CO_2 capture is the most expensive step, between 50-90%, of the process cost. The major concerns for this technology are associated to CO_2 capture efficiency, adsorption rate, energy requirements in regeneration and volume of adsorbent [1]. Thus, it is necessary the development of inexpensive adsorbents to cheapen the cost of the CCS step. In this sense, clay minerals are very available and versatile materials that can be used as ion exchanger, absorbent or catalyst due to their physicochemical properties.

In this research, three commercial fibrous clay minerals, two sepiolites (Pangel and Pansil) and a paligorskite (Millclear), supplied by TOLSA S.A., have been tested to evaluate their potential in CO_2 adsorption. The physicochemical properties of these fibrous clay minerals have been modified by acid treatment and milling. In addition, these materials have been functionalized with amine species to improve CO_2 adsorption, mainly at lower pressure due to the synergetic effect of the molecular sieve of the adsorbent and the chemical interaction between the amine species and CO_2 molecules. These procedures have been carried out by two methods: the incorporation of amine groups by grafting using 3-(triethoxysilyl)propylamine (APTES), or the impregnation of amine-rich polymers using polyethyleneimine (PEI) and tetraethylenepentamine (TEPA) as “basket molecules” [2].



CO_2 adsorption-desorption isotherms at 25 ºC of the raw fibrous clay minerals

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PEDOLOGICAL AND MINERALOGICAL INDICATORS OF SOIL EVOLUTION IN CARBONATED PARENT MATERIALS: A CASE STUDY IN ASTURIAS (NORTHERN SPAIN)

Manuel Rodríguez-Rastrero (1)*, Jaime Cuevas Rodríguez (2), Almudena Ortega Martos (2), Ana Isabel Ruiz García (2), Felipe Yunta Mezquita (3), José Gumuzzio Fernández (2)

(1) Unidad de Conservación y Recuperación de Suelos. Departamento de Medio Ambiente. Centro de Investigaciones Energéticas, Medioambientales y Tecnológicas (CIEMAT), 28040-Madrid, Spain, (2) Departamento de Geología y Geoquímica. Facultad de Ciencias, Universidad Autónoma de Madrid, 28049-Madrid, Spain, (3) Departamento de Química Agrícola y Bromatología, Facultad de Ciencias, Universidad Autónoma de Madrid, 28049-Madrid, Spain

In soil science, clay illuviation (or argilluviation) is the process of mobilization in suspension of silicate clay by the action of gravitational water, from an upper (eluvial) horizon to a lower (illuvial) horizon. Virtually all soil classification systems recognize, at a high hierarchical level, the presence of subsurface horizons enriched in silicate clay. When clay illuviation is manifested with sufficient intensity at a given thickness of the soil, the so-called *argillic* horizon is assigned to a soil profile [1,2]. The definition of the argillic horizon is a practically common diagnostic criterion between the two universal soil classification systems: World Reference Base of Soil Resources [2] and USDA's Soil Taxonomy [1]. The process of argilluviation requires, in geomorphological terms, a great stability of the slopes, as much against erosive as depositional processes. This implies a certain antiquity in the surfaces in which the argillic horizon is present. Thus, in similar climatic zones to those of the studied area, early illuviation features are usually visible from about 2000 years [3]. Furthermore, the developing of illuvial processes as required for the definition of argillic horizons is assumed to appear only in Pleistocene surfaces [3]. In particular, the abundance of kaolinite in temperate regions is assumed to be increasing with the antiquity of the soil, being expected that it generally takes much more than 10000 years to produce a soil containing pedogenic kaolinite as a major constituent [4].

The argillic horizon is widely represented in the temperate zones of the planet, being one of the most common types of diagnostic horizon in the European Atlantic region. However, in certain areas of this region, the argillic horizon is scarce. This is the case of the territory of Asturias (northern Spain), object of this work. From a total of 442 soil profiles studied in this territory, only 40 of them show argillic horizons. Such soil profiles show the highest degree of evolution in the territory (A/Bt/C as a general soil profile) and they are classified within *Alfisols* and *Ultisols* Orders as Soil Taxonomy [1]. Although these soils show significant and positive relationships with calcareous parent materials e.g. limestone or dolomites, they do not constitute the dominant soils in such materials [5]. This role corresponds to soils of lesser evolutionary degree (A/C or A/R soil profiles), included in the *Mollisols* Order and associated to less geomorphologically stable slopes. The mineralogical properties of the studied soils characterized by argillic horizons have shown remarkable differences with those included in the *Mollisols* Order, even when developed under equivalent climatic and lithological conditions. The observed differences in an initial phase of this work refer to the abundance of kaolinite, associated to goethite, in the argillic horizons compared to its absence in soils constituted by mollic horizons. Kaolinite is virtually absent in calcareous parent materials. Mollisols, on the other hand, show appreciable contents of calcite and feldspars that are in turn virtually absent in the argillic horizons. The presence of kaolinite can thus be related to the development of pedological features indicative of a high degree of soil evolution and, consequently, of the geomorphological stability of the slopes during long periods.

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UV PROTECTION USING SPHERICAL CLAY

Kimin Roh (1)*, Daeyoung Kim (1,2), Sung Man Seo (1), Il-Mo Kang (1), Sung-Rock Lee (1)

(1) Korea institute of geoscience and mineral resources, Daejeon, 34132, Republic of Korea, (2) University of science and technology, Daejeon, 34113, Republic of Korea

Because UV radiation of the sunlight is well known for acutely and chronically harmful effects on the human skin such as the sunburn, skin aging and skin cancer, various types of skin creams have been designed for the purpose of UV protection. Most of these creams contain two kinds of UV-protection compounds; organic and inorganic materials. The most commonly used inorganic materials are micronized TiO_2 and ZnO_2 particles, however, these non-natural substances in UV-protection creams are known to cause an unexpected photo-catalytic effect, which may be a serious problem because it takes place on the skin [1]. Therefore, natural materials including clays and clay minerals have received much attention as the formulating agent in the pharmaceutical and cosmetic products in order to reduce the direct contact of TiO_2 particles to the human skin.

In this study, spherical clay powder has been developed by the way of spray drying the composite suspension of bentonite and TiO_2. This spherical functional powder contains uniformly fine TiO_2 particles both to the surface and inside of the bentonite powder. It will be discussed the physical characteristics, UV protect effect, and usability to cosmetics of this clay based functional powder.

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SYNTHESIS, FUNCTIONALIZATION AND BIOLOGICAL IDENTITY OF LAYERED DOUBLE HYDROXIDE NANOPARTICLES FOR BIOMEDICAL APPLICATIONS

Ricardo Rojas*, Cecilia Vasti, Dariana Aristizabal Bedoya, Yadira Estefanía Salguero Salas, Carla E. Giacomelli

INFIQC-CONICET, Departamento de FisicoquímicaFacultad de Ciencias Químicas, Universidad Nacional de Córdoba. Ciudad Universitaria. X5000HUA Córdoba (Argentina)

Layered double hydroxides nanoparticles (LDH-NPs) present excellent properties to grant the complex functionality needed for biomedical applications. They can be easily prepared with a size between 50 and 200 nm and their anion exchange capacity provides a high loading capacity for acid drugs and biomolecules. Besides, they present release mechanisms based on the anion exchange with the anions in the biological media and the dissolution of their layers at slightly acid media [1]. Nevertheless, there are many aspects regarding the physicochemical properties of LDH-NPs and their interaction with the biological media that are still unclear to rationally design LDH-NPs with genuine potential to be applied in biomedical applications.

A precise control of the LDH-NPs size is necessary to ensure their capacity to evade clearing by the mononuclear phagocyte system (MPS) and to optimize the transfection capacity of the cellular membrane [2]. Likewise, new strategies to surface functionalize LDH-NPs are required to increase their colloidal stability in biological media, and to provide site specificity. Another aspect to be addressed is the interaction between serum proteins and the surface of LDH-NPs that produces a biological coating known as protein corona. The protein corona determines the physicochemical properties of LDH-NPs and their interactions with the cellular membrane, which leads to a so-called “biological identity” that can be quite different to that of the as-prepared LDH-NPs. Controlling the biological identity of LDH-NPs is a key aspect to reduce elimination by the MPS and to optimize the interaction with the target cells.

Here we present diverse strategies to control the physicochemical properties and biological interactions of LDH-NPs. In first place, different synthesis routes were explored to intercalate anions such as methotrexate, fluorescein or nalixidate, the best results being obtained with a coprecipitation method at variable pH involving separate nucleation and aging steps [3]. Secondly, different compounds were used to functionalize the synthesized LDH-NPs: risedronate, a bone antiresorptive drug with high affinity for hydroxyapatite, was used to provide bone targeting capabilities, while polylelectrolytes were explored to enhance their colloidal stability. Finally, the interaction between albumin and LDH-NPs was studied as a first insight to the protein corona formation mechanism and its effect on the physicochemical properties of LDH-NPs. Afterwards, the biological identity of LDH-NPs and its modulation by the surface coating with serum proteins was explored in cell culture conditions. The cytotoxicity and transfection capacity of the prepared LDH-NPs were tested in adequate model cell lines.

The use of different synthetic strategies and a careful selection of the operational parameters allowed the synthesis of LDH-NPs with different interlayer anions. In all cases, the drug was selectively located in the interlayer of the LDH-NPs, which allowed their surface functionalization with a minor drug loss. The functionalization with either risedronate and polyacrylate increased the colloidal stability of LDH-NPs even in high ionic strength due to electrostatic repulsion and/or steric impediments. Further, risedronate functionalized LDH-NPs attached to hydroxyapatite due to risedronate bridging. A protein corona was formed on the LDH-NPs surface in all cases upon interaction with serum proteins; albumin was its main component in all cases. The extent of the protein adsorption, as well as the components of the protein corona were affected by functionalization, which ultimately affected the unspecific cell transfection of LDH-NPs. These studies clearly show the potential of rationally and thoroughly designed LDH-NPs to produce drug delivery to specific tissues and cells.

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GAS TRANSPORT IN COMPACTED MX-80 BENTONITE AND COUPLED HYDRO-MECHANICAL PROCESSES

Enrique Romero (1)*, Laura Gonzalez-Blanco (1), Paul Marschall (2)

(1) Department of Civil and Environmental Engineering, Universitat Politècnica de Catalunya, 08034 Barcelona, Spain, (2) Nationale Genossenschaft für die Lagerung radioaktiver Abfälle, 5430 Wettingen, Switzerland
*enrique.romero-morales@upc.edu

The complexity of the coupled THM-C processes associated with gas transport in compacted bentonite gives rise to multiple interacting phenomena, which seem difficult to simulate by numerical models even though they are of potential significance for the long-term safety of engineered and geological barriers for underground disposal of radioactive wastes. Within this context, the present contribution aims at presenting experimental data under well-controlled conditions on the gas transport behaviour of compacted bentonite to complement existing capabilities of the modelling tools, as well as to allow the development of new modelling approaches.

The gas transport processes in compacted bentonite is affected by a number of factors, such as the dry density, the pore size distribution and their connectivity, the heterogeneous distribution of porosity, the saturation state, the stress state, the deformation undergone during gas injection and dissipation, and the gas injection regime (fast and slow injection rates). Therefore, an extensive experimental program using reproducible sample preparation methods has been started on compacted MX-80 bentonite (dry density 1.55 Mg/m^3) to study the influence of some of these aspects on air injection. Controlled volume-rate air injection (0.04 and ≥2 mL/min) followed by shut-off and dissipation stages have been performed under oedometer conditions, which have been focused on the volume change response and the changes in the pore and pathway network. Mercury intrusion porosimetry results have allowed detecting preferential pathways after gas injection / dissipation tests. The opening of these pressure-dependent pathways plays a major role on gas permeability. A complementary insight into the connectivity of these pathways has been quantified by micro-computed tomography. Results have been used to estimate degree of saturation changes on gas injection due to the desaturation of the connected pathways.

In addition, numerical simulations of a test is presented as a first attempt to better understand the air transport process. This simulation has been carried out with a coupled HM model using 2D axi-symmetric finite elements with CODE_BRIGHT, in which stress dependent (dilatant) embedded pathways have been considered (Olivella & Alonso 2008; Gonzalez-Blanco *et al*. 2016). The model handles the combined phenomena of two-phase flow (gas and liquid), the aperture of discrete pathways to account for permeability and capillary pressure variations, as well as the sample volume changes along the air pressurisation and dissipation processes. Three zones with different material properties have been considered: a) central zone of pathway development; b) bentonite matrix; and c) upstream and downstream reservoirs to capture density of the pressurised air mass. The numerical results have allowed reproducing upstream / downstream pressures, outflow volume and bentonite volume changes accurately. The combination of experimental results and numerical simulations have also provided a good insight into the role of the volume change response and pathway development on the gas transport properties of compacted bentonites, confirming that pathway development and aperture occurs during gas injection that later affects the response during the dissipation stage.

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THE USE OF TIME-LAPSE FLUORESCENCE IMAGING TO ASSESS THE IMPACT OF *ACENITOBACTER BAYLYI* ADP1 IN URANYL COMPLEXATION AND TRANSPORT THROUGH POROUS MEDIA

Maria E. Romero-González*, Ali Al-Anizi, Steven A. Banwart

Department of Geography, The University of Sheffield, Sheffield, United Kingdom
*m.e.romero-gonzalez@sheffield.ac.uk

A novel method to visualise the transport of bacterial colloids through porous media in the presence of uranium has been developed. A flow cell packed with sandstone as representative of sub-surface geological media was saturated using *Acinetobacter baylyi* ADP1 (ADP1), on a free phosphate growth medium. The visualisation of the bacteria plume was achieved by staining the cells using fluorescein and monitoring their transport through the flow chamber when irradiated with fluorescent light. Time-Lapse Fluorescence Imaging (TFLI) was used to monitor the transport of the stained cells at different pH conditions and $U(VI)_{(aq)}$ concentration. The amount of cell biomass and concentration of uranium was quantified at the outlet of the flow cell. The rate of cell transport was modelled by fitting breakthrough curves. It was shown that when uranium is adsorbed to ADP1, the mobility of U(VI) is increased. The breakthrough curve for free uranium peaked at pore volume 1.77, while the complexed ADP1-U(VI) peak occurred at pore volume 1.28 and 1.36 at pH 7 and pH 5 respectively. The findings suggest that bacteria-uranium complexes may travel faster through geological media than free uranyl ion, increasing the mobility of this radionuclide in the subsurface.

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MECHANISMS OF PHOSPHATE REMOVAL BY CALCIUM-IRON LAYERED DOUBLE HYDROXIDES AND THEIR HYDROLYSIS PRODUCTS

Al Jaberi Muayad, Mallet Martine, Naille Sébastien, Abdelmoula Mustapha, Ruby Christian*

Laboratoire de Chimie Physique et Microbiologie pour les Matériaux et l'Environnement - LCPME UMR 7564 CNRS-Université de Lorraine, 405 rue de Vandoeuvre, 54600 Villers-lès-Nancy, France

The protection of the water resource is among the major issues of the twenty-first century due to the growing of population, the rapid industrialization and the intensification of agriculture. Among the various pollutants that threaten the water quality, orthophosphate anions (PO_4) are of upmost importance since the excess of PO_4 is mainly responsible of the water eutrophication phenomena. It leads to strong perturbation of the biodiversity and important economic losses, *e.g.* closing of fisheries and groundwater production wells. For eliminating PO_4 from water in rural areas, there is a growing interest for PO_4 passive water treatment that needs low energy and little maintenance. Therefore, new filtration materials should be designed and layered double hydroxides (LDH) are promising constituents for this purpose since they are able to catch phosphate in water by several mechanisms such as adsorption, anionic exchange and dissolution-precipitation [1].

In this study, $Ca^{II}Fe^{III}$ LDH intercalated with chloride ions was synthesized by co-precipitation of Ca^{II} and Fe^{III} species using variable initial Ca^{II}:Fe^{III} ratios in the initial solution (2:1, 3:1 and 4:1). The samples were used for the removal PO_4 in both homogeneous suspensions ("batch reactors") and in hydrodynamic conditions ("column reactors"). LDHs materials were characterized by means of X-ray diffraction and infrared, Raman, X-ray photoelectron and ^{57}Fe Mössbauer spectroscopies.

The isotherms of adsorption of phosphate ions showed that CaFe-LDH prepared at Ca^{II}: Fe^{III} molar ratio of 2:1 revealed the highest rate of uptake. Equilibrium data were well fitted with Freundlich or Langmuir isotherms and led to a maximal removal capacity q_e^{Max} of ~ 385 mg PO_4 g^{-1} LDH. This value is about 3-5 times higher than the value measured for ferrihydrite (Fh) which was determined to be a very efficient adsorbent for phosphate [2] (~ 40 mg PO_4/g ≤ q_e^{Max} ≤ ~ 105 mg PO_4/g). In the case of high initial phosphate concentration ($[PO_4^{3-}] \geq 100$ mg/L), CaFe-LDH is dissolved and released Ca^{2+} ions reacting with PO_4 to precipitate as hydroxyapatite. This was identified to be the main PO_4 removal mechanism (~ 75% of total removal). The excess of phosphate removal (~ 25%) was attributed to the formation of disordered calcium doped Fe oxyhydroxide (Ca-FeOOH). Ca-FeOOH removed phosphate *via* a simple surface adsorption mechanism. In the case of lower initial phosphate concentration ($[PO_4]$ <100 mg L^{-1}), PO_4 was mainly removed by surface adsorption and the formation of hydroxyapatite was not clearly observed.

CaFe-LDH coated pozzolana (Pz), a volcanic rock of Puy de Dome (Auvergne, France) was prepared for the experiments performed in the column reactor. The PO_4 breakthrough occurred at a V: V_p of ~ 180 (V: volume of PO_4 solution, V_p: porous volume of the column). This value was significantly higher than the one observed previously for ferrihydrite coated Pz in similar experimental conditions. However, the drawbacks of using Ca_2Fe-LDH-Cl as a filtration material were the strong alkalinity and the high solubility of Ca in the outflow of the column. Such a high pH is not acceptable for water treatment application (pH should be lower than 9) and soluble Ca can easily precipitate to form $CaCO_3$ inducing a significant increase of the water turbidity.

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INTERACTIONS OF Se(IV) AND Eu(III) WITH THE INDIGENOUS BENTONITE BACTERIAL SPECIE *STENOTROPHOMONAS BENTONITICA*

Miguel A. Ruiz-Fresneda* (1), Jaime Gomez-Bolivar (1), Ivan Sanchez-Castro (1), Andrea Cherkouk (2), Henry Moll (2), Mohamed L. Merroun (1)

(1) Department of Microbiology, Faculty of Sciences, University of Granada, Campus Fuentenueva 18071, Granada, Spain,
(2) Helmholtz-Zentrum Dresden-Rossendorf, Institute of Resource Ecology, Bautzner Landstraße 400, 01328, Dresden, Germany
*mafres@correo.ugr.es

Nowadays, the storage of materials contaminated with radionuclides is becoming a global environmental problem. Deep geological repositories (DGR) consisting on the encapsulation of radioactive wastes in metal containers surrounded by natural and artificial barriers like bentonite clay formations have been proposed as one of the best options for their disposal in the near future. Bentonite clays from the Cabo de Gata Natural Park (Almería, Spain) have been selected for their possible use as an engineered barrier in DGR because of their well-characterized mineralogical and geochemical properties [1]. Several studies evidenced the occurrence and high diversity of microorganisms present in bentonite clay formations that may play an important role in corrosion of container and mobility of radionuclides through the repositories [2].

The main objective of the present work is to study the effect of microorganisms isolated from bentonites collected from Cabo de Gata on the speciation of elements like selenium (Se) and europium (Eu) under alkaline conditions relevant for intermediate level wastes. The speciation of metals determines their transport and migration behaviour in the environment. Selenium is a common component of radioactive wastes produced by nuclear industry [3], while europium is an inactive analogue for trivalent actinides (e.g. Cm(III) and Am(III)) also present in nuclear wastes. The isolate Stenotrophomonas bentonitica BII-R7 [4] showed the ability to reduce selenite [Se(IV)] to less toxic forms [Se(0)] using alkaline (pH 10) conditions under oxic and anoxic atmosphere. The biogenic selenium produced was accumulated extracellular and intracellularly in form of hexagonal crystalline and amorphous nanoparticles (30-200 nm) as revealed by Scanning-Transmission Electron Microscopy (STEM) and X-ray diffraction (XRD). On the other hand, S. bentonitica is also able to interact with Eu(III) mainly by a biosorption process under both aerobic and anaerobic conditions as indicated by STEM, Time-Resolved Laser-induced Fluorescence Spectroscopy (TRLFS) and kinetic studies. TRLFS suggested that most likely phosphoryl and carboxyl containing groups located at the bacterial cell envelope dominated the Eu(III) speciation. In addition indications were found for Eu(III) interactions with cell-released substances.

The results obtained in the present work will provide new insights on the significance of aerobic/anaerobic microbial processes in the safe geological disposal of alkaline, intermediate level wastes.

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Keywords: bentonite, stenotrophomonas bentonitica, repository, selenium, europium.

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SPONTANEOUS SELF ORGANIZATION OF A CHARGED COLLOIDAL CLAY: FROM LIQUID PHASE TO ARRESTED STATES

Roberta Angelini, Emanuela Zaccarelli, Barbara Ruzicka*

Institute of Complex Systems-CNR and Physics Department, Sapienza University, P.zle A. Moro 2, Rome 00185, Italy

One of the most striking features of soft matter systems is their ageing behaviour: the dynamics is not stationary but spontaneously changes with waiting time as the sample evolves from a liquid phase towards an arrested state (gel and/or glass). Ageing dynamics and dynamical arrest in colloidal systems have recently become the subject of intense research activity also because of their theoretical and technological implications. Several mechanisms of dynamical arrest have been identified, even if few real systems are suitable for use as experimental counterparts.

However recent advances in the study of soft materials have led to the discovery of new phases and states besides the ones commonly experienced in atomic or molecular systems. Among these colloidal clays have emerged as suitable candidates to investigate the formation of multiple arrested states.

In this presentation we show the results obtained on dilute aqueous dispersions of Laponite®, an industrial synthetic clay that dispersed in water originates a charged colloidal system of nanometer-sized discotic platelets with inhomogeneous charge distribution and directional interactions. The presence of competing attractive and repulsive terms in the interactions, combined with the directionality of the face-rim charge interactions and with the anisotropic shape of Laponite, determine a nontrivial aging dynamics towards multiple arrested states. Therefore the system spontaneously evolves with waiting time from a liquid phase with low viscosity to an arrested gel and/or glass state. In particular two different disordered arrested states of gel and glass have been obtained respectively for low ($C_w < 2.0\%$) and high ($C_w \geq 2.0\%$) clay concentrations in salt free water conditions.

The arrested state at low concentration is governed by attractive interactions and through DLS and SAXS experiments, supported by numerical simulations, we have found the first experimental evidence of empty liquid and equilibrium gel [1], new concepts formulated for patchy colloids [2] of different shapes, patterns and functionalities.

On the other side the comparison between DLS, dilution and SAXS experiments and theoretical and numerical results have permitted to individuate a high concentration ($C_w \geq 2.0\%$) Wigner glass [3] state, i.e. an arrested state formed by disconnected particles or clusters and stabilized by the electrostatic repulsion. Moreover more recently we have found, through SAXS, XPCS, rheology and numerical experiments, that the attractive interactions are playing a role also in this case and that even in the glassy state the interactions among the colloidal particles are still evolving with waiting time, originating an interesting dichotomic behaviour [4] and a spontaneous glass-glass transition [5]. Two different glassy states are distinguished with increasing waiting time: the system spontaneously evolves from a first glass, dominated by long-range screened Coulombic repulsion (Wigner glass) to a second one, stabilized by orientational attractions (Disconnected House of Cards glass), occurring after a much longer time.

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PROGRESS TOWARDS A PREDICTIVE MODEL FOR SOIL MINERALOGY AND CHEMISTRY IN LOWLAND TROPICAL VOLCANIC ARC LANDSCAPES

Peter Ryan (1,2) *, F. Javier Huertas (2), Lauren Pincus (1,3)

(1) Department, Middlebury College, Middlebury, Vermont 05753 USA, (2) Instituto Andaluz de Ciencias de la Tierra (CSIC-Universidad de Granada), 18100 Armilla, Granada, Spain, (3) School of Forestry and Environmental Studies, Yale University, New Haven, Connecticut 06511 USA

The two main controls on soil composition in the moist tropics are age and climate factors that influence soil moisture and leaching. This is well-exemplified in chronosequences of Holocene to Late Pleistocene uplifted marine terraces, where the effects of time cause alteration of early-stage smectite (ferruginous beidellite) to kaolinite via intermediate interstratified phases (e.g. kaolinite-smectite [K-S]) and halloysite. Cation exchange capacity (CEC) is initially high in smectites from young soil (≤ 8 ka), thendecreases along with loss of layer charge as 2:1 layers are altered to 1:1 layers. Rates have been quantified from a study of three chronosequences (1 ka to 120 ka) of uplifted marine terrace soils on the Pacific coast of Costa Rica. The study locations differ mainly as a function of mean annual precipitation (MAP), ranging from relatively dry (2700 mm/yr, 4 months with < 60 mm rainfall, southern Nicoya Peninsula), to intermediate (3200 mm/yr, 3 months with < 60 mm rainfall, central Pacific Esterillos region), and wet (4250 mm/yr, no months with < 60 mm rainfall, Osa Peninsula). Mean annual temperature (1961-1990) is 25-27 ^{o}C for each chronosequence. Samples of A and B horizons were analyzed for clay mineralogy, CEC, effective CEC (ECEC), bulk mineralogy and chemistry using XRD, FTIR, TEM-AEM and ammonium acetate extraction (1 M NH4OAc, pH=7). Results show that CEC of the clay fraction decreases with increasing soil age, from Holocene soils with pedogenic smectite (CEC 48 to 90 cmolc/kg) to intermediate-stage interstratified K-S (CEC 18 to 45 cmolc/kg) and, finally, to Late Pleistocene halloysite and kaolinite (CEC 2 to 18 cmolc/kg). This mineralogical transition is driven by the leaching of base cations and Si from soil.

Soil weathering reactions and the corresponding drop in CEC occur at a rate at three-to-four times greater in the Inceptisol-Oxisol sequence in the wettest climate (Osa) compared to the drier Esterillos area; in the even drier monsoon climate soils (Nicoya,), this evolved, low-CEC (< 10 cmolc/kg) state does not occur, even after 120 ka of soil formation, and rate is approximately five to ten times slower than at Osa. The dominant exchangeable cation at all sites is Ca. Interlayer K and Al increase relative to Ca over time, resulting in interstratified K-S with smectite layers that become progressively more vermiculite-like and illite-like. The age-related evolution of these moist tropical soils appears to be a predictable sequence in lowland tropical landscapes where periodic tectonism, erosion or volcanism produces unweathered parent material at the land surface. Empirical data from this project has enabled the extrapolation of simple equations that can be tested in tropical arc volcanic landscapes where presence of uplifted marine terrace soils facilitates determination of soil age. The two variables controlling soil composition can be combined into an effective age (age[eff]) that takes into account soil age and weathering intensity (factoring in MAP and wet-dry months from climate data), and equations are of the form, e.g. ECEC = -18.1*ln(age[eff])+77, with an R^2 value of 0.87. Greatest scatter occurs in the youngest soils. Given the apparent prevalence of this sequence and the systematic nature of its reaction progression, these results could be useful for modeling tropical soils.

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HYBRID CLAY-POLYMER NANOCOMPOSITES FOR THE CLARIFICATION OF WATER AND EFFLUENTS

Giora Rytwo (1,2)

(1) Department of Environmental Sciences, Tel Hai College, Upper Galilee, Israel, (2) Environmental Physical Chemistry Laboratory, MIGAL Galilee Research Institute, Kiryat Shmona, Israel

The need for water is increasing in the last decades due to the increase in population and uses. It is obvious that freshwater resources will not be able to meet all requirements and water should not be considered a self-renewable, low cost resource. Thus, the needs for increased amount of water imply adopting several approaches that include (a) intercepting, diverting, storing and transferring water, (b) desalination, (c) water re-use [2]. In all three approaches removal of turbidity and total suspended solids (TSS) is a crucial step, as one of the essential parameters limiting water quality.

The lecture will summarize a series of studies based on the use of clay-polymer nanocomposites, alone or combined with bridging agents for the clarification of water [1-3]. In the case of potable water the process was tested for removal of algae, microbes and other suspended material in surface water, and for the clarification or sea water before desalination. In the water treatment context clay-polymer nanocomposites were used for the clarification of saline industrial effluents, and are commercially in use for almost complete removal of turbidity and suspended solids in several industrial very turbid effluents as dairy industry, wineries, fruit packaging, etc.

Very effective clarification yielding reduction of more than 95% of the turbidity and the suspended solids in several is achieved, with very low sensitivity for conditions: clarification was tested in the range of pH between 3-11, and in temperatures between 5-45 °C, exhibiting efficient results. In some cases even deactivation of microorganisms is observed, even though further research is required to ensure that indeed such treatment could offer an environmentally oriented alternative to chlorination.

The rational beyond the invention is that colloidal suspensions remain stable due to the small size ($<2\ \mu m$), the charge and the density of the colloids. By preparing nanoparticles based on an anchoring denser core (as a clay mineral) to which chains of a polyelectrolyte with charge that opposes the colloidal charges, induces fast formation of neutralized flocs. In such a way all three colloidal stability factors (size, charge and density) are addressed achieving very fast clarification. The size of the flocs might be further increased by the addition of a bridging agent (polymer or low charge nanocomposite), or combining two different polymers bound to the same clay particle, enmeshing several flocs together to very large aggregates. In all cases clarification is obtained in seconds by the formation of 20-500 μm flocs, and their further separation by sedimentation or filtration.

Addition of polymers and clay minerals simultaneously for the treatment of potable water was reported in previous studies. However, the *a-priori* preparation of the nanocomposites and its "aging" for several hours is required to obtain 95-99% turbidity removal in very turbid streams and effluents. *A-priori* preparation of nanocomposites based on montmorillonite or sepiolite and different cationic polymers as poly-DADMAC or chitosan was presented previously in several studies, however in all those studies the role of the nanocomposite was specific adsorption of a *dissolved* pollutant and not the removal of suspended colloids or turbidity.

The good performance observed in a broad range of applications [4,5] is presumably due to the broad versatility that stem from the use of different polymers and clays, and even different clay-polymer rations yielding a wide range of charges. Even though the general rational of the effectivity seems to be explained, and it is ascribed to neutralization accompanied by the formation of large flocs containing a denser anchoring particle, not all the processes are fully understood. For example, sea water requires the use of completely different nanocomposites than industrial non-saline effluents. Thus, additional research is needed to elucidate the influence of those clay-polymer compounds in different water sources.

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MOLECULAR MODELING CALCULATIONS OF SULFONAMIDES ADSORPTION ON PHYLLOSILICATE SURFACES

C. I. Sainz-Díaz (1), M. Francisco-Márquez (2), C. Soriano-Correa (3)

(1) Instituto Andaluz de Ciencias de la Tierra, CSIC-UGR. Av. de las Palmeras 4, 18100 Armilla, Granada, Spain, (2) Instituto Politécnico Nacional-UPIICSA. Té 950, Col. Granjas México, C.P. 08400 México City, México, (3) Química Computacional, FES-Zaragoza, Universidad Nacional Autónoma de México, Iztapalapa, C.P. 09230 México City, México

Sulfamides belong to a great group of antibiotics used for human therapeutics and farm livestock during decades. This intensive use has generated an important environmental risk due to the presence of these compounds in wastewaters and soils close to worldwide farm industries. The molecular structure and physico-chemical properties of these molecules are interesting for evaluating the molecular interactions with surfaces of clay minerals. These interactions are important to know the mobility of these compounds through soils and to design new nanomaterials for drug delivery.

The molecular structure and conformational analysis of the sulfonamides, sulfamethoxypyridazine and sulfamethoxydiazine, as models of sulfonamides, have been studied. These compounds are widely used in therapeutics and represent two families of sulfonamides, sulfonamido-pyrimidines and sulfonamido-pyridazine. This work has been performed by means of quantum mechanical calculations and force fields based on empirical interatomic potentials calculations. All conformers present in the crystal structures of polymorphs of these compounds have been explored at different theoretical levels even at MP2/6-311G** and M06-2X/6-311+G** levels. The adsorption of these drugs on a phyllosilicate surface of (001) plane has been investigated exploring different orientations of the molecules. In all cases explored exothermic processes were obtained for both sulphonamides on the pyrophyllite (001) surface [1]. This result supports the possible application of phyllosilicate as nanocarriers for controlled delivery of drugs.

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FLOCCULATION OF ANISOTROPIC PARTICLES INDUCED BY MODEL POLYELECTROLYTES

Yasine Sakhawoth, Laurent Michot, Pierre Levitz, Natalie Malikova

Sorbonne Universités, UPMC-CNRS, Laboratoire PHENIX, Paris, France

Flocculation is a key process in numerous environmental and industrial technologies [1]. Its optimization relies on understanding the formation and structure of the aggregates forms. There is a clear need to extend the study of flocculation from spherical colloids to anisotropic particles such as the ubiquitous clay colloids (platelets).

We study clay flocculation by ionenes, model cationic polyelectrolytes with a regular charge density, which can be tuned to match/mismatch the clay charge density. We posses extensive knowledge of ionene behaviour in aqueous solutions from SANS and NMR studies [2,3]. Also, we have demonstrated the importance of small angle X-ray scattering (SAXS) in the study of clay flocculation by salts [4,5]. Ionene chains add necessarily complexity to the system, as different conformations on/between the platelets are possible. Moreover, we may expect secondary effects, such as ions-specific effects, to play an interesting role in flocculation of clay-ionene mixtures [2,3,5]. In this study, negative particles used are montmorillonite clays of three different particles sizes.

We suspected that optimal flocculation condition would vary with the charge density of polyelectrolyte and we indeed demonstrated this combining turbidity measurements and zetametry. The linear charge density of available ionenes spanned a range both below and above the average charge separation on the clay particles. For all systems studied (with the exception of the most highly charge ionenes) the onset of optimal flocculation is accompanied by a charge neutralisation of the aggregates, as seen from zetametry. This at first sight indicates a charge neutralisation mechanism responsible for flocculation. However, on our well-defined model system, we see that the onset of optimal flocculation occurs consistently at a ratio of positive and negative charge between ionenes and clay (c+/c-) smaller than 1 (between 0.3-0.8). The aggregates formed are thus highly ionene deficient. Total Organic Carbon measurements confirm that all available ionene is absorbed onto the clay surfaces up to c+/c- ratios significantly higher than the onset of optimal flocculation. In view of these findings we discuss the possible flocculation mechanisms and comment upon the significance of zeta potential measurements and its limits in these systems.

To better understand the structure of clay-ionene aggregates, SAXS measurements were performed. For many of our systems, we observed a correlation peak indicating regular face-to-face stacking of clay particles. This opposes the edge-to-face configuration characteristic of the "house-of-cards" model of clay aggregation [6]. We found that the lower the charge density of ionenes, the higher the interlamellar spacing. Indeed, in our system we suppose thatrod-like structure is observed for the most charged polyelectrolyte whereas loops and tails should be observed for low charge density ionenes and could explain why the interlamellar spacing is higher. These findings will be complemented by our first results of small angle neutron scattering (SANS)under the Zero Average Contrast condition. These allow to match the signal of the clay platelets and thus highlight information about the conformation of ionenes inside the aggregates.

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Mg-Zn-Al LDHS: INFLUENCE OF INTERCALATED ANIONS ON CO_2 REMOVAL FROM NATURAL GAS

Ayat A. A.-E. Sakr (1)*, Tamer Zaki (2), Osama Elgabry (1), Mohamed A. Ebiad (1),
Seham M. El-Sabagh (1), Mostafa M. Emara (3)

(1) Gas Chromatography Department, Analysis & Evaluation Division, Egyptian Petroleum Research Institute, Cairo, 11727, Egypt, (2) Catalysis Department, Petroleum Refining Division, Egyptian Petroleum Research Institute, (3) Faculty of science, Al Azahr University, Cairo, 11651, Egypt
*ayatsakr@yahoo.com, ayatsakr78@gmail.com

Natural gas is considered as cleanest fossil and safe source of energy. It is composed mainly of methane (CH_4). However, in the raw gas steam, other constituents may be present such as CO_2. Carbon dioxide if present in gas stream is considered as diluent as it lowering the heat content of the combusted methane. Also, CO2 can act as an acidic gas if reacted with water in gas stream; consequently, corrosion may occur in the pipelines and equipment. In this consequence; CO_2 should be removed from gas stream. It could be removed by absorption or/and adsorption process (Faramawy et al. (2016)).

One of the adsorbents used is the layered double hydroxide materials. It is an anionic clay type, which consist of metal cations arranged uniformly in staked positively charged layers. The positive charge is compensated by negatively charged anions intercalated in the interlayer space (Cavani et al. (1991)). It is usually used to capture CO_2 at high temperature (Choi et al. (2009)).

In this study, thee components Mg-Zn-Al LDHs were synthesized by microwave assisted homogenous precipitation using urea hydrolysis. The physicochemical properties of the prepared solid were carried out using different techniques such as XRD, FTIR, Elemental analysis, surface characterization measurements, and electron microscope. The results indicate the formation of the layered structure containing the three metals in one phase. By controlling the synthesis condition, carbonates as well as nitrogen containing anions are intercalated within the interlayer space. The type of the nitrogen containing anions depends on the type and concentration of M (II) cation. The nitrogen adsorption -desorption results indicate the presence of type IV isotherm. The surface area decreased with increasing zinc content. However, the high surface area could be related to interparticle agglomeration. The TEM images indicate the presence of nan-particles, its size depending on the concentration of Zn content. The smallest size (~14-25 nm) was detected in Mg-Zn-Al LDH have (Mg : Zn =1:3). The mixed metal amorphous oxide (LDO) phase were obtained after thermal treatment of the as-synthesis LDH at 550 °C.

The ability of the as-synthesized Mg-Zn-Al LDHs and corresponding LDO to capture CO_2 from methane stream was tested using dynamic flow system technique at mild conditions of temperature and pressure. The results indicate that the presence of nitrogen containing anions enhance the adsorption capacity of the LDHs relative to their corresponding oxides.

Keywords: layered double hydroxide, microwave, urea hydrolysis, carbon dioxide, natural gas.

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FRICTION AND COHESION OF PYROPHYLLITE AND MUSCOVITE

Hiroshi Sakuma (1)*, Kenji Kawai (2), Shigeru Suehara (1), Ikuo Katayama (3),
Toshihiro Kogure (2)

(1) National Institute for Materials Science, Tsukuba, 305-0044 Japan, (2) University of Tokyo, 113-0033 Japan, (3) Hiroshima University, 739-8526 Japan
*sakuma.hiroshi@nims.go.jp

Frictional strength of clay minerals is critical on the activity of major creeping faults and landslides. Most clay minerals or phyllosilicates show low friction coefficients relative to other rock-forming minerals in the Earth's crust. The mechanism of the low friction coefficients can be associated with the morphology and layered structure of phyllosilicates. A linear relationship between the interlayer bonding energy (ILBE) of phyllosilicates and friction coefficients of their powders has been discussed to explain the low friction of these minerals [1]. Recent shear measurements [2] and precise theoretical calculations on the ILBE [3], however, showed less relationship between the energy and friction coefficient. While no significant relationship between the friction coefficient and the ILBE was observed, friction between the adjacent layers of phyllosilicates is still a clue for understanding the mechanism of their low friction [4].

Here we conducted the first-principles calculations based on the density functional theory (DFT) for understanding the frictional mechanism between the adjacent layers of pyrophyllite and muscovite. Shear and normal stresses were obtained from the potential energy surface using the method by Zhong and Tománek (1990) [5]. Dispersion interaction was empirically corrected by using the DFT-D2 method [6].

To confirm the reliability of our calculations, the interlayer structures with stable and meta-stable energies calculated for pyrophyllite were compared with the experimental ones observed by high-resolution transmission electron microscopy (HRTEM) [7]. The stable structure reproduced the dominant interlayer structure in pyrophyllite. The meta-stable structure corresponded to a stacking fault found in the HRTEM images. Direct comparison of friction force was performed between the simulations and shear experiments [8] for muscovite. The change of frictional force as a function of sliding direction was consistent between the simulations and experiments. These results indicate that our calculations are reliable to predict the stacking structure and friction of clay minerals.

A large shear stress was required for the sliding between adjacent layers of muscovite rather than those of pyrophyllite. Shear stress (τ) as a function of normal stress (σ_n) for pyrophyllite and muscovite can be described by the equation: $\tau = \mu\sigma_n + c$. Here μ is the angle of internal friction and c is the cohesion. No significant difference was observed for the μ among these minerals, but the cohesion of muscovite was larger than that of pyrophyllite. This is a reason for the large shear stress of muscovite. The cohesion in the friction can be interpreted by the degree of potential barrier along with a sliding direction without load. Therefore the cohesion depends on the sliding direction. The large cohesion of muscovite is ascribed to the presence of interlayer cations which increases the potential barrier along with the sliding directions. We found that potential energy surfaces for various clay minerals is critical for understanding the frictional mechanism of clay minerals.

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COUPLED THCM MODEL OF THE FEBEX *IN SITU* TEST: TESTING, UPDATING AND PREDICTIONS

Javier Samper, Alba Mon*, Luis Montenegro

CICA, Centro de Investigaciones Científicas Avanzadas, Universidade de A Coruña, E.T.S. Ingenieros de Caminos, Canales y Puertos, Campus de Elviña, 15071 A Coruña

The performance assessment of a geological repository for radioactive waste requires the quantification of the evolution of the bentonite engineered barrier. This barrier will be subjected to coupled thermal (T), hydrodynamic (H), mechanical (M) and chemical (C) processes. The FEBEX (Full-scale Engineered Barrier EXperiment) project aimed to study the engineered barrier system designed for sealing and containment of waste in a radioactive waste repository. The FEBEX in situ test included the heating system, the bentonite barrier, the monitoring system and the granitic host rock. The in situ test was performed in Grimsel (Switzerland) and it began in 1997. Heater 1 was switched-off in February 2002 and it was dismantled in September 2002. The test continued to June 2015, where heater 2 was dismantled within FEBEX-DP (Dismantling Project) project.

A coupled THCM 1D axisymmetric model of the in situ test was reported by Zheng el al. (2011). The model accounts for the period from 1997 to 2002. Model results attested the relevance of thermal osmosis and bentonite swelling for the geochemical evolution of the bentonite barrier while chemical osmosis was found to be much less relevant. The THCM model of Zheng el al. (2011) was tested with data collected after the dismantling of heater 1 of the in situ test. The model reproduces reasonably well the measured temperature, relative humidity, water content and inferred geochemical data. However, it fails to mimic the solute concentrations at the heater-bentonite and bentonite-granite interfaces.

The previous model which was constructed with data from 1997 to 2002 has been revised, updated and extended to 2015. Model results have been compared to gravimetric water content data measured after the dismantling of heater 1 in 2002 and heater 2 in 2015 and on line temperature, relative humidity, water content, and pore water pressure in the granitic rock data collected from 2002 to 2015. The model results are within the range of measured data and match the general trend of the data. The limitations, deviations and uncertainties of the previous THCM model have been analysed and overcome by: 1) Extending the previous 1D axisymmetric THCM models to 2D axisymmetric conditions; 2) Improving the numerical implementation of the boundary condition at the heater-bentonite interface; 3) Performing sensitivity analyses to the retention curve, the vapour tortuosity, the thermal conductivity, the permeability, the diffusion coefficient and the kinetic smectite dissolution; and 4) Analysing the back diffusion of solutes from the bentonite into the granite and updating the dispersivities of the bentonite and the granite. Once updated and improved, the THCM model has been used to perform THCM pre-dismantling predictions of the geochemical conditions for the hot and cold sections in June 2015. The predicted concentrations in the hot sections are large near the heater and decrease towards the bentonite-granite interface. The predicted concentrations of Cl^-, dissolved cations and dissolved SO_4^{2-} are generally smaller than those computed in 2002. The predicted pH in 2015 is similar to that in 2002. The concentration of dissolved HCO_3^- in 2015, however, is larger than that computed in 2002 due to the effect of the calcite dissolution front (Samper et al., 2017).

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POLYVINYL ALCOHOL/BENTONITE COMPOSITE HYDROGELS FOR DYES REMOVAL

Laura M. Sanchez, Romina Ollier*, Jimena Gonzalez, Vera Alvarez

Composite Materials Group (CoMP), Institute of Materials Science and Technology (INTEMA), National University of Mar del Plata (UNMdP) - National Research Council (CONICET), Mar del Plata, Argentina

Dye bearing effluents have become an important environmental hazard. In various industrial productions, such as textiles and leather, the dyeing processes are among the most polluting industrial processes because they produce enormous amounts of coloured wastewaters. It has been reported that that more than around 10,000 tons of synthetic dyes are produced every year worldwide. And the estimated amount of dyes discharged in the environment are thought to be 1-2% loss during production, and 1-10% loss during uses [1]. Moreover, in addition to their colour, some of these dyes may degrade to highly toxic and dangerous subproducts.

Hydrogels are three-dimensional polymeric networks capable of imbibing large quantities of water in their structures. Polymer hydrogels have gained attention in many applications due to their unique water absorption along with its retention capacity. However, the use of hydrogels is restricted in some applications because of their poor stability and mechanical properties. Polymer/clay nanocomposite hydrogels have been developed to improve these properties. It is well-known that polymeric nanocomposites reinforced with clays show valuable improvements in their mechanical properties, heat resistance and gas permeability, regarding conventional micro and macrocompounds. This is due to the large contact area between the matrix and the filler [2]. In addition, composite hydrogels that contain clays have shown being useful to do separations in a broader range of work conditions when compared to those needed by the clays themselves [3]. Besides, bentonite is an abundant and low cost smectite-type clay in Argentina.

The general objective of this work is to obtain composite hydrogels suitable to be used as absorbents for the dyes removal. Thus, composite hydrogels will be prepared employing polyvinyl alcohol (PVA) and bentonite as raw materials through a previously optimized physical crosslinking method (through freezing/thawing cycles, a non-toxic and relatively simple method), avoiding the use of potentially damaging components [4-5].

The performance of the resulting nanocomposite hydrogels will be tested to remove methyleneblue, which is a cationic dye. Removal efficiencies and adsorption kinetics will be compared with the respective polymeric matrix and bentonite by themselves.

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QUALITY CONTROL OF COMERCIAL CLAY FACIAL MASKS

Sánchez-Espejo Rita (1), García-Villén Fátima (2), Aguzzi Carola (2), Cerezo Pilar (2), Viseras César (2,3)*

(1) Aguas Termales de Graena, S.A. C/San Antonio, 5, 18517 Cortes y Graena (Granada), Spain, (2) Department of Pharmacy and Pharmaceutical Technology, University of Granada, Campus of Cartuja, s/n, 18071. (Granada), Spain, (3) Andalusian Institute of Earth Sciences, CSIC-University of Granada, Avda. de Las Palmeras 4, 18100 Armilla (Granada), Spain
*cviseras@ugr.es

Cosmetic products are defined as “any substance or mixture intended to be placed in contact with the external parts of the human body (epidermis, hair system, nails, lips and external genital organs) or with the teeth and the mucous membranes of the oral cavity with a view exclusively or mainly to cleaning them, perfuming them, changing their appearance, protecting them, keeping them in good condition or correcting body odours” [1]. Clays are extensively used in the formulation of cosmetics products, both as active ingredients and excipients. Their functional properties lead to their use in several semisolid products, including facial mask, creams, lotions, shampoos and make-up preparations [2]. To be used, clays must comply with a number of requirements [3].

Cosmetics are designed to be placed in contact with external parts of the human body and consequently usually require a consistency suitable for topical application. In particular, semisolid systems used as cosmetics must displayed enough viscosity to remain in contact with the application area at least until their purpose is achieved. Therefore, detail studies on rheological properties are fundamental for these products and viscosity agents are essential cosmetic ingredients.

With these premises, aim of this work was to identify the clay mineral phases in four commercial facial masks (MB, MV, MR and MN) and to determine their rheological properties. X-ray diffraction (XRD) data and chemical analysis (major elements) were used to assess the identity, purity and richness of each sample. XRD analysis was done by using a Philips® X-Pert diffractometer equipped with automatic slit (CuKα, 4-70º 2θ, 6º/min, 40 kV). Major elements were determined by X-ray fluorescence (XRF), using a Bruker® S4 Pioneer equipment, with a Rh X-ray tube (60 kV, 150 mA). Rheological measurements were carried out by a rotational rheometer (Thermo Scientific Haake RV1), in the shear rate range 70-800 s^{-1} and at 25 ºC.

The samples were composed of organic substances (polysorbates, glycerol and derivatives, polysaccharides,…) and inorganic ingredients, including clay minerals. As regards of the minerals, identification results revealed that phyllosilicates and in particular kaolinite were the main mineral component, with other special clay minerals (montmorillonite and stevensite) in minor amounts. In all cases, the studied facial masks showed typical non-Newtonian viscoplastic flow curves with thixotropy, and apparent viscosities adequate for local topical application. Apparent viscosities of the samples were correlated to the presence of smectites (MN>MV>MR>MB).

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SPECIFIC HEATS AND COOLING KINETICS OF SYNTHETIC PELOIDS

Sánchez-Espejo Rita (1), García-Villén Fátima (2), Aguzzi Carola (2), Cerezo Pilar (2), Viseras César (2,3)*

(1) Aguas Termales de Graena, S.A. C/San Antonio, 5, 18517 Cortes y Graena (Granada), Spain, (2) Department of Pharmacy and Pharmaceutical Technology, University of Granada, Campus of Cartuja, s/n, 18071. (Granada), Spain, (3) Andalusian Institute of Earth Sciences, CSIC-University of Granada, Avda. de Las Palmeras 4, 18100 Armilla (Granada), Spain
*cviseras@ugr.es

"Peloids are semisolid natural medicinal products prepared by interposition of organic and/or inorganic solids in mineral medicinal water, that conveniently processes and administered topically locally or in baths, and as a result of a number of biophysical and/or biochemical actions, are used in therapeutics to tread or prevent some pathologies, or to correct their effects in the organism" [1]. Their mechanisms of action are chemical (permeation of ions present in the mud through the skin) and thermal (heat transfer by conduction when its are applied on the surface of the skin) [2,3,4,5]. Therefore, peloids are usually applied at elevated temperature (40-45 ºC) [6] and kept in contact the patient`s skin during time enough to obtain a beneficial therapeutic effect (aprox. 20 minutes). Consequently, to be suitable for thermal therapy, peloids must show low cooling rates and high heat capacities.

With these premises, the aim of this work was to design and develop synthetic peloids with solid phases mainly constituted by clay minerals (pharmaceutical grades kaolinites and smectites from different suppliers) and/or peats (supplied by "Turbera del Agia" S.L., Padul, Granada, Spain). The liquid phase of the designed peloids was in all cases mineral medicinal water from the thermal spring of Graena (Cortes y Graena, Granada, Spain). The relative solid/liquid ratio was maintained to 50/50 w/w. Known amounts of sample were conditioned at 50 ºC in a cylindrical polyethylene terephthalate cell and them immersed in a thermostatic bath at 25 ºC, measuring the cooling of the samples up to 32 ºC, by means of a thermometric probe located in the centre of the cell. Experimental cooling data were fitted by using the Newton law, describing thermal exchange between two bodies in contact at different temperatures. The experimental specific heats, the time required to achieve 32 ºC (temperature of the skin) and the temperature after 20 minutes (minimum typical time of application of peloids) were calculated.

The results were used to evaluate the formulations that optimize the heat transfer between the peloids and the skin in normal application procedures. Clay and clay/peat suspensions showed experimental values of specific heats around 3 J/g K. In all systems, the time required to achieve 32 ºC was greater than 20 min and the temperature after 20 minutes was over 32 ºC. These values were able to assure heat transfer between the systems and the skin in normal application procedures.

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MEDICINAL USE OF CLAYS FROM ANTIQUITY TO THE TWENTY-FIRST CENTURY

Sánchez-Espejo Rita (1), García-Villén Fátima (2), Aguzzi Carola (2), Cerezo Pilar (2), Viseras César (2,3)*

(1) Aguas Termales de Graena, S.A. C/San Antonio, 5, 18517 Cortes y Graena (Granada), Spain, (2) Department of Pharmacy and Pharmaceutical Technology, University of Granada, Campus of Cartuja, s/n, 18071. (Granada), Spain, (3) Andalusian Institute of Earth Sciences, CSIC-University of Granada, Avda. de Las Palmeras 4, 18100 Armilla (Granada), Spain
*cviseras@ugr.es

On behalf of their healing properties, clays appeared in most of ancient Mediterranean/European medical texts, being used to treat both internal and skin pathologies. Nowadays, some of these traditional uses continue in conventional medicinal products in which clays are used as excipients or actives [1,2] and recently as advanced materials with technological uses as nanomatrices and nanocapsules [3,4]. One of the main difficulties in the "archaeomineralogical" study of the medicinal use of clays is the variability during the centuries of mineral names, relying on color, use, location of the deposits or regional areas of use, and so on. In Europe and Mediterranean countries, pharmaceutical ancient historical text of Greek, Roman, Byzantine and Medieval periods include clays as "simples" [5]. Most of "simples" were herbal but also animal parts and minerals. In particular, "Terra sigillata" (Λημνία Γη) or Stamped earth, as well as other clay denominations are included in at least half of the most important historical texts constituting the European materia medica since the "Hippocratic Corpus" (5th-4th century BC) [5]. Clays were mainly used as alexipharmic (antidotes to poison), astringent and desiccative, as well as sudorific and antidiarrhoeal. Their popularity and multiples uses, together with the inherent difficulties to use clays from remote locations resulted in the exploration of alternative types of stamped earths (terra Armenica, terra Florentina, terra Hispanica, terra Lemnia). In mid-eighteenth century, European industrialization changed markedly medical tradition, introducing numerous synthetic substances in therapeutic, at the expense of naturally occurring materials. During XIX century, the presence of clay "simples" in western medicine gradually decreased and at the end of the century only some examples remained in a pharmaceutical encyclopaedia edited in Barcelona and usually with the consideration of obsolete remedies [6]. In the first half of the twentieth century the disappearance of most of the old remedies, the permanence of others and the emergence of new names and uses were confirmed. By mid-century, the major Western pharmacopoeias included clays between the substances used in medicinal products. In the USA pharmacopoeia of 1960 a new clay denomination appeared; "Bentonite". This name came from the location of the clay (Fort Benton, Wyoming, USA). Use of any clay with this designation meant that its composition and properties should be as similar as possible to the American sample. The term "bentonite" was gradually adopted by the British and other European pharmacopoeias and continues being used [2]. Together with "Bentonite", new denominations as "Magnesium trisilicate", "Magnesium aluminum silicate" (or "Aluminium Magnesium silicate", as well as "Attapulgite" were progressively included in pharmacopoeias, being currently considered as pharmaceutical substances [7]. The correspondence with their mineralogical denominations is in some cases difficult, as the names are mainly correlated to properties and uses of the materials in the preparation of medicinal products.

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CONTRASTING DEFORMATION MECHANISMS BETWEEN PLANAR AND FIBROUS PHYLLOSILICATES AT THE MICROSCALE

Catalina Sánchez-Roa (1)*, Blanca Bauluz (2), Fernando Nieto (3), Isabel Abad (1), Juan Jimenéz-Millán (1), Daniel Faulkner (4)

(1) Departamento de Geología and CEACTierra, Unidad Asociada IACT (CSIC-UGR), Universidad de Jaén, Campus Las Lagunillas s/n, 23071 Jaén, Spain, (2) Department of Earth Sciences, Universidad de Zaragoza, Pedro Cerbuna 12, Zaragoza, Spain, (3) Departamento de Mineralogía y Petrología and IACT (CSIC-UGR), Facultad de Ciencias, Universidad de Granada, Avda. Fuentenueva s/n, 18002 Granada, Spain, (4) Rock Deformation Laboratory, Department of Earth, Ocean and Ecological Sciences, University of Liverpool, Liverpool, UK

Active faulting is an important phenomenon triggering chemical and physical processes in the rocks of the fault core and damage zones. Chemical processes involve element mobility and redistribution assisted both by pore fluids and/or fluids running through the faults. Evidence of chemical reactions in these settings includes changes in the mineralogy and elemental-enrichments of the fault gouge. Meanwhile, physical processes mainly involve the accommodation of stress through various modes of deformation that affect the rock fabric and cohesion, and are directly related to earthquake nucleation and propagation.

In this study, we investigate by scanning and transmission electron microscopy (SEM, TEM) naturally- and experimentally-deformed fault gouge samples collected from two main sliding surfaces within the Galera Fault Zone. The two gouges studied have a particular mineral association that includes fibrous clay minerals (sepiolite and palygorskite). In the first mineral assemblage, the fault rock is dominated by smectite with smaller amounts of palygorskite. In the second, the fault rock is dominated by sepiolite (Sánchez-Roa et al., 2016). The aim of the study is to identify the chemical and physical processes taking place within both the fibrous and the platy clay minerals in the samples as a consequence of ongoing deformation.

The microscale deformation mechanisms of smectites and fibrous clay minerals differ significantly. The smectite-rich gouge shows a great number of layer terminations and delamination on the crystals' basal planes that contributes to a distributed mode of deformation in the gouge, possibly resulting in aseismic creep of the fault segment. In contrast, fibre disorientation and the random fabric of the sepiolite-rich gouge result in localised deformation limited to small areas where the needle-like crystals are bent and broken producing "feather-like" structures, without the presence of lattice distortions.

Sepiolite crystals on both naturally- and experimentally-deformed gouges exhibit variability in the (110) d-spacing of sepiolite. This variability suggests the presence of palygorskite polysomes causing polysome width disorder. d-spacings further from the ideal 12.2 Å appear on crystal edges, while values closer to the ideal value appear towards the centre of the fibres. This phenomenon can imply a progressive transformation from sepiolite to palygorskite triggered by a higher Al-input to the system and pore fluid chemistry disequilibrium, as a consequence of exhumation and interaction with the Al-richer wall rock.

Lateral variability of the d-spacing of smectite crystals from 13 Å to 20 Å in the smectite-rich gouge permitted the identification of possible regions of polysomes defined by Krekeler et al. (2005). This lateral change could suggest mineral intergrowth and/or epitaxial transformation between smectite and palygorskite. Furthermore, microanalyses show a progressive and continuous decrease in Mg coupled with an increase in Al+Fe in the octahedral cation content of the sepiolites, palygorskites and smectites in the samples. Therefore, we suggest that in this system palygorskite could be the precursor of smectite.

Deformation mechanisms in planar-expandable and fibrous phyllosilicates are significantly different. Thus, mineral transformations between these two mineral groups, as evidenced in this natural fault, can have important geological implications on fault strength and stability. Furthermore, the presence of these mineral transformations in natural mineral deposits could have important industrial applications for the efficiency of industrial materials, since partial or total transformations between smectites and fibrous clay minerals will drastically change important chemical and physical properties, including surface area and cation exchange capacity.

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IMPLICATIONS OF SEPIOLITE DEHYDRATION FOR EARTHQUAKE NUCLEATION IN THE GALERA FAULT ZONE: A THERMODYNAMIC APPROACH

Catalina Sánchez-Roa (1)*, Olivier Vidal (2), Fernando Nieto (3), Juan Jimenéz-Millán (1), Daniel Faulkner (4)

(1) Departamento de Geología and CEACTierra, Unidad Asociada IACT (CSIC-UGR), Universidad de Jaén, Campus Las Lagunillas s/n, 23071 Jaén, Spain, (2) CNRS, Université Joseph Fourier Grenoble, LGCA, 1381 rue de la piscine, BP 53, 38041 Grenoble Cedex, France, (3) Departamento de Mineralogía y Petrología and IACT (CSIC-UGR), Facultad de Ciencias, Universidad de Granada, Avda. Fuentenueva s/n, 18002 Granada, Spain, (4) Rock Deformation Laboratory, Department of Earth, Ocean and Ecological Sciences, University of Liverpool, Liverpool, UK

A new thermodynamic model for the Mg-phyllosilicate sepiolite was developed and used to calculate its P-T stability conditions and water content for different bulk rock compositions. The standard state thermodynamic properties, entropy (S°) and enthalpy (H°), were initially estimated by oxide summation taking into account the different entropic and enthalpic contributions of the three types of water in sepiolite: zeolitic water, bound water, and structural OH groups. The starting model was then refined with synchrotron XRD data for dehydration of sepiolite and experimental data. The dehydration process follows a step function that allowed us to define end members with decreasing hydration states in a theoretical solid solution.

The stability field of sepiolite is ultimately limited by the reaction sepiolite → talc + quartz + H_2O, which is located at about 325 °C at 1 to 500 MPa. The large stability field of this clay mineral suggests that it could control the mechanical behaviour of crustal faults where it is present and could be stable to 325 °C. The refined model was then applied to the natural case of the Galera Fault Zone (SE Spain) using XRF data of the bulk rock composition of the fault core gouge, which is mainly composed of sepiolite. The dehydration of sepiolite at $T < 300$ °C is modest compared to that occurring during its breakdown, where 62% of water molecules leave the structure to form the association talc + quartz + H_2O; a reaction that also involves a reduction of around 31% of the original solid volume. These significant hydration and volume changes of sepiolite can have important implications on the strength and stability of the Galera Fault and other sepiolite-bearing gouges. In order to estimate the strength changes of the gouge with depth (and hence pressure and temperature), we compare triaxial friction experiments on the sepiolite-rich gouge from the Galera Fault and measurements on a synthetic gouge following breakdown above 325 °C, constructed following the mineral association predicted by the thermodynamic model (93 wt% talc and 7 wt% quartz). The contrasting frictional strength and stability of sepiolite in comparison to talc could be one of the causes of fault instability and earthquake nucleation seen to be concentrated in the upper 10 km of the Galera Fault.

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MULLITE PRODUCED FROM HEATING OF MIXTURES OF ALUMINOSILICATE MINERALS AND ALUMINA RESIDUE

Valmir José da Silva, Geceane Dias, Wherllyson Patrício Gonçalves, Romualdo Rodrigues de Menezes, Gelmires de Araújo Neves, Hélio de Lucena Lira, Lisiane Navarro de Lima Santana*

Academic Unit of Materials Engineering, Federal University of Campina Grande - UFCG, Av. Aprigio Veloso, no 882, Bodocongo, Campina Grande, PB 58109-970, Brazil
*lisiane.navarro@ufcg.edu.br

The use of residue, through studies that are capable to detect its potentialities, is seen today as additional activity that may contribute to preserve natural resources, as well to minimize environmental impact. During the heating of clays different thermal reactions occur and new phases are formed and related to the heating conditions, the chemical composition and the nature of mineral. When aluminosilicate minerals are submitted to temperatures above 1000 ºC, normally the final microstructure contains different forms of mullite crystals and undissolved quartz grains dispersed in the vitreous matrix. The aim of this work is to obtain mullite from aluminosilicates and alumina rich residue, glimpsing the production of refractory ceramic pipes and materials for insulation. The following raw materials were used as precursors: kaolin and bentonite clays and alumina residue. They were submitted to chemical, mineralogical, granulometric and thermal characterizations. To define the content of kaolin, clay and residue in the formulations of ceramics masses, the chemical composition of precursors was calculated based on the stoichiometry of the mullite 3:2 ($Al_2O_3.2SiO_2$). Specimens were prepared by pressing and submitted to thermal treatment using conventional oven at 1100 and 1300 °C, with heating rate of 5 °C/min and dwell time of 60 min. The microstructural analysis by X-ray diffraction (XRD), (scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were carried out and the physical and mechanical properties were measured. By the XRD analysis after the thermal treatment at 1300 °C, the presences of the following phases were evident: quartz, cristobalite, corundum, mullite (major phase) and amorphous phase. The images obtained by SEM reveal elongated crystal in the needle form, typical characteristics of mullite obtained from clay, and grains in round shape typical of corundum. By TEM analysis, to the sintered samples at 1300 °C, it was evident the formation of mullite crystals, whose aspect ratio (length / width) ranged from ~ 8 to ~ 11. With respect to the physical and mechanical properties, it was evident that with the increase in temperature from 1100 to 1300 °C, the mechanical strength of the specimens, for all compositions studied, was increased, and for the compositions containing kaolin the values of this parameter at 1300 °C were higher than obtained with the clays. As for the refractoriness, these showed equivalent Orton pyrometric cone above 36, being considered of high refractoriness.

Keywords: mullite, aluminosilicates, alumina residue.

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CHARACTERIZING THE DIELECTRIC RESPONSE OF COMPACTED FINE-GRAINED SOILS USING IMPEDANCE SPECTROSCOPY

Saranya N.*, Arnepalli D. N.

Department of Civil Engineering, Indian Institute of Technology Madras, Chennai, India
*saranya.nithiyanandan@gmail.com

The geotechnical properties of fine-grained soils are predominantly determined by their electrical diffused double layer (DDL) formed around them upon interaction with the pore-fluid. In the past many empirical and numerical approaches have been proposed to correlate the geotechnical properties such as hydraulic conductivity, compressibility, swelling pressure, etc. in terms of DDL using the concepts of Gouy-Chapman and Stern layer theories [1-9]. In addition, it is also inferred that one of the primary factor that influences the thickness of diffused double layer is the dielectric response of the interacting pore-fluid in the diffused double layer of the soil mass [10,11]. The experimental investigations to quantify the dielectric response of the pore-fluid adsorbed in the Stern and Gouy layers of the compacted soil mass are very limited. In view of this an attempt has been made in this study to quantify the electro-chemical properties such as dielectric response of compacted fine-grained soils using impedance spectroscopy, over a wide range of frequency [12]; further the obtained impedance data of the soil mass was represented using the concepts of equivalent circuit modelling in terms of its resistance, capacitance and inductance [13]. The fitted electrical circuit elements represent the physical significance of the electro-chemical changes that occur within the soil mass due to the change in the pore fluid chemistry [14]. From the fitted equivalent circuit model, the corresponding parallel connected resistance-constant phase elements representing the dielectric response of Stern & Gouy layers has been established. In view of representing broad range of natural soils, the present study has considered high swelling montmorillonite and low swelling kaolinite minerals. The variation in the thickness of diffused double layer of the selected materials upon interaction with different pore-fluids has been assessed based on their measured dielectric response.

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INTERACTION OF MONTMORILLONITE AND PALYGORSKITE WITH STEAM: AN INSIGHT INTO SURFACE ENERGY PROFILES

Binoy Sarkar (1,2,3)*, David L. Bish (2)

(1) Future Industries Institute, University of South Australia, Mawson Lakes, SA 5095, Australia, (2) Department of Geological Sciences, Indiana University, Bloomington, IN 47405, USA, (3) Current address: Department of Animal and Plant Sciences, The University of Sheffield, Sheffield S3 7HF, UK
*binoy.sarkar@unisa.edu.au

Clay minerals are important environmental adsorbents because of their abundance and tremendous variety of uses, including containment of radioactive wastes. However, steam produced in the containment environment during decay of radioactive wastes can irreversibly reduce the osmotic swelling capability of bentonite [1], which is the key mechanism restricting the saturated permeability of the containment barrier. Previous X-ray diffraction, X-ray photoelectron spectroscopy, and nuclear magnetic resonance spectroscopy studies indicated that the crystalline structure of smectite, which is the dominant clay mineral in bentonite, remained unaffected or underwent only subtle changes during steam treatment [2,3]. It has been hypothesized that steam causes release of a small amount of Al^{3+} that would reduce the layer charge of the outermost smectite layer in each floc, making it slightly hydrophobic [2]. Steam may also act at the crystallite edges, causing them to interact with smectite 001 surfaces and flocculate [2]. However, most of these hypotheses are unconfirmed. The current study investigated the surface energy profiles of steam-treated montmorillonite and palygorskite using an inverse gas chromatography surface energy analyser (iGC-SEA). The surface energy analysis was also complemented with N_2-adsorption specific surface area (SSA) and pore size distribution analyses.

Clay minerals (SWy-1 montmorillonite and PFL-1 palygorskite) were treated with steam in a Teflon-lined Parr digestion vessel. Treatments used 4.84 g of clay mineral with 0.34 g of deionised water in a 23 mL Parr vessel, and heating at 200°C for 7 days. The treated and untreated clay mineral samples were characterised by iGC-SEA, and the surface area and pore size distribution were also determined.

The total surface energy as measured by iGC-SEA of palygorskite was greater than montmorillonite both before and after the steam treatment. At fractional surface coverage of 0.04, the untreated palygorskite and montmorillonite recorded 90.2 and 12.4 mJ m^{-2} of total surface energy, respectively. This could be attributed to the difference in the basic layer silicate structures of these clay minerals. The total surface energy of the steam-treated clay minerals was greater than the untreated samples over the entire fractional surface coverage of organic adsorbates (e.g., 140.2 and 112.2 mJ m^{-2} for steam-treated palygorskite and montmorillonite, respectively, at fractional surface coverage of 0.04), and this difference in surface energy for montmorillonite was greater than for palygorskite. As a result of the steam treatment, the SSA decreased by ~26% in montmorillonite and ~13% in palygorskite, which may explain the reduction in total surface energy of the steam-treated clay minerals. Confirming earlier reports [2], the wettability of the clay minerals as measured from humidity controlled iGC-SEA experiments also decreased as a result of the steam treatment, and the effect was more pronounced at higher fractional surface coverage of adsorbates. The changes in wettability were more prominent for steam treated palygorskite than for montmorillonite. The results of this study confirm earlier observations that a steam environment has significant implications for the use of these minerals in radioactive waste containment.

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DESIGN OF ARTIFICIAL FUNCTIONAL SYSTEMS FROM EXFOLIATED 2D OXIDE AND HYDROXIDE NANOSHEETS

Takayoshi Sasaki

International Center for Materials Nanoarchitectonics, National Institute for Materials Science, Tsukuba, 305-0044, Japan
sasaki.takayoshi@nims.go.jp

We have developed a variety of metal oxide and hydroxide nanosheets from appropriate layered compounds as a precursor via inducing their massive swelling and subsequent exfoliation [1,2]. The resulting nanosheets are colloidal 2D nanocrystals, extending laterally up to several tens micrometers. Furthermore, they can be obtained in wide varieties of composition and structure, leading to a range of unique properties. Thus, the nanosheets are useful as a building block to construct "artificial lamellar systems" with a designed nano- to mesoarchitecture through solution-based processes.

The oxide nanosheets can be assembled layer-by-layer into multilayer or superlattice films through sequential adsorption procedure or Langmuir-Blodgett deposition. By selecting appropriate nanosheets, we can design various functionalities, such as superior dielectric and multiferroic properties. On the other hand, simple mixing of oxide and hydroxide nanosheets can spontaneously produce bulk-scale flocculates of unique oxide/hydroxide hybrid structures because they are oppositely charged. We showed that such heteroassembled lamellar composites of reduced graphene oxide (rGO) and transition metal hydroxide nanosheets exhibited superior performances in electrochemical charging/discharging and water electrolysis, showing promise for applications in supercapacitors and electrocatalysts [3,4].

Novel mesoscopic lamellar structures can be realized by inducing enormous hydration-driven swelling of layered metal oxide crystals or organizing exfoliated nanosheets in a diluted suspension under high magnetic field [5]. By controlling an electrolyte concentration, a separation between the oxide layers can be varied from several nm to over 100 nm, which induces a vivid structure color. These mesostructures can be fixed by turning the systems into unique hydrogels, which showed anisotropic optical and mechanical properties.

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STUDY OF Cu-BEARING CLAY MINERALS, FROM CARAJÁS - BRAZIL

Eliana Satiko Mano (1)*, Laurent Caner (2), Sabine Petit (2), Arthur Pinto Chaves (1)

(1) Escola Politécnica - Universidade de São Paulo. Av. Prof. Mello Moraes 2.373 - 05508-900, São Paulo - Brasil, (2) Université de Poitiers, CNRS IC2MP-HydrASA UMR 7285 - Poitiers, France
*elli_mano@hotmail.com

Copper in lateritic ores is associated toiron and/or manganese oxides/hydroxides; to clay minerals and/orto Cu-silicate (chrysocolla) and to Cu-carbonates (malachite and azurite). All these mineralsusually result from the weathering and/or hydrothermal alteration of Cu-sulfides.

The mineral Province of Carajás, northern Brazil, is one of the most important iron oxide, copper and gold ore provinces (IOCG) in the world, often compared to Olympic Dam in Australia. The tropical conditions (high rainfall and temperature) are responsible forthe copper concentrations and secondary minerals formation.

Three samples from the Carajás Province were studied to characterize the Cu-lateritic ore. X-ray diffraction, scanning electron microscopy and Fourier transformed infrared (FTIR) spectroscopy data have shown that Cu is mainly associated to the clay minerals. A DCB (Na-dithionite, Na-tricitrate and Na-bicarbonate solution) treatment revealed that less than 0.1% of Cu is associated to goethite. Unfortunately, goethite represents 40 to 50% of the samples. Nearly 99% of Cu is associated to clay minerals, especially to biotite and secondarily to smectite. Kaolinite was also identified without Cu in its structure.

Keywords: Carajás, IOCG, mineral characterization; Cu-bearing minerals, clay minerals.

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CHLORITE-RICH CLAY ASSOCIATIONS IN INTERBEDDED TUFFS AND MUDSTONES: DIAGENETIC IMPLICATIONS

Roberto A. Scasso (1), Ignacio A. Capelli (1)*, Fernanda Cravero (2), Diego A. Kietzmann (1)

(1) Conicet-IGeBA-FCEN-UBA, Buenos Aires, PC: 1428 Argentina, (2) Conicet-CETMIC, Buenos Aires, PC: 1897Argentina

The Upper Jurassic of two basins in southern South America and the Antarctic Peninsula is characterized by black shale/mudstone-dominated marine successions with interbedded tuff beds milimetric to decimetric thick. Anoxic environment precluded bioturbation and sediment mixing, and favoured organic matter preservation (TOC 2-8%). Some of these successions may form unconventional oil reserves, such as the VacaMuerta Formation, and therefore the study of clay mineralsis critical for the fracking process. As the clay mineral association developed on tuffs is totally diagenetic it may be regarded as a good tracer for the diagenetic grade. It is also remarkably different from the clay mineral association in the background sediments.

Most tuff beds in our case studies (the Ameghino Formation in the Larsen Basin, northeastern Antarctic Peninsula and the VacaMuerta Formation in the Neuquén Basin, western Argentina) are massively replaced by carbonate, chlorite andillite-smectite interlayers (I/S). In the localities selected for this study both units underwent deep burial in the context of high geothermal gradient basins. Chlorite is more abundant than I/S in the tuffs and the opposite is true for the background shales and mudstones.

XRD studies (bulk rock and fraction <2 microns) show similar composition for clays in carbonatized tuffs (early diagenetic carbonatic concretions developed on tuffs) and argilitized tuffs (white/yellow, soft, plastically deformed thin beds). The main clay mineral in the tuffs of the VacaMuerta Fm is Fe-rich chlorite, with variable contribution of interstratified illite-smectite layers (I/S). The I/S have more smectite layers in the tuffs, that are characterized as R1 I/S, in contrast with the R3 I/S in the mudstones. To Max (498-528 °C) from Rock-Eval Pyrolysis indicate the rocks are overmature and were submitted to temperatures about 150 °C (e.g. Peters, 1986).

The tuffs and carbonatized tuffs in the Ameghino Formation also show abundant Fe-rich chlorite, with variable contribution of I/S classified as R1 I/S in contrast with the R3 I/S in most mudstones. The carbonatized tuffs are slightly richer in smectite interlayers, andvitrinite Ro from 0.72 to 1.23 point to diagenetic temperatures from 100 to 120 °C.

The tuffaceous beds in the VacaMuerta and Ameghino Fms. are distal fallout tuffs mostly of siliceous to andesitic composition accumulated in anoxic basins close to a Late Jurassic volcanic arc in the western margin of Gondwana (e.g. Scasso, 2001). Large pumice as well as fine-grained glassy ash, together with the mafic minerals, and sometimes the feldspars and quartz, were replaced by carbonate, clays, pyrite and zeolites. The carbonate precipitated during the early diagenesis forming concretions that precluded later compaction of the beds (e.g. Scasso and Kiessling, 1991). The firstly formed clay mineral phases were probably smectite and a chlorite precursor, coeval with the carbonate precipitation and later transformed into I/S and Fe-rich chlorite during diagenesis. Smectite was transformed to I/S during burial diagenesis and illite interlayers increased substantially.

The clay mineral association in tuffaceous layers is richer in chlorite than the background sediments. The chlorite is entirely diagenetic and may be formed from a metastable precursor (Scasso and Kiessling, 2001) or from smectite transformation during advanced diagenesis (e.g. Foscolos, 1991) favoured by absence of K and limited illitization (Compton, 1991). On the other hand the I/S in the tuffs have more smectite layers than in shales and mudstones, which display poor XRD patterns and may lead to erroneous estimation of the diagenetic grade. A preliminary analysis indicates this may be the result of inherited detritic material in the fraction <2 microns or of the direct precipitation of R3 I/S in shales and mudstones (e.g. Wilson*et al*., 2016).

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BENEFIT OF CLAY IN POLYMER NANOCOMPOSITE FOR BIOMEDICAL ENGENEERING: FROM CLAY PROPERTIES TO POLYMER COMPOSITE PERFORMANCE

Marco Scatto (1)*, Maria Bastianini (2), Michele Sisani (2), Paolo Scopece (1),
Alessandro Patelli (3)

(1) Nadir S.r.l., c/o Campus Scientifico Università Ca' Foscari Venezia, Via Torino 155b, 30172 Mestre (VE), Italy, (2) Prolabin & Tefarm S.r.l., Via dell'Acciaio 9, 06134 Perugia Italy, (3) Department of Physics and Astronomy, Padova University, via Marzolo 8 35122 Padova, Italy

Polymers are key building blocks in the development of smart material for biomedical applications, and a lot of polymers offer unique properties for specific applications. An increased matrix of material options is available through the use of polymer compounds. These compounds can incorporate performance-enhancing fillers, which provide properties considerably different from those of the neat ordinary polymers (e.g., bending stiffness, tensile strength, elongation, torque, biological activity such as antimicrobial properties [1], cell differentiation [2]). In our work we want to demonstrate as the use of synthetic layered double hydroxide (LDH) clays in polymer composites permits to obtain Functional Bionanocomposites with tailor made properties by tuning of morphological and chemical properties of intercalated clay and optimizing processing condition during the compound processing. The LDH/Polymer mixing process is based on melt compounding. This method is a very promising tool, since the modifying of plastic compounds is a custom business and well suited for biomedical application (device, Long-Term Implantable Polymers, Bioresorbable Polymers).

Due to the presence of exchangeable anions in the interlayer regions, LDHs can be used as a host for antimicrobial, antioxidant, antibiotic anions which can be intercalated by ionic exchange process in the metal hydroxide sheets. So the organic guest anions not only improve the compatibility of the inorganic layers with the polymeric matrix, and hence the mechanical, thermal, gas barrier properties of the composite, but also confer to it their typical biological activity. The intercalation of guest anions into LDHs also permits to chemically stabilize them through electrostatic interactions, to physically protect them by the inorganic hydroxide sheets from external harsh conditions (i.e. temperature, oxygen, UV rays and humidity) and to controle the release of the active ingredient with a well known mechanism [3].

Synthetic layered double hydroxide (LDH) clays have attracted particular attention because of their biocompatibility and lack of toxicity and because the chemical composition can be controlled and tuned according to need. For example undesirable trace metals, which are often naturally present in montmorillonite (MMT) clay, can be avoided [4]. Although nanocomposites have been around for a number of years, it has only been recently that researchers discovered the clay purification requirements for maximizing the performance of these compounds. This is due to the high levels of amorphous silica present in clays; the silica substantially degrades the impact and elongation properties of the composite and also increases the haze in film.

The true value of nanocomposites in medical applications is only beginning to be discovered.

A very interesting approach for the production of Bionanocomposite is used in our H2020 Project - FAST "Functionally Graded Additive Manufacturing Scaffolds by Hybrid Manufacturing" (NMP07, GA n. 685825), where processing parameters during Melt Compounding in Twin Screw Extruder, preparation method, feed composition, clay morphology, clay intercalation process were properly modulated until obtaining polymer clay Bionanocomposite with mechanical, reological, and biological properties useful for the preparation of scaffold prototypes for the bone regeneration using a 3D printer device (Bioscaffolder).

In this work the so obtained Bionanocomposite with intercalated/exfoliated morphology will be presented together with results in the tuneable controlled release of antibiotic. The correlation between the morphological properties of LDH intercalated with antibiotic molecules, and the twin screw extrusion processing parameters will be also analyzed and presented.

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INFLUENCES OF THE RECYCLING OF BENTONITE BONDED MOULDING SAND STUDIED BY NEUTRON RADIOGRAPHY

Korbinian Schiebel (1)*, Guntram Jordan (1), Anders Kaestner (2), Burkhard Schillinger (3)

(1) Department für Geo- und Umweltwissenschaften, Munich, 80333, Germany, (2) Spallation Neutron Source Division, Paul Scherrer Institute, Villigen, 5232, Switzerland, (3) Research Neutron Source Heinz Maier-Leibnitz, Garching, 85748, Germany
*Korbinian.Schiebel@lrz.uni-muenchen.de

Bentonite bonded sand is the most commonly used mould material in foundry industries. The mechanical properties of bentonite bonded sand moulds strongly depend on temperature, moisture, and mineralogical composition of the bentonite [1]. During casting, a temperature gradient is introduced into the sand mould. Sand layers next to the mould cavity dehydrate. Steam diffuses into colder mould regions and condensates. The emerging inhomogeneous water and temperature distribution leads to zones of different mechanical properties, notably of different tensile strength [2].

After casting, the sand is retrieved, remoistened, and reused. However, reusability is limited. Statistically, moulding sand is recycled 20 times before removed from the casting process. Bentonites alter at temperatures of 500-750 °C. OH-groups are released from smectites. The bonding capacity decreases [3]. Furthermore, bentonites treated with steam significantly loose swelling capacity [4].

To investigate the effects of temperature driven alteration and cyclical use on the tensile strength of moulding sand, tensile tests were conducted on pre-treated sands. Before applying load, the specimens were heated from above. By heating a temperature and moisture gradient is induced into the specimens that is comparable to the casting conditions. The water kinematics during heating and the location of rupture were imaged by neutron radiography series, which were performed at the imaging facility ICON [5] and ANTAES [6]. After image correction, the local water content was calculated using Beer-Lambert law.

Two series were performed. In the first experimental series, the influence of recycling cycles on the water kinematics and tensile strength were investigated. Therefore, moulding sand (8 wt.% Na-bentonite, 92 wt.% quartz) was dried (120 °C) and moistened (3 wt.% H_2O) several times (1, 13, 21, 25) before tensile testing. In the second series, sand from the same lot had been heat-treated (120, 225, 330, 435, 540, 645, 750 °C) for 24 hours. Afterwards, the altered sand was moistened (3 wt.% H_2O) and the heated tensile tests were conducted.

Both, tensile strength and transport properties did not significantly change when the sand is exposed several times to 120 °C. However, sands treated with temperatures above 500 °C show a significant decrease in tensile strength and a strong increase in drying rate. These results indicate that the exposure temperature is much more relevant for the properties of bentonite bonded moulding sand than the number of recycling cycles.

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LOW TEMPERATURE CAPTURE AND RELEASE OF FLUORINE DURING BRICK MANUFACTURING

Éva Schimek (1)*, Tamás G. Weiszburg (1), Imre P. Varga (2)

(1) Department of Mineralogy, Eötvös Loránd University, 1117, Budapest, Hungary, (2) Department of Analytical Chemistry, Eötvös Loránd University, 1117, Budapest, Hungary
*schimek.eva@gmail.com

The origin and the dynamics of fluorine emission caused by the brick industry have been investigated intensively during the last decade in Europe.

We studied the raw material from a brickyard where, unlike in other Hungarian brick works, fluorine emission had been above the threshold limit before a fluorine absorber unit was installed years ago. Our previous results indicate that local geological factors (e.g. volcanic activity during the deposition of clay) may result in elevated fluorine concentration in the clay which caused the high emissions.

We found that the final brick products, fired at a temperature around 950-1000 °C still contain a substantial amount of fluorine in form of fluorite (CaF_2) grains of several ten micrometres in diameter, indicating that the expected primary cause, the high temperature (> 550-600 °C) fluoride release, caused by the dehydroxilation process of clay minerals (OH^- and F^- release) may have only limited contribution to the elevated fluoride content of the combustion gases.

It is known [1], that during brick manufacturing in industrial tunnel kilns, where water vapour - in contrast to the laboratory kiln experiments - is present, fluorine emission starts at temperatures around 400 °C, far below the start of dehydroxilation in clay minerals. We assume that this lower temperature fluorine release may be responsible for the bulk of the emitted/filtered fluoride content of the gases in the case of the brick factory studied.

In this work the raw material was fired in dry and wet atmospheres at different temperatures in the 300-600 °C range in order to collect data on the low temperature behaviour of fluorine and the influence of water vapour on the emission. We tested also the fixation possibilities of fluorine generated by low temperature wet firing.

The determination of the fluoride content was made using ion-selective electrode technique and the mineralogical composition was analysed by SEM and XRD.

Additional to that low-end temperature study we run systematic tests on how the yield of the alkaline fusion applied as preparatory step in ion-selective electrode technique depends on the used temperature. Since this could affect the accuracy of the measurements a series of experiments were carried out in which we used different firing temperatures and time spans during the fusion.

Our goal is to propose a realistic technological change for the brick factory in order to lower the fluorine emission levels with the enhancement of the retained amount of fluorine.

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THERMAL RESPONSE OF SMECTITE TO THE 2011 TOHOKU EARTHQUAKE IN THE SHALLOW PORTION OF THE JAPAN TRENCH

Schleicher Anja M. (1)*, Boles Austin (2), Van der Pluijm Ben (2)

(1) Helmholtz-Center Potsdam, GFZ German Research Center for Geosciences, Potsdam, Germany, (2) Department of Earth and Environmental Sciences, University of Michigan, Ann Arbor, USA

The hydration behavior of smectite during brief and protracted heating intervals can give critical information about the temperature history of a fault during seismogenic slip and creep. Pelagic-sourced smectite is the most abundant clay mineral that is incorporated into the slip zone drilled during JFAST (Japan Trench Fast Drilling Project) Expedition 343 in the Japan Trench, located at ~820 mbsf. Core samples have been taken to characterize clay minerals in fault rocks of an active plate-boundary fault that produced a displacement of ~50 meters during the Tohoku earthquake of 2011. Sudden slip was postulated to have quickly generated high local heat, with temperatures in a narrow slip zone increasing briefly, as proposed by Fulton et al. [1]. Assuming a slip duration of 50 s and a slip zone thickness <1 mm, they proposed a maximum peak temperature within the slip zone as high as 1250 °C, combined with a very low coefficient of friction of 0.08. In order to analyze the swelling capacity of smectite during brief (2-5 min) and protracted (5 hours) temperature changes, we heated samples in intervals of 25 °C from 25 to 225 °C at different rates, using a temperature stage attached to an X-ray diffractometer [2].

Discrete smectite and illite are the most abundant clay mineral types detected in the core by X-ray diffractometry. The smallest clay size fractions 0.05-0.5 microns show pure smectite with a characteristic interlayer distance of 1.2 nm that increases to 1.7 nm after ethylene glycolyzation, indicating up to 3 water layers. Chemical compositions of the clay size fraction (<2 micron) analyzed by ICP-OES show a significant amount of Fe, and lesser Mg and K in these smectite minerals that are pelagic in origin. We observe that (i) both slow and fast heating causes reduction of water interlayers in smectite between 50-200 °C, with a delay of water-release during quick heating at temperatures up to 150 °C, (ii) smectite recovers more quickly to the original hydration state after brief heating than protracted heating between 50-150 °C, and (iii) non-recoverable collapse of all smectite occurs at temperatures >200 °C, regardless of the heating rate. Based on these results, we conclude that frictional heating cannot exceed a temperature of 225 °C when smectitic clays are present in the fault gouge. With water available at depth and temperatures less than 200 °C, swelling properties of smectite-rich fault rock are preserved. The occurrence here indicates that shear heating at the sampled site of the Tohoku earthquake was relatively low.

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THE DEVELOPMENT OF SLICKENLINED SPOTS IN CLAY-RICH MUDROCK OF THE NANKAI TROUGH ACCRETIONARY PRISM, JAPAN

Ana Crespo-Blanc (1), Anja M. Schleicher (2)*

(1) Departamento de Geodinamica-IACT, Universidad de Granada-CSIC, Granada, Spain, (2) Helmholtz-Center Potsdam, GFZ German Research Center for Geosciences, Potsdam, Germany

Clay minerals are common in the sediments of the Kumano basin and the underlying accretionary prism of the Nankai Trough, Japan, discovered during phases one to three of the NanTroSEIZE (Nankai Trough Seismogenic Zone Experiment) drilling project, which is part of the International Ocean Discovery Program (IODP). During Expedition 348, a riser hole (C0002N/C0002P) was drilled down to 3059 mbsf (meters below surface) into the accretionary prism. Cuttings have been taken throughout the borehole, whereas core was recovered between 1663 and 1712 mbsf. The bulk rock mineralogy determined on board the drillship shows abundant illite and smectite as well as minor chlorite/kaolinite, which makes this site an excellent setting to study the properties of clay minerals in marine sediments of a subduction system, by comparing their role in fluid-rock interaction and faulting in the accretionary prism.

Cuttings from both the 1-4 mm and >4 mm size fractions were investigated, showing abundant slickenlined surfaces and deformation bands together with very few carbonate veins throughout the section from 1045.5 to 3058.5 mbsf. A scaly fabric is increasingly observed below approximately 2400 mbsf. Some clay-rich cuttings and core pieces were selected at different depths for specific SEM-EDS analysis, in order to investigate the development of the slickenlines in more detail. Two end-members of the slickenlined surface types were observed: (i) isolated smooth and uniform planes between 20 and 50 microns long, formed in single grains of smectite clay with marked lineation and frequently jagged boundaries, and (ii) microfaults (longer than 100 microns) with sharp boundaries to the undeformed rock, formed by aggregates of illite and smectite and with well-developed lineation. The transition between these two end-member types show isolated planes that draw a single plane with subparallel lineations. The orientation of the slickenlines seem to be coherent with that observed in an array of conjugated faults, which means all the slickenlines belong to the same plane, in turn sub-perpendicular to the intersection of the conjugated planes. These observations suggest that the slickenlined surfaces initiated along single grains of smectite. With increasing deformation, the planes coherently connected until the formation of a mature slickenline surface (microfault). The described geometry was observed at all depths and the same process of formation seem to be valid for the entire drilled section of the Nankai accretionary prism.

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MOLECULAR MECHANISM OF DISSOLUTION, GROWTH AND ION UPTAKE OF CLAY MINERALS AT THE MINERAL/WATER INTERFACE

René Schliemann (1)*, Inna Kurganskaya (1), Sergey V. Churakov (1,2)

(1) Institute of Geology - University Bern, Bern, 3012, Switzerland, (2) Paul Scherrer Institute, Villigen PSI

Due to the high sorption capacity, clay minerals and clay rich rocks are widely used as backfill material in disposal sites to protect the environment from toxic waste, heavy metal contaminants and radionuclides. The interplay between adsorption and desorption, crystal growth and dissolution and changes in pore water chemistry is of key importance for the prediction of the pollutants transport and retention in geochemical environment over time. Atomistic simulations can help to obtain a deeper understanding of the underlying mechanisms and their respective time scales. Several aspects of the uptake processes have been investigated. Nevertheless, a complete and consistent description of those has not been achieved yet, especially when it comes to the uptake of surface complexing ions. While the exchange reaction of interlayer cations or the adsorption at the basal planes is well understood (Rotenberg et al., 2009) and can be related to hydration energy of the cation, the sorption process on the edge sites is on the other hand quite complex (Churakov & Daehn 2012). The latter is known to be pH dependent, which results from different protonation states of the surface oxygen sites that change the surface affinity towards adsorbed ions. Furthermore, the dissolution and growth of clay platelets at the edge sites most likely modify the surface topography and the availability of sorption sites (Kurganskaya & Luttge, 2013). These processes are responsible for a durable entrapment of contaminants since they involve direct structural incorporation of hazardous ions.

In this study, we investigate the molecular mechanism of clay mineral dissolution at edge sites by ab initio molecular dynamics simulations based on density functional theory. We use the Metadynamics (MtD) approach (Laio & Parrinello 2002) to obtain activation energies for subsequent detachment/attachment of mineral building tetrahedral and octahedral ions at the edge sites. Initial simulations are performed for pyrophyllite which represents a reference model for an uncharged phyllosilicate (TOT structure type). The most stable (110) edge surface was studied first. The system size and the amount of water between the edge surfaces was chosen to minimize the interaction between opposite surfaces and to maintain the water density in the middle of the water slit pore close to 1 g/cm^3. Coordination numbers for different atomic pairs were used as collective variables (CV) for the MtD.

The preliminary simulation results in pH neutral water show that dissolution of the silicon tetrahedron, forming a structural step at the edge, is going through at least three steps by breaking all three oxygen bridges to neighbouring Si-tetrahedrons (Si(t)) and one Al-octahedron (Al(o)). Plotting the free energy surface with CVs as coordinates shows a global minimum that is the initial state and local minima corresponding to the dissolution steps. Activation energies were obtained through the minimum energy pathways between these two types of minima. The information regarding the mechanisms and energies has extreme importance for the parametrisation of the kinetic Monte Carlo (KMC) models of dissolution, growth and surface adsorption. Based on the previous KMC approach (Kurganskaya & Luttge 2013), we are developing a model of montmorillonite particle dissolution and growth as a function of saturation state. In this study, we demonstrate the influence of the activation energies for Mg-O-Si and Al-O-Si bond breaking on the step edge morphology. The corresponding parameter sensitivity study will be further followed by a new ab-initio based parameterization approach, where the above mentioned molecular models incorporating interface water structure and lattice size influence are adopted.

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STATISTICAL ANALYSIS OF CHLORITE COMPOSITIONAL DATA IN CRETACEOUS SEDIMENTS OF THE MAGALLANES BASIN, CHILE

Susanne Th. Schmidt (1)*, Solveig Pospiech (2), Annette Süssenberger (1)

(1) Department of Earth Sciences, University of Geneva, Geneva, Switzerland, (2) Geoscience Centre, University of Göttingen, Göttingen, Germany

Chlorites of three different stratigraphic formations and two lithologies (metapelite, sandstone) were analyzed in order to establish correlations between chlorite chemistry and lithology, stratigraphic units and metamorphic degree. The chlorites originate from the Cretaceous, dominantly metapelitic, deep-marine Zapata, Punta Barrosa and Cerro Toro formations in Patagonia (Chile, 51°S) which were deposited in the Magallanes foreland basin. The thermal evolution of the Magallanes Basin is characterized by a complex pattern of diagenetic, anchizonal and epizonal overprints related to burial, deformational thrusting and contact metamorphic events [1].

The chemical composition of the chlorites (N>1100) from a total of 28 samples was determined by microprobe analysis. Linear discriminant analysis (LDA) was applied to all chlorite measurements in order to determine which element ratios discriminate between the different groups. Prior to statistical analysis the concentrations of elements were transformed into logratios (ilr) in order to avoid spurious correlations in the compositional data.

The statistical analysis reveals (1) that the three formations can be discriminated best by their Mn/Fe ratio in chlorites, but also by the Mn/Si, Mn/Al and Mn/Mg ratios. Other elements such as Na, Ca, K, Ti occurring only in minor quantities are negligible. (2) No change in chlorite chemistry between metapelites and sandstones within the same formation can be observed. (3) Chlorites of epizonal conditions show a feeble tendency of higher Mg, Fe and Al concentration in respect to Ca and Si when compared to anchizonal chlorites.

Chlorites of the Punta Barrosa Formation show an average Mn/Fe ratio of 0.026 compared to 0.011 for chlorites of the Cerro Toro Formation. Chlorites originating from the Zapata Formation display a value of 0.005. The observed discrimination potential of the Mn/Fe ratio was compared and correlates with the Mn/Fe ratio of whole rock X-ray fluorescence analysis data.

The particularly high Mn content of the Punta Barrosa Formation may be explained by higher bottom water O_2 levels during deposition and early diagenesis compared to the Cerro Toro and Zapata formations. Interestingly, different metamorphic conditions from diagenesis up to greenschist facies do not change this trend. Equilibration and recrystallization processes in chlorites associated with thermal events apparently affect only the temperature-dependent Si/Al and Fe/(Fe+Mg) ratios, but not the Mn/Fe ratio. Therefore, the Mn/Fe ratio in chlorites may serve as an additional robust parameter for the discrimination of stratigraphical formations.

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MINERALOGY OF DIAGENETICALLY FORMED IRON SULFIDE CONCRETIONS IN ARCTIC GAS HYDRATE SEDIMENTS: ARE CLAYS THE SOURCE OF IRON?

Jasmin Schoenenberger (1)*, Jochen Knies (1,2), Karl Fabian (1)

(1) Geological Survey of Norway, NO-7491 Trondheim, Norway, (2) CAGE - Centre for Arctic Gas Hydrate, Environment and Climate; Department of Geosciences, UiT The Arctic University of Norway, NO-9037 Tromsø, Norway

Arctic gas hydrate reservoirs are threatened by global warming. Observations of extensive methane venting to the hydrosphere and atmosphere off Svalbard and Siberia raised speculations that rising temperatures in the Arctic could cause destabilization of hydrates. Increased methane release to the atmosphere may contribute to accelerated global warming. To understand the process of methane leakage as well as to locate new methane hydrate occurences, sediment samples were studied from the Yermak Plateau, NW Svalbard (Ocean Drilling Program Sites 910 and 911).

Rock magnetic properties identify high amounts of post-sedimentary formed iron-sulfide concentrations potentially associated with episodic impregnation of ascending methane towards the seafloor.

Preliminary XRDP analyses were performed on both iron sulfide concretions and their sedimentary host rocks. Rietveld quantification indicates the following compositions:

Sedimentary host rock	*Iron sulfide nodules*
quartz (~36 wt%)	goethite (~20 wt%)
K-feldspar (~13 wt%)	lepidocrocite (~18 wt%)
plagioclase (18 wt%)	greigite (~29 wt%)
chlorite (~12 wt%)	sulfur alpha (~23 wt%)
mixed-layered illite-smectite (~21 wt%)	quartz and (Fe-)kaolinite (each ~5 wt%)

The occurrence of *greigite* can be associated with anaerobic oxidation of methane or with the formation of gas hydrates. It forms under more reducing conditions than pyrite [1,2], and its preservation requires a delicate balance between (hydro)carbon, sulfide and reactive iron.

A partial aim of this study is to shed light on the sources of sulfur and particularly *iron*. Sulfur as H_2S most likely resulted from CH_4-driven sulfate reduction [3]. Iron could have been leached from iron oxides in the host sediments. However, XRDP results confirmed their absence and rather indicate chlorite as the only Fe-bearing mineral phase. Under acidic conditions, Fe^{2+} (and Mg^{2+}) can be leached from chlorite and the released ions could have been transported as organic chelates [4].

Further studies (SEM combined with EDS, microscopy) are necessary to confirm this assumption so that the complete formation process as well as the significance of associated clay minerals can be understood.

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STABILITY OF TETRABUTYLPHOSPHONIUM BEIDELLITE ORGANOCLAY - DFT AND EXPERIMENTAL STUDY

Eva Scholtzová (1)*, Ľuboš Jankovič (1), Daniel Tunega (2)

(1) Institute of Inorganic Chemistry of Slovak Academy of Sciences, Dúbravská cesta 9, 845 36 Bratislava, Slovakia, (2) Universität für Bodenkultur, Institut für Bodenforschung, Peter-Jordan-Strasse 82, Wien A-1190, Austria
*eva.scholtzova@savba.sk

Modification of clay minerals by organic cations is a subject of a great interest because of possibility to develop new materials with specific properties for new technological applications e.g. polymer-clay nanocomposites, active sorbents, drug release retardation from biocomposite hydrogels, storage of radioactive waste, reinforcement of anti-microbial paper packaging improving its tensile strength, etc. In a recent time, closer attention is also paid to phosphonium-based organic cations that could be used to prepare organoclays with improved properties and higher stability than organoclays prepared with conventional alkylammonium cations [1,2].

This work reports experimental and modeling study of organoclays prepared from tetra-alkylphoshonium cations and beidellite (Bd). Beidellite is aluminosilicate smectite with predominant cation substitutions in tetrahedral sheet, in contrast to frequently used smectite montmorillonite (Mt), in which octahedral substitutions prevail. This leads to a different charge distribution in layer that can improve a stability of prepared organoclays from beidellite. Tetrabutylphosphonium-beidellite (TBP-Bd) organoclay was synthetized by intercalation of the organic cation into the purified sodium beidellite form and was characterized by X-ray Diffraction (XRD), Differential scanning calorimetry (DSC), and Fourier transform infrared spectroscopy (FTIR) methods. Observed main thermal decomposition peak at 444 °C uncovered the enhanced thermal characteristic of this unique TBP-Bd in comparison to TBP-Mt organoclay. Infrared spectra exhibited typical beidellite vibrations at 417, 474, 534, 1041, and 3658 cm^{-1} assigned to the vibrations of beidellite structure whereas the bands at 2962 and 2872 cm^{-1} were assigned to the C-H stretching vibrations of the organic cation.

Further, density functional theory (DFT) method was employed to study a stability and detailed structure of beidellite intercalated with tetrabutylphosphonium cation. The eight models with different mutual positions of TBP cation and Al/Si substitution in the tetrahedral sheet were proposed for this study. The calculated intercalation energies showed a much better stability of all TBP-Bd models in comparison to the TBP-Mt model. The lowest calculated intercalation energy of the TBP-Bd (-96.5 kJ/mol) was ~25% higher (in absolute value) than for the TBP-Mt (-72.2 kJ/mol, [2]). The predicted higher stability of the TBP-Bd organoclays is in accord with experiment.

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K-Ar AGE DETERMINATIONS ON THE CLAY SIZE FINE FRACTIONS OF ILLITE "CRYSTALLINITY" INDEX STANDARD (CIS) SAMPLES

Anna Christine Schomberg (1), Klaus Wemmer (1), Laurence N. Warr (2)*, Georg Grathoff (2)

(1) Georg-August University, Göttingen, Germany, (2) University of Greifswald, Germany
anna.schomberg@posteo.de

Eight clay mineral "Crystallinity" Index Standards (CIS) [1] from the Palaeozoic rocks of southwest England were investigated systematically for the first time in five sub-fractions per sample. Together with illite "crystallinity" data measured by the Kübler Index (KI), a detailed determination of the mineralogical and illite polytype composition, K-Ar ages and extrapolated ages were performed. Grain size separation was carried out by the combined Atterberg-centrifuge method and results were monitored by laser particle sizer and SEM images. CIS calibrated KI values were used to determine the regional metamorphic grade of the samples applying the the Kübler-equivalent [2] anchizonal boundary limits of Warr & Mählmann (2015) [3]. Our results are consistent with previous studies, exhibiting a range of grades from diagenetic to epizonal values for samples SW1 to SW7. Illite polytype compositions also conform to that expected from the KI data with diagenetic and anchizone samples (SW1-SW5) containing mixtures of 1M (largely 1Md) and epizone rocks(SW6-SW7) with only the $2M_1$ polytype. The K-Ar age values for the diagenetic and anchizonal samples of the Upper Carboniferous rocks of the Culm Basin show a strong trend of becoming younger with decreasing grain size. Following the procedures of illite age analysis documented by Grathoff & Moore (1996) [4] and Pluijm et al. (2001) [5], the extrapolated 1M illite ages for two of these samples yield Permo-Triassic (ca. 233-265 Ma) ages indicating prolonged neocrystallization of the illite probably related to early Mesozoic hydrothermal fluid events. The origin of the detrital component in the Upper Carboniferous samples was probably derived from Lower sequences Palaeozoic rocks in the north. In contrast, the epizonal grade samples, SW6 and SW7, from the Tintagel High-Strain Zone (THSZ), that reached the highest grade of metamorphism in southwest England [5], do not show significant differences between the grain-sizes and yield Permian ages of 268-294±7 Ma and 273-282±5 Ma. These ages match previous whole rock K-Ar ages, recalculated from Dodson & Rex (1971) [6]. As these rocks reached temperatures in excess of 350 °C and there is no indication of detrital age contamination of the size fraction separated, the ages of the$2M_1$ polytype are considered to represent cooling ages that post-date the peak of metamorphism. However, the possibility of are juvenating event influencing the smallest fine fractions cannot be excluded, especially as the< 0.2 µm SW6sampleyieldsa young age of 268±6 Ma, which is equivalent to the proposed age of authigenic 1M illite formed in the Upper Carboniferous Culm rocks. In contrast, the K-Ar values of upper anchizonal Devonian slates (SW3-2012 and SW4)to the south of the THSZ show again larger age ranges between the finer and coarser grain size fractions (286-339±5 Ma and 308-349±7 Ma), similar to that recorded in the Upper Carboniferous anchizone grade rocks sampled to the north of the THSZ. Here, the age of the authigenic1M illite also indicates Late Carboniferous/Early Permian or younger events. These ages are significantly younger than those previously interpreted from published whole rock K-Ar and Ar-Ar ages [7].

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MONTMORILLONITE NANODEVICES AS FUNCTIONAL DRUG DELIVERY SYSTEMS

Luciana Sciascia (1)*, Filippo Parisi (2), Giuseppe Lazzara (2), Marcello Merli (1), Stefana Milioto (2), Alessandro Pavese (3)

(1) Dipartimento di Scienze della Terra e del Mare, Palermo, Italy, (2) Dipartimento di Fisica e Chimica, Palermo, Italy, (3) Dipartimento di Scienze della Terra, Torino, Italy

The topic of drug administration captures the interest of many scientists and engages them in solving the cogent problem of either over-dosing or under-dosing windows. Considerable efforts have therefore been devoted to the design of appropriate drug delivery systems (DDS) aimed at improving the efficiency and the safety of the product. In this context, montmorillonite (Mt), attracted a great deal of attention because of its noteworthy properties including large specific surface area, good adsorption ability, cations exchange capacity, adhesive ability, and drug-carrying and releasing capability.

In the present work the potential applicability of Mt, and surfactant-modified Mt as delivery systems for two different class of drugs, namely the antibiotic metronidazole (MNE) and the cinnamic acid (CA) were evaluated.

The pharmacokinetic profile of the conventional tablet of both drugs indicates the requirement of effective strategies for the administration of drug, aiming at minimizing secondary effects, increasing drug bioavailability and stability or even exhibiting high accuracy in reaching the target has become significant.

In this perspective a series of drug/clay hybrids were prepared by varying the pH and the amount of loaded drug. Complementary kinetic and equilibrium studies were carried out in order to elucidate the adsorption mechanism and to establish the nature of the interactions involved. Moreover the interactions sites of the clay surface were proposed on the bases of the XRD results.

Very useful information was obtained by the in vitro release studies, and from the comparison with the commercial formulation of the drug, which reveal not only that the new-tailor made formulation could be fruitful exploited for successfully prolonged the action of drug in the target site but the use of these nanodevices reduce both time and costs for the drug delivery.

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PREPARATION OF CROSS-LINKED CHITOSAN HYDROGEL AS A DRUG DELIVERY CARRIER OF PODOPHYLLOTOXIN

Soheila Sedaghat*, Mona Eslami

Department of Chemistry, Islamic Azad University, North Tehran Branch, Tehran, Iran
*s_sedaghat@iau-tnb.ac.ir

In biological fluids, drug delivery systems can reduce side effects of toxins and create an appropriate concentration of drug at the treatment site. Chitosan hydrogel have become a potential drug delivery systems for carriers of bioactive compounds. Biodegradable and biocompatibility of chitosan have been interested in preparation of carrier systems. Chitosan film was prepared by solvent casting method and evaluated them in terms of uniformity, swelling rate and disintegration time, it was used as a drug delivery system of podophyllotoxin. The drug release rate follows the first order model. Converting chitosan to co-polymer chitosan-acrylamide improves drug delivery rate and provides the opportunity to use it. We prepared chitosan, montmorillonite (MMT) nanocomposite as a natural- based nanocomposite film. It was made by mixing of two different concentration of clay particles suspension in a chitosan solution. The preparation of organo-montmorillonite removed trapped water molecules from the montmorillonite, and formed composite film without bubble, as shown by the DSC analysis.

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ON THE OCCURRENCE AND ORIGIN OF EOGENETIC Fe-Mn NODULES IN THE POST-WÜRMIAN ALPINE SEDIMENTS OF GENEVA BASIN, WESTERN SWITZERLAND

Branimir Šegvić (1)*, Stéphanie Girardclos (2, 3), Giovanni Zanoni (1), Carlos Arbiol González (5), Tara Steimer-Herbet (4), Marie Besse (4)

(1) Department of Geosciences, Texas Tech University, Lubbock TX 79409, USA, (2) Department of Earth Sciences, University of Geneva, 1205 Genève, Switzerland, (3) Institute for Environmental Sciences, University of Geneva, 1205 Genève, Switzerland, (4) Laboratory of Prehistoric Archaeology and Anthropology, Department F.-A. Forel for Environmental and Aquatic Sciences, University of Geneva, 1211 Genève 4, Switzerland, (5) Department of Earth Sciences, Memorial University of Newfoundland, St. John's NL A1B 3X9, Canada
*branimir.segvic@ttu.edu

The soils and surface sediments of Geneva basin located in western Switzerland are intrinsically tied to the last Alpine glaciation that reached its maximum around 20 to 22 ky BP. Substantial areas have thereafter become free of ice due to the global warming and subsequent glacier retreat [1]. Colluvial and alluvial processes are considered parental to the young Holocene sediments featured by some remarkable eogenetic phenomena like the formation of ferromanganese nodules, which is discussed in this contribution. Namely, along the hillside of Grand-Saconnex, a locality situated within the Geneva city limits, recent archaeological excavations have revealed a nicely developed ~1.5 m thick exposure of post-glacial sediments. The sequence consists of reworked glacial till, preceded by several distinct layers of clayey to sandy deposits [2]. At the interface of two colluvial units, the upper very fine grained and the lower marked by the brown-orange alterations, a cm-thin zone rich in Fe-Mn nodules has been reported. A detailed X-ray elemental mapping coupled with XRD and XRF investigations has been performed in order to understand occurrence modes as well as the origin of such mineralization. The nodules host layer mainly consists of illite, chlorite, several mica varieties, mixed-layer illite-smectite, quartz and amorphous matter. In addition, myriad ferromanganese concretional forms are present, attaining up to 1.5 mm in diameter size. Compared to adjacent layers, 10 to 15 times higher concentrations of Fe and Mn were reported in nodule-rich domains. The nodules are spherical to subangular, with an onion-like quasi-layered internal architecture marked by selective enrichments of Fe and Mn. Iron is preferentially encountered along the rims, whilst Mn is mostly concentrated in the nodules' cores. An increasing porosity gradient has been reported toward the centre of the nodules, which points to the secondary pore filling that must have commenced tangentially to the nodules' rim. Mineralogy of nodules reflects the composition of the host sediment with an exception of very low crystalline, practically amorphous, Fe-Mn aggregates present solely within the studied concretional forms. In comparison to the neighbouring colluvial layers, the nodule-rich sediment level is 10 to 100 times enriched in igneous and metamorphic phases such as olivine, Cr-spinel, clinopyroxene, amphibole, garnet, chlorite and biotite. Furthermore, this layer shows different clay mineral content, which is devoid of hydroxyl-interlayered minerals typical for the rest of the colluvium.

The above-mentioned Fe-rich mineral suite of magmatic and metamorphic origin, reported in the nodule-rich layer, is believed to have served as a feedstock of Fe and Mn. Most probably, the morphology of terrain receptive to water retention, caused favourable pH-Eh conditions that enhanced mobilization of Fe and Mn in their soluble forms eventually leading to their dispersion within the host sediment. Electron microscopy identified exfoliated chlorite, and presumably metamorphic vermiculite (mixed 10-14 Å sheet silicates), as the most evident sources of iron. Oscillating redox conditions triggered the precipitation of Fe and Mn in the form of low-crystalline aggregates attached to the outer surfaces of illite crystallites. This process ultimately saw an end with the formation of nodules thoroughly cemented by Fe-Mn mineralization.

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GENERATION AND TRANSPORT OF CLAY COLLOIDS FROM BENTONITE BARRIERS IN NUCLEAR WASTE REPOSITORIES - AN OVERVIEW OF THE BELBAR PROJECT

Patrik Sellin (1)*, Amy Shelton (2), Tiziana Missana (3), Thorsten Schäfer (4), Radek Červinca (5), Kari Koskinen (6), Mary Westermark (1)

(1) SKB, Stockholm, Sweden, (2) RWM, Harwell, United Kingdom, (3), Ciemat, Madrid, Spain, (4) KIT, Karlsruhe, Germany, (5) ÚJV Řež, Czech Republic, (6), Posiva, Eurajoki, Finland

The BELBaR project was a collaborative project based on the desire to improve the long-term safety assessments for geological disposal facility concepts for spent fuel/ high level waste that combine a clay engineered barrier system (EBS) with a fractured rock. BELBaR partners included national radioactive waste management organisations (WMOs) from a number of countries, research institutes, universities and commercial organisations working in the radioactive waste disposal field.

The main aim of the BELBaR project was to increase the knowledge and reduce uncertainties with respect to the processes that control clay colloid generation, stability and their ability to transport radionuclides and reduce uncertainties in the description of the effect of clay colloids in long-term performance assessments.

The mechanisms of bentonite erosion from the compacted bentonite barrier of a waste repository, leading to the generation of (colloidal) particles detaching from the clay, are being deeply investigated in the BELBAR Project. Different possible scenarios were considered: the static system, where the transformation of the hydrated bentonite gel to a sol is mainly a chemically driven process and the dynamic one where other hydraulic aspects, as water velocity or fracture geometry must be considered.

Colloid mobility controlling processes in the geosphere and the effect of the mobile colloidal phase on the transport of radionuclides in the far-field environment of a deep geological repository in crystalline formations were investigated. The investigations focussed on one hand side on microscale investigations and on the other hand side on macroscale investigations including work in near-natural systems. Another main focus was on the process understanding of radionuclide colloid interaction with a special emphasis on sorption reversibility.

Because colloid stability depends on the chemistry of the aqueous environment, the stability studies were performed to analyse whether or not clay colloids aggregate depending on several chemical and physical parameters, such as pH, ionic strength, temperature, presence of different inorganic ions and organic ligands.

The overall aim of the project was to use the experimental data obtained to produce quantitative models that could be used to estimate the magnitude of bentonite colloid generation and transport in a waste repository. The key focus has been on a dynamic model for pure smectite swelling and colloid release that accounts for competing attractive and repulsive forces between the smectite particles as well as on them by thermal movement (Brownian motion) and gravity. Important factors in the model are gel/sol behaviour and expansion, ion exchange and influence of calcium and other divalent ions and friction in fractures.

The key outcome of the BELBaR project was a list of recommendations for the potential to review the treatment of colloids in future performance assessments.

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BENTONITE AS A PHEROMONE DISPENSER

Sung Man Seo (1)*, Daeyoung Kim (2), Ki-Min Roh (1,2), Il-Mo Kang (1)

(1) Advanced Geo-materials R&D Department, Pohang Branch, Korea Institute of Geoscience and Mineral Resources, Pohang 37559, Korea, (2) Department of Nanomaterials Science and Engineering, University of Science and Technology, Daejeon 34113, Korea

Because of climate and cropping system changes, sap sucking insects (Oder: Hemiptera) have become major agricultural pests in Korea and other Asian countries [1]. The adults and nymphs of Hemiptera cause damage by feeding on crops and transmission of plant viruses [1,2]. For effective control of the insect pests, synthetic aggregation pheromone traps have been used commercially. Recently, cation modified zeolites were studied as pheromone dispensers for insect attractants [1]. Aggregation pheromone of *Riptortus clavatus* (Thunberg) (Heteroptera: Alydidae) consisted of three components: (E)-2-hexenyl-(Z)-3-hexenoate, (E)-2-hexenyl-(E)-2-hexenoate, and myristyl isobutyrate in a ratio of 1:5:7. To prepare a pheromone adsorbed dispenser, dehydrated powder bentonite was combined with an amount of aggregation pheromone, dissolved in methylene chloride and soaked to obtain the desired sorption loading after homogenization for 3 days. For comparable of adsorption capacity and diffusion rate, mesoporous molecular sieves MCM-41 and microporous titanosilicate ETS-10 were also prepared using the same procedure. The contents of adsorption and desorption into/onto three materials were investigated by gas chromatography analysis. While the adsorption capacity followed the trend bentonite > ETS-10 > MCM-41, the desorption rates were MCM-41 > ETS-10 > bentonite, suggesting that bentonite has potential as an outstanding material for the development of a pheromone dispenser.

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CLAY MINERALS ASSEMBLAGE: EVIDENCE OF THE HYDROTHERMAL ALTERATION ACTIVITY IN NEFZA AREA (NORTHWESTERN TUNISIA)

Dalel Sghaier (1)*, Fredj Chaabani (1), Slim Boussen (2), Faten. Hammami Ben Zeid (1)

(1) Laboratoire de Ressources Minérales et Environnement, Université de Tunis El Manar, Faculté des Sciences de Tunis, Département de Géologie, Campus Universitaire, 2092 Tunis. Tunisia, (2) Office National des Mines 24 rue 8601- 2035 La Charguia I Tunis (Tunisia)
*sghaierdalel@yahoo.fr

The Oued Belif structure belonging to the Nefza district (northern Tunisia) results of the post-collisional Cenozoic magmatism of the Mediterranean Maghreb margin. This structure, previously interpreted as a salt diaper coeval with Late Miocene magmatic activity, represents an elliptic configuration rimmed by Upper Miocene ferruginous breccias [1]. It encloses saliferous Triassic formation [1,2,3,4,5,6]. Through these chaotic deposits, calc-alcaline magmatic and metamorphic rocks were emplaced. They are represented by Ragoubet el Alia granodiorite (Serravallian), Ragoubet es Seid and Oued-Arra rhyodacites (Tortonian) and skarn deposits [1,2,3,4,5,6]. The borehole carried out by the Tunisian Office of Mines indicated that these felsic igneous and the Triasic evaporates rocks are deep-rooted [6]. Furthermore, recently gravity and aeromagnetic data of northwestern Tunisia [7] has shown that the intrusive rocks were probably emplaced in the shallow levels of the crust. This concealed magmatic-hydrothermal complex cross-cut the allochthonous Numidian flysch.

Below the tectonic breccia of Boukhchiba, mineralized veins and veins intercalated in the sedimentary series have been encountered. They are filled with clayey mineralization represented mainly by vermiculite, smectites, interstratified illite/smectites and kaolinite associated with 2M1-phengite.

The occurrence of these post magmatic clay mineral assemblage is thought to be a late stage hydrothermal infilling which can be related to the Late Mio-Pliocene reactivation of shear zone inherited from Hercynian orogeny.

Keywords: Oued Belif structure; diapir; magmatic activity, clayey mineralization; hydrothermal.

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CYCLODEXTRIN-MONTMORILLONITE COMPOSITES FOR SIMULTANEOUS REMOVAL OF BISPHENOL A AND DISSOLVED ORGANIC MATTER

Itamar A. Shabtai*, Yael G. Mishael

Dept. Soil and Water Sci., The Robert H. Smith Faculty of Agriculture, Food and Environment, Hebrew University of Jerusalem, Rehovot 7610001, Israel

One of the challenges of water technologies is treating trace concentrations of emerging organic pollutants in complex matrices, such as treated wastewater (TWW). In this study, polymeric cyclodextrin-montmorillonite (polyCD-MMT) composites were designed as sorbents to remove both micro-pollutants and dissolved organic matter (DOM) from TWW. CDs are cyclic oligosaccharides which form complexes with many organic compounds due to their small hydrophobic cavity. CD can be polymerized and adsorbed to MMT to obtain composites with potentially high affinity towards organic micro-pollutants. On the other hand, adsorbing PolyCDs substituted with cationic trimethylammonium forms composites which may possess a positive charge, promoting the removal of negatively charged DOM compounds. Hence, we designed polyCD based composites to specifically target micro-pollutants and simultaneously remove DOM compounds from TWW. The composites were employed for the removal of bisphenol A, a model hydrophobic micro-pollutant and DOM from TWW.

Neutral (N) and cationic (C) PolyCDs were characterized by SEC-MALS, H NMR, zeta potential, FTIR and elemental analyses and adsorbed to MMT to obtain N-polyCD-MMT (zeta potential -22 mV) and C-polyCD-MMT composites (zeta potential 32 mV), respectively. The adsorption of C-polyCD (0.3 g/g clay) was lower than that of N-polyCD (0.6 g/g clay), due to electrostatic repulsion between the highly charged C-polyCD. Initial composite optimization revealed almost complete removal of bisphenol A (BPA) (97% of 1 mg/L) by N-polyCD-MMT (0.5 g/L), indicating that the CDs retained their ability to form a complex with BPA upon adsorption to MMT. Furthermore, the removal of BPA from spiked TWW was equally high. The removal of DOM itself by N-polyCD-MMT was negligible, indicating the specificity of N-polyCD-MMT for BPA. However, very high removal of DOM (95%) was reached by the C-polyCD-MMT composite, indicating the significant role of the cationic groups in DOM removal. On the other hand, BPA removal (mmol/g polyCD) was significantly lower in the case of C-polyCD-MMT. This may be due to different configurations of adsorbed polyCDs (C-polyCD vs. N-polyCD) or steric hindrance introduced by the cationic groups. Thus, a combination of composites possessing different characteristics may be efficiently employed to remove a variety of hydrophobic micropollutants and DOM from TWW.

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EXPERIMENTAL STUDY ON STABILIZATION OF MOUNTAINOUS SOIL WITH LIME: APPLICATION FOR THE CONSTRUCTION OF ROADS

L. K. Sharma*, T. N. Singh

Department of Earth Sciences, Indian Institute of Technology Bombay, Mumbai- 400076, India
*lksharmaiitb@gmail.com

Mountainous land is widely distributed throughout the world and the soils in such area are subjected to many construction projects. The long term durability and fitness of the projects depend upon the soundness of the engineering behaviour of the soil. The analyses of the physical, mechanical and mineralogical properties of soil is extremely important for better and safe construction. The evaluation of the geotechnical properties of mountainous soil and its treatment with lime are fairly limited. In the study area (Orang-Kalaktang-Shergaon-Rupa-Tenga road, Arunachal Pradesh, India), most of the soil failure problems are encountered during roads construction and their widening. The present study was aimed to stabilize potentially expansive mountainous soil using lime, which is easily available and an eco-friendly additive. Geotechnical properties were assessed by measuring pH values, consistency limits, free swell index, compaction characteristics, unconfined compressive strength, modulus of elasticity, shear strength and wave velocity. Mineralogical and textural changes induced by the stabilization process were studied by X-ray diffraction (XRD), scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR) analyses. The outcomes of the study indicate that the geotechnical and microstructural properties of the mountainous soil are considerably affected by the addition of lime. Additionally, the compressive strength of samples cured for 28 days increased four times than that of the untreated specimen, thereby suggesting the influence of curing time on the strength parameters. The results obtained from X-ray diffraction analysis, SEM and FTIR spectroscopy indicate the development of cementitious compounds. We suggest that this occurred due to cation exchange and pozzolanic reactions and it also produced noticeable changes in the engineering behaviour of mountainous soil. The results of the study show that mountainous soil can be stabilized satisfactorily with the addition of about 5% of lime.

Keywords: mountainous soil, lime, roads, stabilization.

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CRYSTALLINE POLYMORPH OF CHITOSAN WITH CLAY NANOPLATELET

Sergei Sarin (1), Irina Postnova (1,2), Yury Shchipunov (1)*

(1) Institute of Chemistry, Far East Department, Russian Academy of Sciences, 690022 Vladivostok, Russia, (2) Far East Federal University, 690072 Vladivostok, Russia

Mineralized tissues or biominerals of living organisms serve as examples of composite materials with highly hierarchically organized structure from the nano- to the macroscale. A well-known example is provided by crustaceous shells containing highly structurally ordered crystalline chitin. When biomimicking the biomineral construction at nano/microscopic levels, material scientists could prepare bionanocomposites in which biopolymers were in a disordered state. By studying the formation of films from chitosan and saponite nanoplatelets by a new technique in which it proceeds in the self-organized manner [1,2], we have found out a novel crystalline polymorph considered in the presentation.

Bionanocomposite films were prepared by a method that includes the initial formation of building blocks through the association of saponite nanoplatelets with chitosan macromolecules charged in situ and then their evaporation-induced self-assembly into highly ordered nanocrystalline narrow rectangle microparticles with uniform thickness and high aspect ratio [3]. Their characterization by the SAXS, WAXS, SEM and TEM revealed the presence of crystalline polymorph unknown for chitosan with nanosized particles before. This polysaccharide classified as semi-crystalline demonstrates rich polymorphic behaviour. There are six known polymorphs called "*tendon-chitosan*" because of its preparation from a lobster tendon chitin, "*annealed*" or anhydrous form obtained by annealing at ca. 200 °C, "*form I*", "*form II*", "*I-2*", "*L-2*", separated from solutions with transition metals, mineral and organic acids.

New polymorph possessed a nacre-like structure from alternating layers of two chitosan macromolecules and saponite nanoplatelets. The nanocrystalline narrow rectangle microparticles are stable, insoluble in water and organic solvents owing to the strong polysaccharide - nanoparticles association through numerous electrostatic interactions and hydrogen bonds that enabled one to separate them by a simple procedure. They might go to work as alternative to nanofibrils of chitin and cellulose, of which separation meets with severe difficulties, in such applications as reinforcing nanofillers in (bio)nanocomposites, packaging, biomedical materials, biomimetic optical nanomaterials, etc.

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CHITOSAN-CLAY BIONANOCOMPOSITES PREPARED THROUGH REGULATED SELF-ORGANIZATION

Irina Postnova (1,2), Vladimir Silant'ev (1), Sergei Sarin (1), Yury Shchipunov (1)*

(1) Institute of Chemistry, Far East Department, Russian Academy of Sciences, 690022 Vladivostok, Russia, (2) Far East Federal University, 690072 Vladivostok, Russia

Biopolymers possess insufficient mechanical strength, high gas and water vapor permeability, low heat degradation temperature, etc., ranking much below petroleum-derived plastics in properties. However, they have decided advantages over the latter being in the biocompatibility, biodegradability and abundant renewable sources. Properties and performance are improved in substantial manner as ever biopolymers are combined with clay nanoparticles. These composites are separated into an individual class of materials called "bionanocomposites" because of the particular preparation methods, properties and functionalities [1].

Here bionanocomposites are considered that are prepared from chitosan with clay nanoparticles (mainly saponite or sepiolite) by a new approach [2,3]. It is based on the property of this cationic polysaccharide to be in the charged/uncharged state in accordance with the solution pH. By taken it in the uncharged form at pH a little higher than its pK value, chitosan is dispersed initially in a solution of exfoliated clay nanoparticles bearing negative charges. To make the polysaccharide charged, solution is gradually acidified. The transition of uncharged carbohydrate macromolecules into charged state results in electrostatic interactions *in situ* with neighbour anionic clay nanoparticles. If the pH change was made in a progressive way, the process proceeds in a self-organization manner, leading to the jellification without common precipitation. The method can be applied to prepare both monolithic hydrogel and homogeneous films [2-4]. Structure, morphology and properties of both the types of bionanocomposites were well characterized by various physico-chemical techniques including dynamic rheology, dynamic thermomechanical analysis, scanning and transmission electron microscopy, small-angle and wide-angle X-ray scattering. It was found that the tuned charging of polysaccharide macromolecules provided the jellification through the formation of a three-dimensional network consisting of fibrils. The films had pronounced stratified layer (nacre-like) structure from stacked nanoparticles and separated by aligned chitosan macromolecules.

This approach provides an opportunity to prepare hydrogels of chitosan that belongs to nongelable polysaccharides. Its advantage is that a chemical modification is not needed. Therefore, chitosan retains its main properties - biocompatibility, biodegradability, antimicrobial and wound-healing in full measure. Its films with clay nanoparticles served as a good barrier decreasing permeability to water vapor. When fruits and vegetables were coated, it extended their shelf life without signs of infection over long period owing to reducing moisture loss and antimicrobial protection.

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SYNTHESES OF COPPER NANOPARTICLES AND TRIANGULAR NANOPLATES WITH SAPONITE BY PHOTOREDUCTION

Akane Shibusawa*, Masaya Miyagawa, Kaho Maeda, Hideki Tanaka

Department of Applied Chemistry, Chuo University, Tokyo, 112-8551, Japan
*ashibu0609@gmail.com

Since Au, Ag and Cu nanoparticles (NPs) show surface plasmon resonance (SPR) and high catalytic activity, various synthetic methods have been reported mainly by chemical reduction, which requires hazardous reducing agents. Hence, photoreduction method has recently attracted attention due to its environmentally-friendly condition. Because absorption wavelength of SPR is dependent on their shape, syntheses of anisotropic NPs have been investigated energetically. Au triangular nanoplates (TNPs) have been synthesized by a combination of seed-mediated growth and addition of iodide ions, by using selective adsorption of I^- on the {111} facet of the Au NPs [1]. Morphology control has also been achieved by arrays of Au or Ag NPs with protective agents on layered materials [2]. In spite of many reports on Au and Ag, Cu TNPs have yet been reported with high yield. Even so, we have assumed that the Cu TNPs would be obtained by the combination with saponite (Sapo). To apply the metal NPs to a catalyst, it is important to control their diameter and dispersibility. We have assumed that the diameter of the Cu NPs could also be controlled simply by [Cu^{2+}]. In addition, because the Cu NPs could be synthesized on Sapo with the aid of the adsorption of Cu^{2+}, they are expected to be dispersed with no protective agents due to electrostatic repulsion originating from the negatively-charged nanosheets. In the present study, we have synthesized the Cu NPs on Sapo by photoreduction, and controlled their diameter and dispersibility. We have also synthesized the Cu TNPs by the combination described above. Synthetic saponite (Kunimine Ind. Co.) was dispersed in Milli-Q water, and copper acetate aqueous solution and ethanol were added to the dispersion drop by drop. The mixed solution was irradiated by UV light to obtain a nanocomposite of the Cu NPs and Sapo (Cu−Sapo) [3]. To synthesize the Cu TNPs, a small amount of NaI aqueous solution was added to the photoirradiated solution, followed by further UV irradiation. We call a sample synthesized from x mmol L^{-1} of Cu^{2+} and y g L^{-1} of Sapo {x:y}, hereafter. The mixed solution turned red by the UV irradiation, which was characteristic of the SPR of spherical Cu NPs. We confirmed production of the oxide-free CuNPs by XRD measurement. An average diameter of {0.5:0.5} was determined to be 11±4 nm. In contrast, that of {0.2:0.5} was decreased to 8±2 nm. This result suggests that the lower [Cu^{2+}] is, the smaller the diameter is. Therefore, we concluded that the diameter can be controlled by [Cu^{2+}]. Dropping speed of the copper acetate solution also changed the diameter. While the average diameter of {1:1} was 13±3 nm obtained by the drop-by-drop method, it got larger (20±2 nm) when the solution was added at once. Similarly, the diameter was also increased to24±6 nm from 13±3 nmin {2:2} by changing the dropping speed. These results imply that Cu^{2+} was segregated on Sapo by adding the solution at once. Thus, it was found that the dropping speed could control the diameter. It should be noted that Cu−Sapo in {1:1} was dispersed independently of the dropping speed, and no large aggregates were observed with the naked eye, while large aggregates were observed with flocculation in {2:2}, when the photoirradiated solutions was kept in darkness for 24 h. Therefore, we concluded that the dispersibility was related to the formation of the large aggregates, and could be controlled without changing the diameter by [Cu^{2+}] and [Sapo]. The Cu TNPs with sharp edges were obtained by the combination described above. Their edge length was between 100 and 200 nm, which was much larger than the diameter of the seed (ca. 30 nm). Thus, it was suggested that anisotropic crystal growth to form the sharp edges was induced due to the selective adsorption of I^-on the {111} facets of the seed. Correspondingly, a new absorption band appeared at 820 nm in the UV-vis-NIR extinction spectrum, which may originate from the in-plane dipole plasmon resonance of the Cu TNPs.

In summary, the oxide-free Cu NPs were synthesized by photoreduction of Cu^{2+} adsorbed on Sapo. The diameter of the Cu NPs were controlled by [Cu^{2+}] and the dropping speed. The dispersibility of Cu−Sapo was also controlled by [Cu^{2+}] and [Sapo]. In addition, the Cu TNPs with the sharp edges were obtained by the combination of the seed-mediated growth and the addition of I^-.

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FORMATION AND STABILITY OF SMECTITE UNDER HYPER-ALKALINE CONDITIONS AT NARRA IN PALAWAN, PHILIPPINES

Misato Shimbashi (1)*, Tsutomu Sato (1), Tsubasa Otake (1), Naoki Fujii (2),
Minoru Yamakawa (2), Masanobu Nishimura (3), Yukinobu Kimura (3), Carlo Arcilla (4),
Hisao Satoh (5), W. Russell Alexander (6)

(1) Graduate school of Engineering Hokkaido University, Sapporo 060-8628, Japan, (2) Radioactive Waste Management Funding and Research Center, Tokyo 104-0052, Japan, (3) Obayashi Corporation, Tokyo 108-8502, Japan, (4) University of the Philippines, Quezon 1101, Philippines, (5) Mitsubishi Materials Corporation, Naka 311-0102, Japan, (6) Bedrock Geosciences, 5105 Auenstein, Switzerland

Montmorillonite, which belongs to the smectite group, will play an important role as buffering materials for the geological disposal of radioactive waste due to the favorable features of smectite such as low permeability and high cation exchange capacity. However, it is frequently proposed that montmorillonite may dissolve by hyper-alkaline leachates from cementitious materials in a disposal site and results in the loss of its favorable properties as buffering materials. Although many experiments have been conducted to elucidate the reaction after montmorillonite dissolution under hyper-alkaline conditions, there is a significant disparity between complexiety of the reaction involved in laboratory experiments and actual disposal environments. Previous studies observed the interaction between montmorillonite and hyper-alkaline groundwaters in natutal settings and reported that montmorillonite has altered to Fe-rich smectite [1] or palygorskite[2]. If smectite forms by hyper-alkaline leachates after montmorillonite dissolution in the actual disposal sites, the properties ot buffering materials would not damage seriously compared to the case montmorillonite alter to non-swelling minerals. Therefore, understanding the formation condition of smectite under hyper-alkaline conditions is important. In this study, the focus is on observable interaction between smectite and hyper-alkaline groundwaters in an actual field site to understand the effect of hyper-alkaline fluids on the formation and stability of smectite. Sampling of clays and natural hyper-alkaline groundwaters took place at Narra in Palawan, Philippines, where hyper-alkaline groundwaters by modern-serpentinization has been flowing up as several springs. XRD analysis of both of solid samples which contact with hyper-alkaline fluids and do not contact with current hyper-alkaline groundwaters at least revealed the presence of smectite in weathered serpentinite sediments. Here, there are 3 possibilities of smectite formation under hyper-alkaline conditions. (1) Smectite was originally produced by weathering process and persists under current hyper-alkaline conditions. (2) Smectite was produced as alteration products from ultramafic minerals by hyper-alkaline groundwaters. (3) Smectite was directly formed from hyper-alkaline groundwaters. XRD analysis of less than 2 μm samples before and after heat treatment revealed stevensite only in those samples which contact with hyper-alkaline groundwaters. Based on EPMA analysis of the solid samples which contact with hyper-alkaline groundwaters, Fe-Mg-smectite formed as alteration products of primary ultramafic minerals and stevensite formed as precipitates in pores of the sediments. Thermodynamic calculations based on the hydrochemistry of the natural hyper-alkaline fluids support the formation of magnesium silicate hydrate from hyper-alkaline fluids, which could be precursor of Mg-smectite such as saponite and stevensite. Therefore, the observed stevensite would be precipitated from hyper-alkaline groundwaters. To further understand the effect of hyper-alkaline fluids on the formation of smectite, it is important to understand whether Fe-Mg-smectite as alteration products from some ultramafic minerals may formed under hyper-alkaline conditions or initially produced by weathering and persists under current hyper-alkaline conditions. In this study, we documented the formation of Fe-Mg-smectite under hyper-alkaline fluids to understand the effect of hyper-alkaline fluids on the formation of smectite. To discuss the potential forming of smectite after montmorillonite dissolution in the actual disposal sites, it is necessary to elucidate the formation condition of smectite under hyper-alkaline conditions by further understanding smectite formation under hyper-alkaline groundwaters at Narra.

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NANOSTRUCTURES FROM PYROLYSIS OF Ni-BASED LAYERED DOUBLE HYDROXIDE

Caroline Silva de Matos (1)*, Antonio D. dos Santos (2), Koiti Araki (1), Vera R. L. Constantino (1)

(1) Instituto de Química - Universidade de São Paulo, São Paulo, Brazil, (2) Instituto de Física - Universidade de São Paulo, São Paulo, Brazil
*matos@iq.usp.br

The fine tuning of layered double hydroxides (LDHs) composition permits engender nanocomposites containing metal nanoparticles and/or nanocarbons for information storage, energy conversion, catalysis, electrochemical sensing and environmental remediation [1,2]. A bottom-up approach can be design to the direct formation of multifunctional structures *via* pyrolysis of LDHs containing transition metals in the brucite-like layers and intercalated organic anions in the gallery region. In this way, the inorganic matrix can act as a template for carbon and a source of metal [2].

In this work, Ni_2Al-LDH intercalated with carboxymethylcellulose (abbreviated LDH-CMC) was synthetized by one pot reaction. As-prepared LDH-CMC was thermal treated at 70 °C for 24 h and subsequently pyrolyzed at 200 - 1000 °C under inert atmosphere. The isolated materials were characterized by X-ray diffractometry (XRD), infrared (FTIR) and Raman spectroscopies, thermal analysis (STA-MS), elemental analysis (CHN), scanning electron microscopy (SEM) and vibrating sample magnetometry (VSM). For comparison purposes, Ni_2Al-LDH intercalated with chloride anions (LDH-Cl) was also prepared and submitted to the same thermal treatment as LDH-CMC.

XRD data show the conversion of LDH-Cl into NiO and $NiAl_2O_4$ after pyrolysis process: from 500 to 1000 °C, the presence of peaks (2θ) at 37.3, 43.3 and 62.9° attributed, respectively, to (111), (200) and (220) plans confirm the NiO formation while $NiAl_2O_4$ phase is observed only when sample is treated at 1000 °C. On the other hand, LDH-CMC pyrolized materials exhibit the nickel XRD pattern when heated at 600 °C and higher temperature values, suggesting the Ni^{2+} reduction to Ni^0. FTIR spectra of LDH-CMC precursor and its derivatives obtained at 200 and 350 ^oC present bands at 1057 (δ CO) and 1572 cm^{-1} (ν_{as} COO^-). The disappearance of these bands at higher pyrolysis temperatures indicates CMC thermal decomposition. Production of graphitic carbon from pyrolyzed LDH-CMC at 600 - 1000 °C was confirmed by the presence of bands around 1600 and 1350 cm^{-1} on Raman spectra, attributed to typical G and D bands, respectively. TG-MS curves (air) of LDH-CMC pyrolyzed at 600, 700, 800 and 1000 °C show two main steps of mass change: *(i)* room temperature to 200 °C, attributed to dehydration and *(ii)* 200 to 500 °C, related to carbon and residual CMC oxidation, releasing CO_2, and conversion of Ni^0 to NiO. Elemental and thermal analysis reveal that the carbon and nickel content (m/m) vary respectively from 18.7 and 9.9% (at 600 °C) to 10.6% and 48% (at 1000 °C) in the pyrolyzed products. SEM micrographs show spherical nickel nanoparticles growing as higher is the pyrolysis temperature, and some wrinkled regions of Al_2O_3, as suggested by EDX analysis. Magnetization curve for LDH-CMC carbonized at 1000 °C shows a hysteresis loop. Saturation magnetization (M_s), remanence (M_R) and coercivity (H_c) values are equal to 5.1 emu g^{-1}, 1.1 emu g^{-1} and 104 Oe, respectively. The set of characterization techniques suggests that pyrolysis of LDH-CMC hybrid material at high temperatures (600 - 1000 °C) results in promising multifunctional materials mainly composed by nickel nanoparticles and graphitic carbon in a layered double oxide matrix.

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GRAIN SHAPE PREFERRED ORIENTATION(GSPO) MEASUREMENT FOR THE MICRO-SIZED CLASTS IN FAULT GOUGE

Ho Sim (1)*, Yungoo Song (1), Ha Kim (1), Changyun Park (1), In-Chang Ryu (2)

(1) Mineralogy Laboratory, Dept. of Earth System Sciences, Yonsei University, Seoul 120-749, Korea, (2) Department of Geology, Kyungbuk National University, Daegu 702-701, Korea

Grain shape preferred orientation (GSPO) of various sized fragments in fault gouge is influenced by the forces acting at and after the fault activity. Especially, the GSPO of brittle quartz and feldspar clasts surrounded by clay matrix reflects the environment of matrix formation timing and direction of shear at the latest stage. In this study, we firstly attempted to measure the GSPO of the tens of micro-sized clasts representative fault gouges by using Scanning Electron Microscope (SEM) on the Backscattered Electron (BSE) Images. The oriented samples were collected and prepared as polished sections with perpendicular and parallel directions to the fault plane. The GSPO data were presented as contour plot on the stereonet and as rose diagram using Ellipse fit, Stereonet, and Dips program.

The GSPO mesurement results are close to the P-shear and R-shear directions of macroscopic fault activity as revealed in the outcrops. The graphs for each extent of GSPOs with different axial ratio show that the GSPOs of clasts tend to be close to the P-shear direction as the axial ratio value increases. As the result of this study, the GSPO of micro-sized fault clasts showed an useful evidence indicating the shear sense directions to the brittle fault zone.

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CRYSTALLOCHEMICAL FEATURES OF GLOBULAR LAYER SILICATES FROM CHIM−LOPTIUGA PYROSCHIST DEPOSIT

Yulia Simakova

IG Komi SC UB RAS, Syktyvkar, 167982, Russia, yulia5-07@mail.ru

The results of crystal chemical study of globular layer silicates of glauconite-illite composition from Chim−Loptyuga pyroschist deposit, North Urals (Jarenga shale-bearing region, Mezen' syneclise) are presented. Upper-Jurassic rocks of Chim-Loptiuga deposit consists of clay and combustible shales, calcareous dark gray and greenish-gray clays and clay-marls with infrequent sandstone layers. In Oxford and Kimmeridgian sediments of the upper division of the Jurassic system ($J_{3\ of+km}$) glauconite is present as the lithological datum.

Globular layer silicates were studied using modern chemical and physical methods: X-ray analysis, scanning electron microscopy (SEM), chemical and microprobe analysis, IR spectroscopy and others.

1. The globular phyllosilicates from Chim−Loptyuga pyroschist deposit are presented by differently colored grains (dark green, green, light green) and their green beans and dark green color glauconite are low in potassium and, accordingly, low degree of diagenetic mineral maturation [1]. Glauconite with ideal crystallochemical composition is absent. Green globules are presented by dioctahedral mica with a deficit of interlayer cations and close in composition to the glauconite with low interlayer charge whereas bleached grains contain in its composition smectite component in addition to glauconite.

The diffraction patterns of dark green globules display presence of several phases related to layered silicates: mica (glauconite), smectite and mixed-layered mineral of illite/smectite type. Glauconite is predominant mineral of globules and set of non-basal reflections on diffractograms corresponds to 1M polytype although peaks are slightly broadened.

IR spectra of the studied samples are typical of dioctahedral micaceous minerals. Dark green globules show intensive band at 3551 cm^{-1} corresponding to FeOHFe vibrations and weak band at 3623 cm^{-1} (A1OHFe^{3+}), IR spectra of bleached globules show more intensive band at 3593 cm^{-1} corresponding to AlOHAl vibrations in smectite.

Glauconite-bearing rocks are also widely altered what is resulted in widespread mixed-layered minerals containing expandable layers. Interstratified minerals could be formed by the transformation of the initial layer silicates under the influence of organic matter during diagenesis. With this stage is also associated the intensive authigenic formation of zeolite, glauconite and iron sulfides (in some stratigraphic intervals - sulphides of zinc, cobalt and nickel) which are widespread throughout the section of the Upper Jurassic rocks [2]. The presence of pyrite in the surface of the globules may indicate that the formation of glauconite was interrupted and not completed due to changes of environmental redox conditions.

2. Crystal chemical features of glauconite allow considering this mineral to be an indicator of a weak degree of diagenetic transformation of sediment. We propose that smectite was a "precursor" for the glauconite formation and the change rate of sedimentation and permeability the surrounding environment prevented the completion of the process.

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USE OF VITREOUS WASTE AND WASTEWATER SLUDGE AS ALTERNATIVE RAW MATERIALSTO OBTAIN GEOPOLYMERS

L. Simão (1A), D. Hotza (1B), M. J. Ribeiro (2), J. A. Labrincha (3), O. R. K. Montedo (4), F. Raupp-Pereira (1A)

(1) Graduate Program in Materials Science and Engineering (PGMAT), ADepartment of Mechanical Engineering (EMC), BDepartment of Chemical Engineering (EQA), Federal University of Santa Catarina (UFSC), PO Box 476, 88040-900 Florianópolis (SC), Brazil; (2) UIDM-ESTG, Polytechnique Institute of Viana do Castelo, 4900-348 Viana do Castelo, Portugal; (3) Department of Materials and Ceramic Engineering / CICECO- Aveiro Institute of Materials, University of Aveiro, Campus Universitário de Santiago, 3810-193 Aveiro, Portugal; (4) Graduate Program in Materials Science and Engineering (PPGCEM), Laboratory of Technical Ceramics (CERTEC), University of Southernmost Santa Catarina (UNESC), 88806-000 Criciúma (SC), Brazil

Ceramics chemically bonded by geochemical reactions also known as geopolymers, normally use traditional raw materials such as metakaolin [1]. Metakaolin is obtained by heating kaolin (typically between 700 and 850 °C) for dehydroxylation. Alternatively, some industrial wastes can be also involved in the formulation of geopolymers, including fly ash [3], red mud [4] and glass [5,6]. These raw materials should assure the needs of Al_2O_3 and SiO_2 of the geopolymers composition, being environmentally more adequate, since their preparation requires less energy than the production of metakaolin. The potential of urban vitreous waste from non-returnable glass bottles (UVGB), and sludge generated from the wastewater treatment of a ceramic pigment industry (WWTS), for the production of geopolymers was the main objective of the current work. Chemical analyses (done by XRF) showed that UVGB contains SiO_2 (71.10 wt.%), and Na_2O (13.71 wt.%) as main components, while WWTS is rich in SiO_2 (59.10 wt.%) and Al_2O_3 (8.5 wt.%). Both wastes show high amorphous phase (revealed by XRD), which might be crucial for their chemical activation reactions. In fact, the use of NaOH solution (10 M) easily hardened the tested waste mixtures. The optimal formulations showed compressive strength of ~5 MPa after 7 days curing in 40 ^{o}C. In order to adjust the SiO_2/Al_2O_3 molar ratio, additions of other Al_2O_3-bearing wastes will be test.

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NON-EQUILIBRIUM SIMULATIONS OF FLOW IN CLAY NANOPORES USING A WALL THERMOSTAT

Pauline Simonnin (1,2)*, Benoit Noetinger (1), Carlos Nieto-Draghi (1), Virginie Marry (2), Benjamin Rotenberg (2)

(1) IFP Energies nouvelles, 1 & 4, avenue de Bois-Préau, 92852 Rueil-Malmaison Cedex, France, (2) Sorbonne Universités, UPMC Univ. Paris 06, CNRS, Laboratoire PHENIX, 4 place Jussieu, 75005 Paris, France

Fluids transport through nanoporous media is a key issue for unconventional hydrocarbons recovery or for cap rock integrity in the context of CO_2 sequestration. The thermodynamic behaviour of a fluid in a clay nanopore depends on the nature of the clay itself and on the physico-chemical effects induced by the confinement.

Nonequilibrium molecular dynamics (NEMD) simulation has allowed to investigate the validity of continuous hydrodynamics of simple systems under confinement. Most studies on the hydrodynamics of confined fluids on the molecular scale are based on model systems such as a Lennard-Jones (LJ) fluid between LJ walls [1], though some applications to more realistic systems have been published, as water in silica nanopores [2] or between two montmorillonite layers [3,4]. Such molecular dynamics (MD) simulations are necessary in the contexts previously described to bridge molecular descriptions and continuous models in order to upscale transport properties from the microscopic to the macroscopic scale.

Several recent studies underlined that simulations with rigid walls and/or using a thermostat acting directly on the fluid should be taken with caution. Rather, it is possible to thermostat highly confined fluid by a wall thermostat [5]. We currently apply this strategy for the case of fluids in clay nanopores. We will present results on the ionic force and surface charge effect on mass transport. We will also present results on confined diphasic systems containing water/methane and water/carbon dioxide.

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COMPARISON OF SINGLE ELEMENT AND COMPETITIVE SORPTION OF HEAVY METALS ON SOIL CLAY AND IRON-OXYHYDROXIDE PARTICLES IN SOILS

Peter Sipos (1), Réka Balázs (1)*, Viktória Kovács Kis (2), Tibor Németh (1)

(1) Institute for Geological and Geochemical Research, Research Centre for Astronomy and Earth Sciences, Hungarian Academy of Sciences, Budapest, H-1112, Hungary, (2) Institute for Technical Physics and Materials Science, Centre for Energy Research, Hungarian Academy of Sciences, Budapest, H-1121, Hungary

Direct observation of the sorption capacity of individual soil mineral particles is expected to allow a much deeper insight into the sorption process of heavy metals in soils compared to studies of bulk soil samples. To support this idea, batch single element and competitive Cd, Cu, Pb and Zn sorption experiments were carried out on smectitic soils characterized by contrasting physico-chemical characteristics and by clay mineral and iron-oxyhydroxide accumulation. The sorption capacities of the bulk soil samples were described by sorption curve evaluation whereas that of the individual soil mineral particles was studied by TEM-EDS analyses.

The generally observed phenomenon that Pb and Cu can be characterized by higher sorption in the bulk soil than Cd and Zn was also found in our case. However, relating soil sorption capacities (derived from the sorption curves) to the major physico-chemical properties of soils have failed, primarily for metals with higher sorption. This can be due to the complex nature of soils where many parameters affect the sorption of certain metals to varying degrees.

Metal sorption capacity of the individual soil mineral particles decreased in the order of Fe-oxyhydroxide > Fe-rich smectite > smectite both in acidic and alkaline soils and in single element and competitive situations. As expected, the same type of soil mineral particles exhibited larger sorption capacity in the alkaline than in the acidic soils. Additionally, sorption of Cu and Pb on the individual mineral particles was generally higher than that of Cd and Zn in harmony to the results of the sorption experiments carried out on the bulk soil samples. In single element situations, a strong linear relationship was found between the Fe content of smectite particles and their metal sorption capacity for Cu, Pb and Zn. On the contrary, this phenomenon was observed for Cd only in the alkaline soils, and this metal showed the lowest sorption on the soil mineral particles generally. In competitive situations, however, such a linear relationship was not found (e.g. the sorbed metal amount did not increase with the Fe content of the smectite particles), although differences in sorption capacities of soil mineral particle types was still observed. Additionally, sorbed metal amounts on the soil mineral particles were generally significantly lower in competitive than in single element situations, and this difference was much more expressed for metals with lower sorption (Cd and Zn) than for those with higher sorption (Cu and Pb).

Consequently, results of sorption experiments carried out on bulk soil samples provide insufficient information about the role of soil mineral phases in sorption processes. With the direct study of the sorption capacities of soil mineral particles, however, this gap can be filled effectively, and when such data are used, the behaviour of distinct mineral groups in the metal sorption in soils can be evaluated.

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LAYERED COMPOUNDS AS ACTIVE FILLERS OF BIOPOLYMERIC NANOCOMPOSITES FOR 3D PRINTED FUNCTIONALLY GRADED BONE SCAFFOLDS

Michele Sisani (1)*, Maria Bastianini (1), Marco Scatto (2), Paolo Scopece (2), Alessandro Patelli (3), Alberto Sanchez (4), Sara Villanueva (4), Ainhoa Egizabal (4)

(1) Prolabin & Tefarm S.r.l., Via dell'Acciaio 9, 06134 Perugia Italy, (2) Nadir S.r.l., c/o Campus Scientifico Università Ca' Foscari Venezia, Via Torino 155b, 30172 Mestre (VE), Italy, (3) Department of Physics and Astronomy, Padova University, via Marzolo 8 35122 Padova, Italy, (4) Sustainable Construction Division, Health Division, TECNALIA, Área Anardi 5, 20730 Azpeitia, Spain

In bone regeneration, autografts are considered the gold standard used for medical procedures, but several complications might occur for patients treated with autologous tissue due to the limited availability and also possible tissue morbidity. Alternatively, bone allografts from cadaveric tissue are also used, but there have been some reports of disease transmission where these tissues were applied. Synthetic- and natural-based biomaterials such as polymers, ceramics, or composites of these materials are a promising alternative to human tissue. In particular scaffolds produced by means of Additive Manufacturing (AM) technologies allows the control of the pore architecture of the fabricated scaffolds [1]. This results in 3D matrices with controlled mechanical properties matching those of the tissue to be replaced. Scaffolds production for tissue regeneration is one of the main fields where the "Design for Function" feature of AM make the difference relative to the other production techniques if in the production process all the needed "Functions" can be introduced: mechanics, geometry (porosity and shape), biomaterial, bio-active molecules and surface chemical groups. In this scenario the use of polymeric nanocomposites with bio-functionalised layered fillers in a 3D printing device is a smart and effective solution for the production of scaffolds for bone regeneration. In fact biocompatible layered fillers, like hydrotalcites [2], also known as anionic clays or layered double hydroxides and zirconium or titanium phosphate [3], can be modified through the intercalation of active species with biocidal activity and then dispersed in a proper bioresorbable polymer using the melt blending technique. The exfoliation of these layered fillers into the polymer allows the preparation of bionanocomposites with better mechanical, cell differentiation [4] and drug delivery [5] properties that greatly enhance the effectiveness and the stability of bone scaffolds. In this work MgAl-hydrotalcites and zirconium phosphate intercalated with high loading (up to 54 wt%) with ciprofloxacin and gentamicin antibiotics respectively were successfully employed as active fillers of polyethyleneoxide terephthalate/polybutylene terephthalate (PEOT/PBT) copolymer, already used for clinical applications in orthopedic surgery thanks to its special properties of biocompatibility, elasticity, strength, wettability and biodegradation rate [6]. The fine dispersion of the fillers, confirmed by XRD and SEM/TEM analyses, was obtained using a twin screw extruder in the melt blending process that allows a good exfoliation/intercalation of the layered compounds into the polymeric composite materials. Several composites with different loading of active fillers (from 5 to 20 wt%) were prepared and characterized in order to determine the mechanical (tensile, flexural and compression test). The evaluation of the biocidal activity on *Staphylococcus epidermidis* (Gram +) and *Pseudomonas aeruginosa* (Gram -) strains was also carried out by means of a Dose Response screening assay. With the aim of optimize the suitable features of the final manufacts, selected nanocomposites were employed for the preparation of scaffold prototypes for the bone regeneration using a 3D printer device. After the optimization the final scaffolds will be prepared at c-GMP level and tested in pilot *in vivo* trials.

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MINERALOGICAL AND GEOCHEMICAL CHARACTERISTICS OF KAOLIN OF VERKHNE-ASHUTSKOE KARST DEPOSIT IN KAZAKHSTAN

Dmitriy Sivkov (1,2), Yulia Bocharnikova (1), Natalia Boeva (1)

(1) IGEM RAS, Moscow, 119017, Russia, (2) MSU, Moscow, 119991, Russia

Kaolin clays in the structure of Verkhne-Ashutskoe karst bauxite deposit (Central Kazakhstan) are localized in large sinkholes and often block the bodies of industrial bauxite.

Within the structures of the folded basement the deposit is localized in areas of carbonate rocks which control the accumulation process of kaolin and bauxite. Bauxite in these areas is usually enclosed in the largest karst sinkholes. Genetically bauxite are associated with continental lacustrine-marsh, predominantly clayey sediments, within which horizons of kaolin refractory clay occur, which contain free alumina and fine variegated and black lignite-bearing rocks.

Clays and bauxites were formed in a warm, variably humid climate which comparable to the current climate of tropical savanna.

A distinctive feature of the layered lithology profile is the presence of lignite layers, below which within the profile is the process of bleaching of clays and bauxite, that are usually brown colored because of impurities of iron oxides.

In this study, a profile parallel to the quarry wall was selected and 12 representative samples with varying intervals were collected from an exploratory pit. Of these, 7 samples belonged to the bauxite ores, 3 — to the clay, and 2 to the lignites.

The chemical composition of the ore deposits has the following average content of main components: Al_2O_3 = 40.0-44.9%; SiO_2 = 11.5-14.5%; Fe_2O_3 = 15.3-23.3%; TiO_2 = 3.0—3.7%. The average silicon module is 3.4. Kaolin clays form thick (up to 30 m) layers in the upper, middle and lower parts of the lithological profile and it’s a high-alumina refractory raw materials.

The analysis of clay and bauxite substance by the complex of precision methods allowed us to identify a number of mineralogical and geochemical features. For the first time by the SEM (Scanning Electron Microscopy) and STA (Simultaneous Thermal Analysis) perfect biogenic gibbsite crystals that grew on the surface of the lignite film in bauxite and biogenic discoid aggregates (crystal twins) of nanohematite in the ferruginous nodules of kaolin clays were discovered.

The highest silica content among all samples (25.5-45.8% SiO_2) was detected in samples of kaolin clays. The amount of alumina varies from 23.4% to 44.8%. In some samples the high content of iron oxide (40% Fe_2O_3) was observed. According to the results of XRD analysis the iron oxides are present in samples in form of goethite and hematite. The average loss on ignition is 14.5% of the initial mass and doesn’t exceed 21%. The bulk of water in these clays is enclosed in the crystal lattice of kaolinite. Values of silicon module of clay samples don’t exceed 1.5.

All samples were studied by simultaneous thermal analysis instrument STA 449 F1 Jupiter “Netzsch”. The heating rate was 10°/min till a temperature of 1050 °C in argon atmosphere. Before filling the chamber with argon the air was deflated from the chamber. The weight of the portion ~ 40 mg.

According to the analysis results it can be argued that the bulk of bauxite and clays is composed by kaolinite and gibbsite in different proportions. The maximum value of the enthalpy of kaolinite dehydroxylation corresponds to the temperature range 524.1-538.3 °C.

The biggest amount of gibbsite from all the studied samples was found in the sample of stony iron-poor bauxite, kaolinite - in the sample of clay. These features can be observed on the DSC (Differential Scanning Calorimetry) plots of samples: among all samples that contain gibbsite, the most intense endothermic effect that corresponds to gibbsite (-776.2 J/g) were present on the DSC plots of the iron-poor bauxite sample, and among all samples that contain kaolinite - on DSC plot of clay sample (-383.3 J/g).

According to the TG (Thermal Gravimetry) plot clay samples have relatively small total losses on ignition that can be explained by the high organic matter content.

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POZZOLANIC REACTIVITY AND REACTIVE SITES OF CALCINED CLAYS FROM A COMBINATION OF CHEMICAL METHODS AND SOLID-STATE NMR SPECTROSCOPY

Jørgen Skibsted, Cristina Ruiz-Santaquiteria, Nishant Garg

Department of Chemistry and Interdisciplinary Nanoscience Center (iNANO), Aarhus University, DK-8000 C Aarhus, Denmark

The use of calcined clays as supplementary cementitious materials (SCM's) may provide a valuable contribution to the reduction in CO_2 emissions associated with cement production since calcined clays can be produced at significantly lower temperatures and do not involve a decarbonation reaction. Thermal activation of clay minerals involves dehydroxylation of the aluminate and silicate sheets which introduces a progressive degree of disorder in the heated material. ^{27}Al and ^{29}Si MAS NMR spectroscopy have the advantage that amorphous and crystalline phases are detected in an equal and unambiguous manner and thus, these tools are ideal in studies of the thermal activation of both pure and impure clay minerals [1-3]. In addition, ^{27}Al and ^{29}Si MAS NMR can provide the degrees of reaction for the principal cement and calcined clay phases which can be utilized in thermodynamic modeling of the hydrate phase assemblages in these blends [4]. Moreover, valuable structural information is also achieved about the calcium-silicate-hydrate phase (C-S-H) [5], formed as the principal hydration product in Portland cement - calcined clay blends.

A common approach to evaluate the reactivity of SCM's is the Chapelle's test which probes the pozzolanic reactivity by measuring the amount consumed $Ca(OH)_2$ in $Ca(OH)_2$ - SCM suspensions. For these experiments, additional information can be achieved by studying the solid residues by ^{29}Si and ^{27}Al MAS NMR, which allows identification of the formed hydration products and the remains of SCM in a semi-quantitative manner. In addition to this approach, the present work employs a combination of chemical methods and solid-state NMR to identify the reactive species in clay minerals calcined at different temperatures.

Highly pure samples as well as commercial samples of kaolinite and montmorillonite have been examined at heating temperatures in the range 400 - 1100 °C. For each sample, the degrees of dissolution in acidic and basic media have been determined, using a 1% (v/v) HF solution and an 8.0 M NaOH solution, respectively. The solid residues from these experiments are analysed along with the calcined starting materials by ^{27}Al and ^{29}Si MAS NMR. A comparison of these spectra, before and after dissolution, enables a clear differentiation of the silicon and aluminium environments that are present in each sample, providing direct information about the aluminate and silicate species which are dissolved under basic and acidic conditions, i.e., identification of the active sites in calcined clays. Moreover, this procedure facilitates the structural assignment of the different silicon environments observed by ^{29}Si NMR, shedding light on the dehydroxylation process and on the structural changes that occur for kaolinite and montmorillonite upon heat treatment.

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INACTIVATION OF *STAPHYLOCOCCUS AUREUS* USING A LASER LIGHT-ACTIVATED METHYLENE BLUE EMBEDDED IN COLLOIDAL MATERIALS

Miroslava Smolinská, Lucia Černáková*, Helena Bujdáková

Comenius University in Bratislava, Faculty of Natural Sciences, Department of Microbiology and Virology, 842 15 Bratislava, Slovakia
*cernakova@fns.uniba.sk

Resistance of *Staphylococcus aureus* to common used antibiotics represents a big medical issue. Nowadays, nanotechnology brings new possibilities in an effective inactivation of bacterial cells. Colloidal materials with embedded photosensitizers represent prospective agents from environmental and medical viewpoints. Colloids based on synthetic layered silicates of saponite type, including those modified with dodecylammonium chloride (C12) and methylene blue were studied in this experimental work. The Gram-positive bacterium *Staphylococcus aureus* CCM 3953 and diode laser source, which emits light with a wavelength of 665 nm were selected for this study. The colloidal dispersions effectively absorbed the laser light and upon illumination with visible light, generate singlet oxygen in aqueous solution. This was proved by EPR spectroscopy using a spin trapping agent. Photodynamic efficiency depended on the growth phase in which the bacteria were tested, and increased with preincubation with the photosensitizer. Probably, surface properties of the smectites were important for the contact with bacterial cells. The saponite-C12-methylene blue ratio played a significant role in the interaction with cells. Modification of saponite with the C12 surfactant led to the significant enhancement of methylene blue photophysical activity. The presence of C12 cations with disinfectant biocide properties would additionally be predicted to suppress dye molecular aggregation. Therefore the choice of the clay mineral, saponite-methylene blue ratio, or the presence of C12 surfactant adsorbed on silicate particles significantly influenced the antimicrobial properties of colloid systems. After methods optimalization (testing of different concentration of immobilized methylene blue with different ratios of inert compound as also amonia salt, testing of different times of irradiation exposure, intensity of irradiation and conditions of preincubation) was chosed suitable combination of parametres of tested complexes in regard with expected influence on growth of *S. aureus*. Enhanced antimicrobial efficiency of immobilized methylene blue (26 µmol/l) was demonstrated after 10 s of irradiation with laser source (5.58 J/cm^2). Immobilized methylene blue on smectite (0.65 mg/ml) and free form of methylene blue were preincubated for 30 min at 37 °C, 3.4-log$_{10}$ reduction of *S. aureus* cell survival rate was achieved. Significant decrease in surviving bacteria cell count was observed in the case of testing modification of saponite and methylene blue with quaternary ammonium salt C12 (0.17 mg/ml) in the same experimental conditions. It was stated that 3.7-log$_{10}$ reduction in cell survival rate of *S. aureus* was achieved. Another observed important feature of colloidal material was a high adherence of bacteria to these materials what was documented by optical microscopy and scanning electron microscopy. Experiments revealed that the organoclay mineral is the adequate carrier for an immobilization of cationic methylene blue molecules. Photosensitization process with methylene blue embedded in clay minerals using laser illumination is an effective method for inactivation of Gram-positive bacteria. This study exhibited that the interaction of methylene blue with clay minerals could lead to the formation of new materials with effective antibacterial properties.

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PREPARATION OF NANOSHEET-MONTMORILLONITE HYDROGEL FOR REMOVING Pb(II) FROM WATER

Yunliang Zhao (1), Shaoxian Song (1)*, Jian Cai (2)

(1) School of Resource and Environmental Engineering, Wuhan University of Technology, Luoshi Road 122, Wuhan, Hubei, 430070, China, (2) Suzhou Design and Research Institute of NonmetallicMinerals Industry, Sanxiang Road 999, Suzhou, 215004, China

Montmorillonite is widely used as an adsorbent in wastewater treatment for removing contaminated ions and organic composites because of the layered structure. But the small interlayer openings and the low specific surface area limit the applications. In this study, an eco-friendly montmorillonite nanosheets-chitosan (MMNT-CS) hydrogel was prepared to develop a new and effective adsorbent. The fabrication of the MMNT-CS hydrogels were realized through the self-assembly of MMNT and CS chains. The prepared MMNT-CS hydrogels were characterized by AFM, SEM, TEM and nitrogen adsorption, and were tested on the adsorption of Pb(II) at the interface of water/hydrogel for the Pb(II) elimination from water. The effect of solution pH, contact time, initial Pb(II) concentration and temperature on Pb(II) adsorption from water were investigated. The experimental results indicated that the exfoliated MMNT enhanced the removal efficiency and adsorption rate of Pb(II) compared to pillared montmorillonite owing to the increase of the effective adsorption sites. The Langmuir and Freundlich adsorption models have been applied to evaluate the adsorption efficiency and the data correlated well with the Langmuir model. The adsorption mechanism was found to be due to the ion exchange according to the analysis of XPS and FTIR.

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ANODE MATERIALS FOR LITHIUM ION BATTERY SYNTHESIZED FROM LAYERED DOUBLE HYDROXIDES

Noriyuki Sonoyama*, Yoshitaka Ogasawara, Testuya Tsukada, Satoshi Yoshida

Department of Materials Science and Engineering, Nagoya Institute of Technology, Gokiso-cyo, Showa-ku, Nagoya 466-8555, Japan

A new conversion type anode material for lithium ion battery utilizing the redox activity of aluminum (III) ion has developed. Conversion type materials are known to have a serious weak point as anode materials, that is the high reaction voltage in spite of its high capacity (over 600 mAh/g). This high reaction voltage originates in high redox potential of transition metal oxide such as NiO or CoO, those are known as representative conversion anode materials for lithium ion battery. In order to improve this high reaction voltage, it is effective to use oxides of light metal with lower redox potentials such as aluminum oxides, titanium oxide and so on. However, aluminum oxides are difficult to use as the electrode materials owing to the low electric and ionic conductivity. We have synthesized solid solution of nickel oxide and aluminum oxide with nano level particle size by calcination of Ni-Al layered double hydroxides (LDH). In the previous studies, we have investigated the structure and electrochemical properties for the solid solution of NiO with TiO_2 or V_2O_5 [1-3]. The fine structure of calcinated materials are determined by XRD and XAFS: Ni^{2+} and Al^{3+} ions are randomly locating metal ion sites of NiO with rock salt structure and cation vacancies are introduced to compensate the excessive charges brought by the aluminum ions. In this structure, electron and lithium ion are expected to be supplied via NiO type host structure and cation vacancies, respectively.

The charging capacity of the half cell with lithium metal counter electrode from 0.03 V to I.5 V, that corresponds to the discharge capacity of the full cell was improved to 600 mAh/g, whereas that for pristine NiO was 230 mAh/g. This improvement of capacity in the lower voltage region is expected to originate in redox of aluminum ion. The redox activity of aluminum ion was confirmed by ex-situ XANES measurement at Al K edge. The absorption edge of aluminum ion shifted to lower energy direction with discharge from 1560 keV to 1556 keV. With charging, the absorption edge of aluminum shifted back to the initial position. This directly indicates the redox activity of aluminum ion during charge-discharge. This is the first report of anode material for lithium battery that utilizes redox of aluminum ion as far as we know.

In order to investigate the detailed reaction mechanism, ex-situ XRD and XAFS measurements were carried out. On the basis of these results, the reaction mechanism of Ni-Al binary metal oxide was concluded as follows. In the higher voltage discharge process (OCV-1.0 V), lithium intercalation into the cation vacancy and lithium ion adsorption to the surface of Ni-Al binary metal oxide with the partial redaction of nickel ion are proceeding [1]. In the lower voltage discharge (1.0-0.03 V), the conversion reaction proceeds with the reduction of Ni and Al ions. In the lower voltage charge process (0.03-1.0 V), only aluminum ion is oxidized to form an intermediate state, where aluminum ion makes complex with surrounding oxide ions. In the higher voltage charge process, nickel metal is oxidized to re-form the Ni-Al binary metal oxide with the rock salt structure.

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OPTICAL PROPERTIES OF Eu (II), (III) IONS DOPED METAL OXIDES OBTAINED FROM SINTERING LAYERED DOUBLE HYDROXIDES

Noriyuki Sonoyama, Keita Takagi, Satoshi Yoshida, Yoshitaka Ogasawara

Department of Materials Science and Engineering, Nagoya Institute of Technology, Gokiso-cyo, Showa-ku, Nagoya 466-8555, Japan

Eu^{3+} has a stable valence in sintering process in air and can be easily activated, therefore it is used as a luminescent center in many materials. The luminescence shows a large number of linear luminescence due to the $^5D_J$to^7F_J transition, a magnetic dipole transition at the transition of $^5D_0$to $^7F_1$ (near 580 nm), and an electric dipole transition at the transition of $^5D_0$to $^7F_2$ (near 600 nm). In order to develop an excellent red phosphor, it is necessary to promote electric dipole transition with high purity and suppress the magnetic dipole transition. The intensity ratio of these two luminescence depends largely on the local structure of the host, and in the inverted asymmetric structure, the electric dipole transition is the center. Therefore, in this study, we used a layered double hydroxide (LDH) doped with Eu^{3+} as a precursor to form a structure not including inverted symmetry in the local structure of binary metal oxide with solid solution of the tri-valence metal ion in $M^{II}O$ structure. We have investigated the correlation between its structure and luminescent properties

$Mg(NO_3)_2$ 6 H_2O, $Al(NO_3)_3 \cdot 9H_2O$, $Eu(NO_3)_3 \cdot x\,H_2O$ was dissolved in distilled water at a ratio of Mg: Al:Eu = 66: 33: 1 and was kept constant LDH was synthesized by a coprecipitation method in which the pH of the solution was controlled by dropping NaOH-Na_2CO_3 mixed solution.

The synthesized LDH was calcined at 500 °C. for 12 hours to obtain a target metal oxide. The structure of the obtained sample was evaluated by XRD and XAFS, and the fluorescence characteristic was evaluated by a fluorescence spectrophotometer. XAFS measurements were carried outat High Energy Accelerator Research Organization (KEK) Photon Factory BL-7C or BL-9A.

The synthesized LDH was identified by XRD measurement. As a result, the 003, 006 reflection unique to LDH disappeared, and 200, 220 reflections of MgO rock salt type structure newly appeared. The local structure of the metal oxide obtained by calcining LDH at 500 °C estimated from the XAFS analysis result is that Al^{3+}, Eu^{3+}, and cation defects are randomly distributed in the Mg^{2+} site of the rock salt type structure as shown in Fig. 1

The fluorescence spectrum of the obtained sample is shown in Fig. 2. When excited at 250 nm, emission maxima appearing at 613 nm is assigned to electric dipole transition. On the other hand, the emission appearing near 580 nm, is assigned to the magnetic dipole transition, and its emission intensity was about half of that of the electric dipole transition. Originally, since the MgO type structure has inverted symmetry, emission due to electric dipole transition does not appear. However, in the sample obtained in this study, luminescence due to electric dipole transition showed higher intensity than luminescence by magnetic dipole transition. This is because the inversion symmetry is lost by the strain caused from randomly distributing Al^{3+}ion at the Mg^{2+} site.

In the presentation, we will discuss about the adjustable luminescence color of Eu^{2+} ion doped sintered LDH.

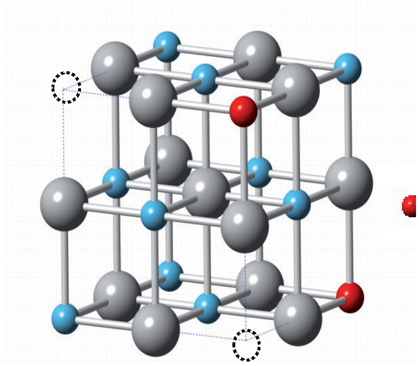

Fig.1. Structure model sintered LDH

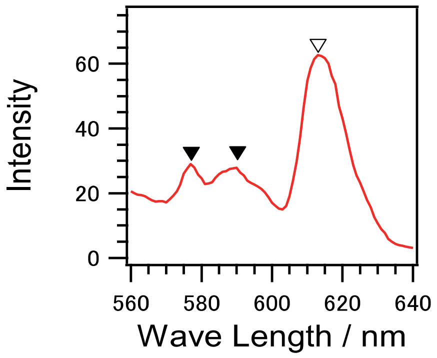

Fig. 2. Photoluminescence of Eu^{3+}dopedsintered LDH

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PHOTOCHEMICAL BEHAVIOR OF PORPHYRINS INCORPORAETD IN ALTERNATIVE STACKED FILMS OF METAL-DOPED TITANATE NANOSHEET

Wasusate Soontornchaiyakul*, Takuya Fujimura, Ryo Sasai

Interdisciplinary Graduate School of Science and Engineering, Shimane University, Matsue, Shimane, 690-8501, Japan
rsasai@riko.shimane-u.ac.jp

Highly efficient photo-induced water-splitting reaction is one of the goals of the artificial photosynthesis researches. Accordingly, many researchers reported various photocatalytic systems for water-splitting reaction such as Z-scheme [1]. Moreover, to achieve the photo-induced water-splitting reaction under visible light irradiation, transition metal doping to metal oxide framework [1,2] and hybridization of photosensitizer with metal oxide [3] were investigated. The hybrid systems of photosensitizer with metal oxide nanosheets have gret potential as photo-harvesting ability, effective photoelectron generation under light irradiation, and others. In this study, we prepared a series of hybrid system of α,β,γ,δ-*tetrakis*(1-methylpyridinium-4-yl) porphyrin ($[H_2TMPyP]^{4+}$) deposited on metal-doped titanate nanosheet (TiNS:A*z*, where A is Rh, etc., and *z* is a doped amount of A), then the photochemical behavior of $[H_2TMPyP]^{4+}$ in the prepared hybrid materials system was investigated.

The $Na_2Ti_{3-x}Rh_xO_7$ was synthesized by solid state reaction, and exfoliated as a TiNS:Rh*z* colloidal suspension in TMAOH aqueous solution [4]. The hybrid of TiNS:Rh*z*/$[H_2TMPyP]^{4+}$ were synthesized as a thin solid stacked films on quartz substrate by conventional layer-by-layer (LbL) method [5]. Photochemical behavior of the TiNS:Rh*x*/$[H_2TMPyP]^{4+}$ hybrid systems were examined by sequentially monitoring absorption spectra with light irradiation under low pressure, and various atmospheric conditions (dry N_2, wet N_2, and Ar gases).

A series of UV/Vis absorption spectra of LbL thin solid films containing of both TiNS:Rh*z* and $[H_2TMPyP]^{4+}$ was observed in every step of immersing process. As a result, the soret absorption band of $[H_2TMPyP]^{4+}$ shifted from 422 nm (in water solution) to 438 nm. This red shift indicated that the environment surrounding $[H_2TMPyP]^{4+}$ molecule has less polarity [6], thus $[H_2TMPyP]^{4+}$ molecules could be intercalated into interlayer space between TiNS:Rh*z* by the present method.

The TiNS:Rh*z*/$[H_2TMPyP]^{4+}$ hybrid film was irradiated for 2 hours by UV of 254 nm which more than 99% of incident UV could be adsorbed by TiNS:Rh*z* due to their wide energy band gap. At steady irradiation, the film changed from red-brown to clear color. The soret adsorption band of $[H_2TMPyP]^{4+}$ at 438 nm was decreasing as the increase of irradiation time. This result showed that the photodegradation of $[H_2TMPyP]^{4+}$ could be found under UV light irradiation. Additionally, the effect of Rh dopant was also found. Consequently, the rate constants of photo-degradation reaction of $[H_2TMPyP]^{4+}$ was increased with an increase in amounts of Rh dopant. Hence, Rh dopant in part of Ti sites can enhance photocatalytic activity of TiNS:Rh*z*.

In addition to visible light of 400, 450, 500, and 600 nm irradiation, it exhibited no detectable change both of soret absorption band of $[H_2TMPyP]^{4+}$ and film color after 24 hours irradiation time. This revealed the stability of hybrid film under the visible light. However, fluorescence quenching of $[H_2TMPyP]^{4+}$ was observed when the hybrid film was irradiated by the visible light of 450 compared to its free particle in water or ethanol solution. Hence, it could be indicated that the electron transfer from $[H_2TMPyP]^{4+}$ to TiNS:Rh*z* occurred when the TiNS:Rh*z*/$[H_2TMPyP]^{4+}$ hybrid film was irradiated by visible light; which shows a possibility to use the TiNS:Rh*z*/$[H_2TMPyP]^{4+}$ hybrid film for photocatytical reaction such as a visible-light-driven hydrogen production.

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MODIFICATION OF CLAY MINERALS WITH ω-AMINOACIDS FOR USE IN DENTAL CEMENTS

Jeroen S. Van Duijneveldt (1), Michele E. Barbour (2), Martha Laura Sosa Madrid (1,2,3)*

(1) School of Chemistry, University of Bristol, Cantock's Close, Bristol BS8 1TS, UK, (2) Oral Nanoscience, School of Oral and Dental Sciences, University of Bristol, Lower Maudlin St, Bristol, BS1 2LY, UK, (3) Bristol Centre for Functional Nanomaterials, University of Bristol, Tyndall Avenue, Bristol, BS8 1TL, UK
*ms15149@bristol.ac.uk

Amines adsorb strongly to smectites such as montmorillonite resulting in intercalated materials/organoclays. Adsorption of omega-amino acids (ω-AA) has the added interest that the modifier itself can be polymerised into a nylon, thus allowing for in-situ polymerisation resulting in a clay nanocomposite [1].

One potential use of such ω-AA modified clay is as a nanofiller in dental filling material known as a glass ionomer cement (GIC). A GIC is an acid-based cement composed primarily of alumina-silica-calcium fluoride glass embedded in a polyacrylic acid matrix. GICs are widely used in dentistry and have many clinically favourable properties, but they lack strength and this limits their applications. Thus methods to enhance the strength of GICs are of interest to the dental materials community. One study observed that adding 12-aminododecanoic acid (ADA) to a clay helped to increase the compressive strength of the GICs. [5,6]. Nevertheless, it has beenmentioned that one of the challenges for mixing clays with GICs is the technique used to get the clay well dispersed into the GICs [7].

The overarching aim of this work is to establish whether ω-AA modified clays could be used to increase tensile and compressive strength of GICs. In this study we treated clay with ADA and with 6-aminohexanoic acid (AHA) and characterised the organoclays using elemental analysis and X-ray scattering. Treatment is done from an aqueous dispersion of montmorillonite (MONT), either by room temperature mixing or by treatment at 80 ºC in acid medium [8].

Small-angle X-ray scattering (SAXS) revealed that ADA treatment resulted in a larger increase in basal layer spacing than AHA, in line with the difference in chain length. However, for AHA an excess had to be added in order to achieve a good intercalation. In contrast with the ADA-MONT, the clay modified with AHA fully exfoliates into water.

Initial compressive strength testing results of GICs modified with 2 wt% of these clays will be presented.

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VALORIZATION OF VARIOUS TYPES OF METAL(LOID) S-CONTAMINATED WASTES FROMCLAY/METAKAOLIN-BASED ALKALINE ACTIVATED MATERIAL: ENVIRONMENTAL AND SANITARY IMPACT

Soubrand Marilyne (1), Joussein Emmanuel (1), Courtin-Nomade Alexandra (1),
Monneron-Gyurits Matthias (1), Rossignol Sylvie (2)

(1) Université de Limoges, GRESE "Groupement de Recherche Eau Sol Environnement", Limoges, France, (2) Université de Limoges, SPCTS, Limoges, France

In a context of circular economy, the valorization way of contaminated mineral waste management (e.g. mining sediments, industrial by-product such as phosphogypsum, slags, sewage-sludge…) is up to date particularly in terms of alkali activated material and geopolymers. In fact, this can be effective if (i) the valorization by alkaline activation uses only untreated wastes, (ii) the environmental and sanitary risks are reduced up to inexistent (dependant of the potential use of the final product), and (iii) the human acceptation of wastes-based material is better (i.e. needed that people are in accordance to have wastes-treated materials in their direct environment). As expected, these types of wastes, as well synthesized materials, are classically highly contaminated in metallic elements which can induce environmental and sanitary risks. So, it is quite important to evaluate the metal(loid)sbehaviour and speciation in wastes as well in the synthesized materials then their leaching behaviour. It is then needed to well characterize by X-ray diffraction, infrared spectroscopy, and electron microscopy the waste, as well their amount and type of clay minerals. About the presence of metal(loid)s element content, the use of modified BCR is a quite useful tool to estimate thechemical speciation (waste and synthesized material), as well the leaching behaviour according for example to EN12-457 or TCLP. Finally, the sanitary risks for each synthesized material may be also estimated using a derived protocol of the UBM - BARGE by taking into consideration various scenario relative to their potential use.

Examples of various effect of geopolymer-based material to incorporate wastes and stabilize the contaminants (elemental dependant) will be done, as well the potential environmental and sanitary risks.

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REMOVAL OF Pb^{2+} AND Cd^{2+} BY ADSORPTION ON A ZEOLITE Y

Ait Hamoudi Souhila (1,2)*, Yahnine Elhossyne (2), Soufi Belkhir (2)

(1) Centre de Recherche scientifique et technique en Analyse Physico-Chimique (CRAPC), BP 384, Siège ex-Pasna Zone Industrielle Bou-Ismail CP 42004 Tipaza Algeria, (2) Laboratoire LPCMAE, Faculté de Chimie, Université des Sciences et de la Technologies Houari Boumediene (USTHB), B.P32 EL ALIA, Bab Ezzouar Alger, Algeria

Heavy metal pollution is a problem associated with areas of intensive industry. However, roadways and automobiles now are considered to be one of the largest sources of heavy metals. Zinc, copper, and lead are three of the most common heavy metals released from road travel, accounting for at least 90 of the total metals in road runoff. Lead concentrations, however, consistently have been decreasing since leaded gasoline was discontinued. Smaller amounts of many other metals, such as nickel and cadmium, are also found in road runoff and exhaust. With the acceleration of the modernization process, excessive use of industrial chemicals, organic compounds and fossil fuels have attracted intensive attention. The use of zeolites can be a solution to this problem. In this present study, a commercial zeolite called CBV was used and tested in the elimination of two inorganic pollutants Lead and Cadmium; retention properties towards both pollutants and a real effluent were studied. This is an industrial discharge of a factory that manufactures batteries and which is located in the industrial zone east of Algiers.

The Lead and Cadmium retention properties were evaluated by adsorption isotherms of CBV, by introducing 60 mg of solid in 50 mL of (Pb^{2+}, Cd^{2+}) aqueous solution at different concentrations (25, 50, 100, 150, 200, 300, 400, 500, 600, 700, and 800 mg/L) for 24 h. These experiments were carried out under experimental conditions (pH 4.5 and 5 (solution pH for Pb^{2+} and Cd^{2+} respectively), and fixed stirring rate) at 298, 308, and 318 K, in order to examine the temperature effect on (Pb^{2+}, Cd^{2+}) removal. CBV is very effective in lead and cadmium retention. Adsorption capacity is pH dependent. CBV has more affinity for lead than Cadmium. Indeed, The adsorption capacity of Pb^{2+} ions increases from 24.83 to 106.66 mg / g when pH increases from 4 to 6. For Cd^{2+}, the adsorbed amount increases from 6.5 to 44.91 mg/g.

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USE OF 2D AND 3D ALUMINOSILICATES IN MODIFIED DRUG DELIVERY

Iane Souza*, Artur Oliveira, Sibele Pergher

LABPEMOL - Universidade Federal do Rio Grande do Norte, Natal, Brasil

The use of aluminosilicates as a drug delivery vehicle has enabled advances in the pharmaceutical industry related to several factors, such as improving the release of poorly soluble drugs in water, delivery in specific and/ or difficult to reach places, access of large molecules to sites intracellular actives and the combination of several active ingredients in a single drug [1,2].

Aluminosilicates are materials with Al, Si and O as main chemical elements of their structure, in which the presence of other elements, as well as the organization of these atoms, lead to the existence of several different types of structures and properties, classified in two-dimensional and three-dimensional [2].

The two-dimensional, also known as lamellar, are mostly clays structurally formed by sheets of SiO_4 tetrahedral connected by sheets of AlO_6 octahedral [2]. The zeolitic materials are three-dimensional aluminosilicates, natural or synthetic, with SiO_4 and AlO_4 tetrahedral connected by oxygen atoms, resulting in a well-defined pore and cavity structure [3,4].

Based on this information, the objective of this study was to evaluate how aluminosilicates with different geometries and accessibility influence the adsorption and desorption of organic molecules such as olanzapine. This understanding shall result as a basis for to know the interactions, advantages, and limitations in the use of different types of aluminosilicates as a drug delivery vehicle.

In this study, the adsorption capacity of a lamellar aluminosilicate, montmorillonite, and a three-dimensional, beta zeolite, were compared using olanzapine as the drug. Sample of zeolite beta and montmorillonite were preheated at 105 °C for 4 h in stove with air recirculation to remove the physically adsorbed water. After this, a mass of 0.5 g of the aluminosilicate was added in a becker with 50 mL of solution of olanzapine (3.0 mg/mL) and left to stir for 72 h. The samples were centrifuged for 20 minutes at 2000 rpm. The supernatant was analyzed to evaluate the drug adsorbed and the decanted solid was characterized by FTIR, XRD and MEV.

For the dissolution test, a mass of developed material, equivalent to 10 mg of olanzapine, was submitted to three types of solutions with different pH (1.2, 6.8 and 7.4) equivalent to the regions of the stomach, first and second region of the intestine under agitation and temperature control (37 ºC). At pre-determined time intervals, aliquots were collected and analyzed for drug concentration.

As a result, it is possible to prove that both montmorillonite and beta zeolite have high adsorption capacity of olanzapine, in which for both cases about 90% of the drug present in the solution was stored in the zeolite pores or in the montmorillonite lamella. In the release test for zeolite beta was verified that even after 10 hours the material did not release to the different solutions. The percentage of drug released was only 27% in the medium to zeolite beta. However, the clay was able to release more than 90% of incorporated drug. The results shows that the pore and cavity organization in 3D aluminosilicate are factors that control the availability of the drug. Finally, the characterizations proves that different types of interactions between the species involved in each case, accentuating the feasibility of applying in modified drug delivery.

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USE OF BRAZILIAN CLAY FOR CONTROLLED-RELEASE OF FERTILIZERS

Iane Souza (1)*, Artur Santana (1), Mauricio Bômio (2), Juan Ruiz (3), Antonio Medeiros (3), Alberto Paskocimas (2)

(1) LABPEMOL - Federal University of Rio Grande do Norte, Natal, Brazil, (2) LSQ - Federal University of Rio Grande do Norte, Natal, Brazil, (3) CTGÁS-ER, Rio Grande do Norte, Natal, Brazil

As a result of population growth and the need to increase food production, the fertilizers to supply the macronutrients critical to plant growth, such as nitrogen, phosphorus and potassium, are an important tool to increase agricultural productivity [1]. Among these macronutrients, nitrogen plays an important role in fundamental functions, making nitrogen fertilizers widely applied to agricultural soils, where the urea fertilizer is the most used due to its high concentration of nitrogen (46.6% wt), low cost, good solubility and easier mixing with other components [2]. However, high volatilization capacity of ammonia and nitrate leaching reduce its efficiency when applied to alkaline and coarse-textured soils. These losses could be significant, for example 50 to 70% of nitrogen can be lost through volatilization when applied through urea to soils [1,3]. An alternative is to optimize the use of fertilizers by encapsulation or mixing with other inert and environmentally friendly materials that promote the controlled release of nutrients to the soils, reducing losses, the need of successive applications and minimize environmental pollution. Among these materials, clay-based formulations due to its high adsorption capacity, easily cation exchange and high surface area can reduce the leaching, photodegradation and volatilization of these fertilizers [4]. Montmorillonite, a clay mineral abundant in bentonites, presents high capacity of cation exchange, being possible to storage NH_4^+ ions from urea hydrolysis, controlling its release to the soil. With this objective, fertilizers based on urea and bentonite, obtained from deposits in Boa Vista(PB-Brazil), were formulated for this study. The formulation was made by compacting mixtures in the form of pellets with 7mm diameter and 4mm thickness. Both urea and bentonite were ground and separated to a 45 mesh size, and subsequently mixed in various mass proportions. For the bentonite: urea composite, a 0.05 g / L polyvinylpyrrolidone (PVP) solution was added to granulate the mixture, making possible to flow during the compacting process, so that each tablet has approximately the same mass. All the materials were characterized using XRD, FTIR, TG / DSC, TPD-NH3, in order to determine physical, chemical and morphological aspects of the raw materials used, as well as the formulated fertilizers. In order to evaluate the volatilization of N_{NH3}fromthe fertilizers, a greenhouse experiment was carried out using the methodology SALE N_{NH3} [5]. The soil used was a sandy-textured Planosol Haplico, collected from 0-20cm depth. The experiment consisted of 33 experimental units evaluating five types of fertilizers, i.e. B1U4, B1U8, B1U16, tablet urea, pearled urea as reference, and soil without fertilization as control. For each fertilizer treatment, two dosages equivalent to 100 and 200 kgha^{-1} of nitrogen were used, with three replications of each treatment, in which the distribution of the experimental units occurred in a random manner.

The results showed that the formulation that reduced more the ammonia volatilization was the one that had less amount of clay, called B1U16 fertilizer, with reduce of ammonia volatilization of 11.20% and 15.98% for the dosages of 100 and 200 kg.ha^{-1} respectively, this result was obtained by comparing the percentage volatilization from pearled urea with formulated fertilizers. Was also observed that using only the technique of compaction and the addition of PVP solution, it is possible to obtain significant reductions in ammonia volatilization applied through urea. Therefore, we conclude that it is possible to reduce the volatilization of ammonia from urea only by changing its geometry and adding elements to control its hydrolysis, as bentonite and PVP which have significantly reduced the losses of urea in the form of ammonia.

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ALUMINUM-HYDROXIDE BASED-WASTE AS AN ABSORBENT FOR WASTEWATER TREATMENTS

Marcelo T. Souza (1), Fabiano Raupp-Pereira (1)*, Rui M. Novais (2), João A. Labrincha (2), Manuel J. Ribeiro (3), Antonio P. Novaes de Oliveira (1)

(1) Laboratory of Glass-Ceramic Materials / VITROCER - Federal University of Santa Catarina, Campus Reitor João David Ferreira Lima, 88040-900, Florianópolis (SC), Brazil, (2) Department of Materials and Ceramic Engineering / CICECO - Aveiro Institute of Materials, University of Aveiro, Campus Universitário de Santiago, 3810-193 Aveiro, Portugal, (3) UIDM-ESTG, Polytechnique Institute of Viana do Castelo, 4900-348 Viana do Castelo, Portugal

Wastes from refineries, food and beverage industries [1], Solvay or ammonia-soda production [2], acetylene gas generation [3], aluminium production from Bayer process [4], steelworks slags [5], air pollution control [6] and chromite ore processing [7] are all examples of alkali-rich materials, composed mainly by calcium and sodium, with recovery potential. However, these are commonly discarded in controlled landfills [8]. In this work it was investigated the feasibility of using Al-anodizing waste (AAW) as an alternative material to treat alkali-rich effluents. This whitish material is highly hygroscopic, is composed by fine particles and shows certain plasticity. It presents similar features to mineral clays commonly used in wastewater treatment applications [9]. The AAW is produced in large quantities and, despite many applications have been proposed [10-13], is still mostly cast in landfills after previous treatment. In this work, the waste was tested as an alkali-exchange material. Its characterization involved chemical (XRF) and mineralogical (XRD) determinations, while zeta potential and electrical conductivity measurements of aqueous suspensions containing calcium or sodium hydroxides were conducted to test its cationic exchange potential. The results revealed amorphous aluminum hydroxide as the main present compound. Zeta potential and electrical conductivity analysis showed the waste as an amphoteric material in neutral medium, however, presents high reactivity in alkaline environments. XRD analisys displays calcium and sodium compounds precipitated as from alkali reactivity of the waste.

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INFLUENCE OF MAGNESIUM OXIDE IN THE ACTIVATION OF BENTONITIC CLAYS OF THE CITY OF SOSSEGO, PARAÍBA, BRAZIL, FOR APPLICATION IN WATER BASED DRILLING FLUIDS

Ivna Daniele Souza Pereira*, Isabelle Albuquerque Da Silva, Vanderlane Cavalcanti Da Silva, Romualdo Rodrigues Menezes, Gelmires De Arújo Neves

Academic Unit of Materials Engineering, Federal University of Campina Grande - UFCG, Bodocongó, Campina Grande-PB, 58109-970, Brazil
*ivnadaniele@hotmail.com

Bentonite clays allow large modifications planned in their microstructure, thus allowing specific properties to be obtained, making these materials to be applied in an immense range of industrial uses, among the several applications, it stands out its use in drilling fluids. Thus, this work aims to characterize physically, mineralogically and technologically bentonite clays of the City of Sossego, PB, Brazil, for use as a thixotropic agent in the formulation of drilling fluids. For this, the clays were characterized by the following techniques: laser granulometry (AG), X-ray diffraction (XRD), chemical analysis (EDX), cation exchange capacity (CTC), thermogravimetric (TG) And thermal differential (DTA). Then the clays were transformed into sodium by treatment with sodium carbonate (Na_2CO_3) and activated with combinations of (Na_2CO_3) and magnesium oxide (MgO). Subsequently, the rheological behavior of the dispersions was studied in order to determine apparent viscosity (VA), plastic viscosity (PV) and pH. The results showed that the samples studied presented typical characteristics of the bentonite from the State of Paraíba, showing the typical clay minerals, smectite, kaolinite and accessories. Concerning the use of clays as a viscosifying agent for drilling fluids, it was observed that clays activated with Na_2CO_3 partially accord the specifications required for use in water based drilling fluids. However, the combination of Na_2CO_3 and MgO, for the activation of the clays, produced an improvement in the properties of the fluids produced, proving to be applicable in well drilling.

Keywords: bentonites, drilling fluids, rheological properties.

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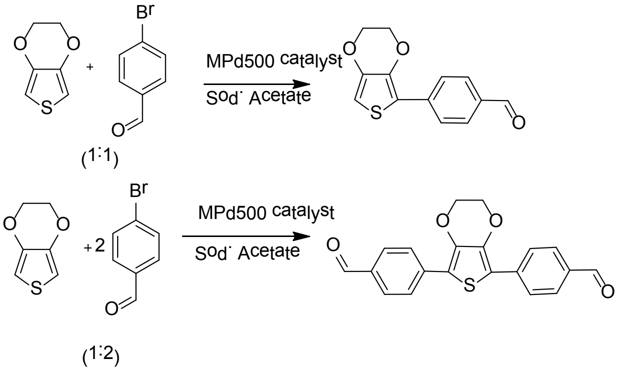
EFFICIENT SYNTHESIS OF MONO- AND BIS-ARYLATED 3,4-ETHYLENEDIOXYTHIOPHENE-BASED FUNCTIONAL π-CONJUGATED MOLECULES VIA CLAY SUPPORTED PALLADIUM CATALYSED DIRECT ARYLATION REACTIONS

Sneha Sreekumar (1), Sowmya Xavier (2), Kannan Vellayan (3), Beatriz González (4)*

(1) College of Integrated Studies, University of Hyderabad, Telangana, India, (2) Department of Applied Chemistry, Cochin University of Science and Technology, Kerala, India, (3) Department of Chemistry, Government College, Kattappana, Kattappana, Kerala, India, (4) Dep. Química Inorgánica, Univ. de Salamanca, 37008- Salamanca, Spain

Among all the thiophene derivatives, 3,4-ethylenedioxythiophene (EDOT) based π-conjugated polymers have been extensively investigated for the past decade, because they exhibit unique properties such as electrochromic as well as electrooptic behaviour. They form part of low band gap polymers. The EDOT based thienyl oligomers are mostly synthesized using in situ prepared 3,4-ethylenedioxythiophenyl-2-magnesium bromide [1]. Additionally, the synthesis of EDOT based thienyl oligomers has been also achieved using stable 2-tributylstannyl-3,4-ethylenedioxythiophene [2] and the 2-pinacol-boronate ester of 3,4-ethylenedioxythiophene [3]. Recently, a direct C-H arylation of heteroarenes with aryl iodides was reported, using a palladium catalyst [4]. A procedure for the synthesis and characterization of the EDOT based π-conjugated molecules through clay supported Pd-catalysed direct C-H bond activation (arylation) is reported in the present communication. EDOT and halobenzene derivatives (dibromobenzene, 4-bromobenzaldehyde, 4-iodo nitrobenzene, 4-bromoanisole and 9,10-dibromoanthracene) are taken in the ratio 2:1 or 1:1 in 10 mL of dry dimethylacetamide/dimethylformamide in three-necked round bottom flask under nitrogen atmosphere. To this, sodium acetate (2 mmol), tetrabutylammonium bromide (8 mmol) and clay supported palladium catalyst (MPd500) (10 mg) was added. The reaction mixture was allowed to stir at 80 ºC for 12 hours. The mixture was poured into water and extracted with dichloromethane. The organic layer was washed several times with brine, water and dried using $MgSO_4$. The product was recrystallized using chloroform. The products were analysed with LCMS, and comparison with reported spectral data (FT-IR, ^{1}H NMR) and melting points. The yield of the products correlated well with the expected electronic effects of the substituents. Reusability of clay supported palladium catalyst towards direct arylation reaction was tested for three reaction cycles without significant loss of catalytic activity.



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HYDROTHERMAL ALTERATION OF THE EDIACARAN BASALTS OF THE EAST EUROPEAN CRATON: A MODEL FOR MARTIAN CLAYS?

Jan Środoń (1)*, Oksana Kuzmenkova (2), Jan J. Stanek (3), Sirle Liivamägi (1)

(1) Institute of Geological Sciences, Polish Academy of Sciences, Krakow, Poland, (2) Republican Unitary Enterprise "Belarussian State Geological Center", Minsk, Belarus, (3) Jagiellonian University, Krakow, Poland
*ndsrodon@cyf-kr.edu.pl

140 thousand km^2 Ediacaran basalt trap, up to 500 m of lavas and volcanoclastics, covers the western margin of the East European Craton (SW Belarus, NW Ukraine, N Moldova, NE Romania, and E Poland). These rocks underwent a pervasive hydrothermal alteration. They have been studied for decades, mostly by microscopic and chemical techniques. In particular, glassy-looking accumulations of dark material, known under name "chloropheite" were found even in very fresh-looking basalts. This contribution reports the investigation of mineral composition of basalts, including those with chloropheite, based on the bulk rock quantitative XRD, chemistry, Mössbauer spectroscopy, and XRD of clay fractions.

Quantitative XRD of the bulk rock provided the content of major primary minerals of basalt: basic plagioclase, pyroxene, magnetite, ilmenite and pseudobrookite. In the investigated samples their sum, used as an index of basalt alteration, ranges from 93% to 4%, but never reaches 100%. Down to 80%, additional minerals present are quartz, dioctahedral and trioctahedral smectite, subsequently also Kspar and hematite. Below 80%, the contents of all these minerals increase, appear chlorite and chlorite-saponite as common components, and rare zeolites: analcime and clinoptilolite. Finally dioctahedral smectite (or illite-smectite in parts of the province which underwent burial diagenesis) and chlorite become dominant rock components.

The alteration of basalts took place in oxidizing conditions, as recorded by the appearance of hematite and by good positive correlation between the percent primary minerals and Fe^{2+}/Fe^{3+} ratio of the bulk rock, measured by the Mössbauer spectroscopy. The Mössbauer ratios can be reasonably well modeled using the XRD mineral composition, if both di and trioctahedral smectite are assumed to contain more Fe^{3+} than Fe^{2+}, while chlorite contains more Fe^{2+}.

Chloropheite inclusions are composed of di and trioctahedral smectites and quartz, in proportions analogous to those measured in the surrounding basalt. In more altered samples, traces of smectite chloritization are detectable. The volcanic glass, reported earlier based on petrographic observations, was not detected. Fe^{2+}/Fe^{3+} ratio of the chloropheite inclusions is identical as of the surrounding basalt. These observations offer no clue to solve the puzzle of smectites origin: whether they are products of final crystallization from the basaltic lava, altered latter by the hydrothermal action, or purely hydrothermal minerals.

The chemical composition of basalts changes during the hydrothermal alteration in a systematic manner, but without major mass gain or loss: CaO decreases from 9 to 2%, Na_2O decreases slightly, except of the rocks with analcime, MgO increases twice, from 4-5 to 9-10%, and B increases three times. Only in the most altered rocks an increase in K_2O is noted. LOI (bound water + OH) increases ten times: from 0.4-0.5 to 5-6%. No clear trends were noted for other major or trace elements.

These chemical and mineral alteration trends are even more pronounced in tuffs interbedded with basalt flows, which also are much more acidic (SiO_2 higher by 10-20% than in basalts). Locally tuffs contain also up to 37% of 1Mtv aluminoceladonite, a mineral not noted in basalts. In such cases enrichment in K_2O instead of MgO is observed.

Top surface of the basalt series underwent intense Ediacaran weathering of lateritic type, producing vertical succession of dioctahedral smectite, mixed layer smectite-kaolinite and pure kaolinite, accompanied by increasing amount of hematite and characterized by an intense loss of mass of the primary rock.

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ZEOLITE- AND/OR BIOGENIC OPAL-RICH TUFFS AND CLAYS, AND THEIR USE IN OLIVE OIL MILL WASTE TREATMENT

George Stamatakis, Michael Stamatakis*, Ioanna-Stefania Stamataki

Department of Geology and Geoenvironment, National and Kapodistrian University of Athens, Zografou, 15784, Attica, Greece
*stamatakis@geol.uoa.gr

Europe's olive oil production is estimated at about 2,2×10^6 tons annually, most of which comes from the Mediterranean Countries, particularly Spain, Italy and Greece. During its extraction a large volume of olive oil mill waste [OOMW] is generated and subsequently discarded in the environment. OOMW is considered an important pollution factor mostly due to its heavy organic load, having Biochemical Oxygen Demand (BOD) and Chemical Oxygen Demand (COD) that can reach up to 100 and 220 g/L, respectively. Several methods for the degradation of the OOMW have been proposed, the majority of which involve physicochemical and microbial treatment of the wastes. Natural absorbents of diverse origin have been successfully tested for OOMW treatment, zeolite tuffs, clays and diatomite being among them. The aim of the present study is to characterize and test the OOMW absorption capacity of rocks containing biogenic and/or volcanic-derived micro-porous components. The absorbent materials tested were: 1- biogenic opal-A-rich clayey rocks, mainly with the form of cylindrical diatom frustules [central Greece], 2- opal-CT- and zeolite [clinoptilolite]-rich clayey rocks [Cyprus]. 3- zeolite [chabazite]-rich tuffs [Tuscany, Italy], and 4- saponite/montmorillonite and zeolite [chabazite and minor phillipsite]-rich tuffs [Samos Island, Greece]. All the samples were analyzed to define their mineralogy, chemistry, micro-texture, apparent density, particle size distribution, pH, CEC, SSA, Cumulative Volume of Pores, Cumulative Surface Area of the Pores, Average Pore Width and Oil Absorption Values for two grain size fractions, <0,25mm and 0,25 -1,4mm. The OOMW used, was collected on January 2016 from a three-phase centrifugal olive processing plant, located in western Peloponnesus, Greece. The pH, BOD, COD and TOC content of the OOMW were also measured. Despite the presence of common minerals in the studied samples, they all exhibited diverse mineralogy defined by the major element chemistry. Significant differences were found in the micro-structure of the samples and the other physicochemical characteristics. Regarding the OOMW absorption capacity, the clayey rock of Cyprus exhibited the best results in both granulometries and was the sample with the most complex mineralogy, containing all three active components: smectite clays, zeolites and biogenic opal. Correlating the parameters measured it was revealed that the OOMW absorption capacity of the samples depended on their Cumulative Volume of Pores and not their Specific Surface area or CEC. It is therefore concluded, that the coexistence of multiple micro-porous components in the clayey sample, a case that rarely occurs in sedimentary deposits, is the main reason of its efficiency to act as functional OOMW absorbent.

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MICROBIAL DIVERSITY IN COMPACTED BENTONITE UNDER DEEP GEOLOGICAL HIGH-LEVEL RADIOACTIVE WASTE REPOSITORY CONDITIONS

Jana Steinová (1)*, Rojina Shrestha (1), Alena Ševců (1), Roman Špánek (1), David Dobrev (2), Václava Havlová (2), Milan Zuna (2)

(1) Institute for Nanomaterials, Advanced Technology and Innovation, Technical University of Liberec, Bendlova 1407/7, Liberec, CZ-460 01, Czech Republic, (2) UJV Rez, a.s., Hlavní 130, Rez, Husinec, CZ-250 68, Czech Republic

Deep geological repository (DGR) is the globally accepted solution how to treat and manage spent nuclear waste (SNF) and high level waste (HLW). The safe disposal is based on the so-called multi-barrier safety concept, employing several engineered and natural barriers in order to ensure no harm to man and biota. The Czech deep geological repository (DGR) concept assumes that waste packages containing spent nuclear fuel (SNF) assemblies will be enclosed in steel-based canisters placed in vertical or horizontal boreholes at a depth of ~ 500m below the surface. The void between the canisters and the host crystalline rock will be backfilled with compacted bentonite which will make up the final engineered barrier. Processes that can influence any barrier, leading toward potential loss of its safety functions, need to be defined, described and understood. Canister material corrosion in the contact with bentonite belongs to one of those processes that can be influenced by microbial presence. Therefore, the microbial abundance and diversity need to be studied even during the experiments focused on corrosion process description.

In this work, we studied the composition of bacterial communities present in compacted bentonite samples recovered from long-term experiment of the MACOTE (Material Corrosion Test) project. The experiments have been performed in the Grimsel test site (Switzerland), simulating the initial phase of canister corrosion process at elevated temperatures after the repository closure. Samples of selected metal materials (copper, copper-coated steel, carbon and stainless steel) were placed into individual test modules and surrounded by either sodium bentonite (MX-80) or calcium-magnesium bentonite of Czech origin. Five identical modules (UJV design) were positioned in boreholes around 5 metres deep in granitic massive (2015). The modules have been constantly heated. Those would be removed after 1, 2, 5, 7 and 10 years. The first module was removed from the borehole after one year (2016) and the bentonite samples collected from this module were subjected to microbiological analysis.

Molecular biological approach was chosen to determine the composition of bacterial communities present in bentonite samples, namely NGS amplicon sequencing of V4 region of 16S rRNA gene and quantitative PCR analyses targeting sulphate-reducing bacteria (SRB), nitrate-reducing bacteria (NRB) and methanogenic archea. In addition, sample of groundwater, surrounding bentonite sealing, is being analysed using the same methods. When interpreting the results, we will focus on the differences in microbial consortia among different bentonite types, and between bentonite and water samples. The results of presented work will help to understand the microbial processes taking place during canister material corrosion in contact with compacted bentonite under repository conditions and their possible effect on engineered barrier systems.

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STRUCTURAL MODIFICATIONS OF KAOLINITE AND SMECTITE INDUCED BY THERMAL ACTIVATION

ANNETT STEUDEL (1)*, RAINER SCHUHMANN (1), PETER THISSEN (2), FELIX DATHE (3), CLAUDIA SCHMIDT (3), FRANK DEHN (3), GISELA GUTHAUSEN (4), KATJA EMMERICH (1)

(1) Karlsruhe Institute of Technology, CMM, Karlsruhe, Germany, (2) Karlsruhe Institute of Technology, IFG, Karlsruhe, Germany, (3) University Leipzig; IMKM, Leipzig, Germany, (4) Karlsruhe Institute of Technology, MVM and EBI Water Chemistry and Technology, Karlsruhe, Germany

Heat-treated kaolinite is currently one of the main raw materials for the production of geopolymers, which can be seen as an alternative binding material in concrete instead of cement. As kaolinite is applied in diverse applications (e.g. ceramic, paper, rubber, plastics, paint) and locally available only, common clays are considered to be a promising alternative which is less expensive compared to other raw materials to produce geopolymers. Common clays consist of several clay minerals comprising kaolinite and 2:1 layer silicates. For their optimized thermal activation before geopolymer production, the thermal (inter-)reactions of these clay minerals up to 1000 °C have to be understood. In the first step, the coordination of octahedral Al will be studied. While 6-fold coordinated octahedral Al (Al^{VI}) of kaolinite is transformed into 4-fold coordinated Al (Al^{IV}) during dehydroxylation (DHX), the octahedral Al^{VI} of montmorillonite is transformed into 5-fold coordinated Al (Al^{V}) [1]. However, Al^{V} is very often observed for dehydroxylated kaolinite [2] and the nature of the 5-fold coordination will be studied in comparison to Al^{V} in dehydroxylated 2:1 clay minerals.

For this purpose, a kaolinite (KBE1-M2) and a montmorillonite (BP-M0.2Na) were investigated. Both materials were obtained by separation of the <2 and <0.2 µm fraction of a kaolin and a bentonite, respectively. Comprehensive mineralogical characterization was performed by XRD, XRF, STA, CEC and layer charge measurement. Afterwards, the samples were thermally treated at elevated temperatures (200/275, 420/480, 555/600, 615/750, 900/900 °C) to achieve full dehydration, partial dehydroxylation (DHX), full DHX and structural decomposition before recrystallization of high temperature phases. The heat treated samples were prepared in the STA (heating rate 10 K/min, cooling rate 20 K/min) in streaming air to record the degree of DHX. The Al coordination and the structural changes were studied by ^{27}Al magic angle spinning nuclear magnetic resonance (MAS NMR) spectroscopy using a Bruker Avance 400 (magnetic field 9.40 T, ^{27}Al Larmor frequency 104.28 MHz, spinning rate 12 kHz, and zirconium rotor 4 mm).

Both clay minerals showed one resonance signal around 0 ppm, characteristic for Al^{VI}. The ^{27}Al MAS NMR spectra of BP-M 0.2 Na showed one small resonance signal at 63 ppm, which revealed the presence of tetrahedral Al^{IV}. The integral of this signal (0.8%) corresponds to the amount of Al^{IV} (0.7%) in the smectite structure. The ^{27}Al MAS NMR spectra of KBE1-M2 also showed a small signal at 66 ppm of Al^{IV} that confirmed the presence of 5% dioctahedral mica with Al substitutions for Si in the tetrahedral sheet. With increasing sample treatment temperature, the overall intensity of the ^{27}Al MAS NMR signals of both samples decreased drastically, while they increased again in the spectrum of BP-M0.2Na after heating to 900 °C due to the incipient recrystallization. Both samples showed a decreasing Al^{VI} signal with progressive DHX. In the ^{27}Al NMR spectra of BP-M 0.2 Na, a new signal appeared at 49 ppm (46 and 51 ppm), which intensity increased with the advanced degree of DHX. The observed Al signal displays a much higher chemical shift than so far published data for Al^{V} (20-35 ppm) and it is more closely to common chemical shifts of Al^{IV} (50-70 ppm) in clay minerals. In the ^{27}Al NMR spectra of KBE1-M2 thermally treated at 555 °C two signals at 22 ppm (Al^{V}) and 54 ppm were observed. The signal at 54 ppm shifted to 45 ppm with rising temperature. In the course of the present study, we are going to identify the nature of the Al^{V} in heated kaolinite and the structural changes responsible for the low chemical shift of Al^{V} in dehydroxylated smectite, which will have a tremendous influence on the geopolymers properties.

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CLAYS IN HYDROCARBON RECOVERY: ADSOPTION AND STACKING BEHAVIOR INVESTIGATED USING COMPUTATIONAL MODELING

Stanislav R. Stoyanov (1,2)*, Feng Lin (1), Yuming Xu (1)

(1) Natural Resources Canada, Canmet ENERGY in Devon, Devon, Alberta T9G 1A8 Canada, (2) Department of Chemical and Materials Engineering, University of Alberta, Edmonton, Alberta T6G 2V4 Canada
*stanislav.stoyanov@canada.ca

Unconventional hydrocarbon resources, such as the oil sands deposits in Western Canada, are increasingly important for addressing the global energy demand. Currently, bitumen is recovered from mined oil sands using hot water extraction (HWE), a flotation process that involves phase separation and leaves large amounts of water trapped in a stable suspension of fine clay particles. Non-aqueous extraction (NAE), an alternative process based on the use of mainly hydrocarbon solvents, eliminates water usage but faces technological and environmental challenges related to solvent recovery [1].

This presentation will discuss the results from previous studies on the stacking and adsorption behaviour of clays representative of the oil sands. A research approach based on computational modelling correlated with experiments is employed to study the stacking and adsorption behaviour of clay minerals representative of the oil sands so as to address important challenges to NAE and HWE. The 3D reference interaction site model (3D-RISM) is employed to calculate the structure and thermodynamics of adsorption of petroleum fragments on clays in solution, as well as the potential of mean force for stacking of kaolinite nanoplatelets in a range of thermodynamic conditions. This model predicts correctly the surface adsorption energies and kinetic barriers related to the liquid organization near a solid surface that have to be overcome by molecules approaching the solid surface [2]. Multilayer adsorption and molecular recognition interactions of heterocyclic compounds representative of heavy oil components with kaolinite in aromatic and aliphatic extraction solvents are calculated and analysed to elucidate the mechanism of adsorption. The isotherms for adsorption for heterocycles are determined experimentally and analysed to calculate the adsorption affinity and capacity [3,4]. Hydrocarbon adsorption on clay in liquid and supercritical CO_2 solvent is also investigated [5]. The effect of flocculant additives on the stacking interaction of kaolinite platelets in aqueous electrolyte solutions is explored to help understand the mechanism of action of hydrophilic and hydrophobic polymers for enhanced flocculation and dewatering of aqueous clay suspensions [6].

The results showcase a powerful computational modelling platform for understanding the mechanism of adsorption and stacking on clays and design of additives to control particle organization in solution. The computational results correlate well with the experiment to present a detailed mechanistic picture of the clay-molecule interactions in solution. The results highlight the importance of this advanced research approach for helping decrease the environmental impact and enhance hydrocarbon recovery from challenging resources, such as the oil sands.

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SORPTION OF Se^{VI} USING NANOCOMPOSITES OF ZEOLITE-NANOPARTICLES ZERO VALENT IRON AND MONTMORILLONITE-NANOPARTICLES ZERO VALENT IRON

Jonathan Suazo (1)*, Katherine Bobadilla (1), María de la Luz Mora (1), Nicolás Arancibia-Miranda (2)

(1) Center of Plant, Soil Interaction and Natural Resources Biotechnology, Universidad de La Frontera.UFRO. Temuco, 4780000, Chile, (2) Faculty of Chemistry and Biology, CEDENNA, Universidad de Santiago de Chile. USACH. Santiago, 8320000 Chile
*j.suazo06@ufromail.cl

The incorporation of selenium (Se) into the environment mainly by anthropogenic activities such as agricultural drainage, oil refinery residues and thermoelectric plants [1] has produced an accumulation of this element in groundwater, affecting drinking water, as reported in Canada and the United States [2]. Se in low concentrations is an essential micronutrient for humans, however when its ingested concentration exceeds 10 $\mu \cdot L^{-1}$ may cause to fatigue, cytotoxicity and genotoxicity [3]. In oxidizing environments the predominant form of this oxanion is selenate (Se^{VI}), in addition Se in natural aqueous matrices is coexisting with other anions, such as arsenate (As^{V}), which could affect the selectivity and removal capacity of the adsorbents used. Among these are the nanoparticles of zerovalent iron (nZVI), which can be immobilized on natural porous substrates such as zeolite (Z), and montmorillonite (Mt), to reduce its mobility and agglomeration [3]. In the present work, nZVI and composites of Z-nZVI and Mt-nZVI were synthesized and was evaluated for the adsorption of Se^{VI} in the presence of As^{V} by means of pH studies (pH 3.0-10.0), kinetics and sorption isotherms. The synthesis of the composite was performed with a theoretical 2:1 mixture of clay:nZVI(w/w) (Z-nZVI and Mt-nZVI). The kinetic studies were performed with 50 mg of material and solutions of 200 $mg \cdot L^{-1}$ Se^{VI} and As^{V} at different times of agitation. For the isotherms 50 mg of absorbent and solutions of Se^{VI} and As^{V} between 0.5-200 $mg \cdot L^{-1}$, NaCl 0.01 M (support electrolyte) at pH = 7.0 in a monocomponent system (MS) and in a binary system (BS). The pH study showed that the maximum sorption of Se^{VI} in a MS using nZVI, Z-nZVI and Mt nZVI between pH 3.0 and 10.0, was 69.4, 40.9 and 24.4%, respectively. On the contrary, in the BS the removal of Se^{VI} decreased for nZVI to 56.9%, whereas for Mt-nZVI and Mt-nZVI to 13.3% to 13.2%, respectively. According to the kinetic studies the model that best describes the sorption process for nZVI was that of pseudo second order, whereas for Z-nZVI and Mt-nZVI it was the pseudo first order. The immobilization of nZVI in Z and Mt generated an increase in Se^{VI} removal of about 8.1 and 28 times, respectively, with respect to the pristine material. Sorption isotherms showed that the model describing the sorption process in MS is that of Freundlich, suggesting that the adsorption in the three adsorbents occurs in a heterogeneous surface and multilayer. With respect to the null adsorption of Se^{VI} determined in the kinetics and isotherms sorption in BS, it may be related to the fact that the functional groups of the absorbents ≡Fe -OOH and ≡Fe-OH have a higher affinity for As^{V} compounds. Therefore it is proposed that the Z-nZVI composite is a better alternative to be used in the removal of Se^{VI} in aqueous systems in which As^{V} is not present.

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STRUCTURAL COLOR OF THE INORGANIC NANOSHEET/POLYMER COMPOSITE GEL

Keiichiro Sueyoshi*, Shinya Yamamoto, Nobuyoshi Miyamoto**

Department of Life, Environment and Materials Science, Fukuoka Institute of Technology 3-30-1, Wajirohigashi, Higashiku, Fukuoka, Japan
**corresponding author: miyamoto@fit.ac.jp

Inorganic nanosheets are obtained by dispersion and exfoliation of inorganic layered crystals in a solvent. Under a certain condition, nanosheets dispersed in a solvent are spontaneously ordered by excluded volume effects, to form crystal phase with regulated structures. We call these kinds of nanosheet colloids as "nanosheets liquid crystal". Further, some of nanosheet liquid crystals show structural colors [1]. Structural color arises from diffraction, reflection and refraction of light. The observed color and layer spacing of the liquid crystal phase is basically correlated based on Bragg's law and Snell's law. Since the color is not due to absorption of light upon electron transition, structural color materials have high durability and, in the case of soft materials, responsiveness to structural changes triggered by external stimuli. In this study, we demonstrate immobilization of the nanosheet liquid crystal with structural color in polymer gel matrix by in-situ polymerization technique, [4] in view of applications as stimuli-responsive soft material.

The layered perovskite nanosheets liquid crystal was synthesized using the method reported previously, [5] followed by removable of excess salt. Into the 2 g of nanosheets liquid colloid, 1.29 mmol of the monomer (*N*-isopropylacrylamide; NIPAm), 649 µmol of crosslinker (*N,N'*-methylenbisacrylamide) and 0.00609 µmol of initiator (2-Hydroxy-2-methylpropiophenone) were dissolved. The mixture was irradiated with UV-light to finally obtain the nanosheet/pNIPA composite gels with structural colors by radical polymerization.

We observed changes in structural color of as the synthetic step proceeds. The nanosheet colloid (2.0 wt% and above) showed pearl-like structural colors of green, purple, and yellow, depending on the view-angle and the concentration. However, the colors disappeared by adding the monomer, cross-linker and initiator. After polymerization and swelling to equilibrium state, colors appeared again. Meanwhile, we confirmed strong birefringence in the samples before and after polymerization by observing the gels with crossed polarizers.

Structural analysis was then performed by small angle X-ray scattering measurement. In the gel with the structural color (nanosheet concentration is 3.0 wt%), the peaks due to lamellar structure with basal spacing of 117 nm was observed. In contrast, no peak was detectable in the sample with no structural color (nanosheet concentration = 1.0 wt%). Thus, the structural color is due to the existence of orientation order and position order of nanosheets in the gel.

The color of the gel was reversibly changed between green and blue by mechanically compressing the gel. The change in the color was confirmed by using reflection spectrum measurements. In the spectrum, a peak is observed at 517 nm before compression and it shifted to 458 nm after compression.

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COMPOSITIONAL CHARACTERS OF FINE SEDIMENTS FROM THE MONTESCAGLIOSO LANDSLIDE (BASILICATA, SOUTHERN ITALY)

Vito Summa (1)*, Agnese Emanuela Bonomo (2), Barry Cameron (3), Erwan Gueguen (1), Salvatore Margiotta (1), Eleonora Paris (4)

(1) IMAA, Istituto di Metodologie per l’Analisi Ambientale, CNR, C.da S. Loja, Z.I., 85050 Tito Scalo, Potenza, Italy, (2) Dipartimento di Scienze, Università degli Studi della Basilicata, 85100 Potenza, Italy, (3) Department of Geosciences, University of Wisconsin-Milwaukee, P.O. Box 413, 53201, Milwaukee, WI, USA, (4) Scuola di Scienze e Tecnologie, Università degli Studi di Camerino, 62032 Camerino, Macerata, Italy

Plio-Pleistocene fine sediments in Southern Italy are often affected by erosion processes and landslides, which are very important hazards to anthropic environments, causing serious socio-economic damage and the loss of human life. Previous research has highlighted the importance of using a multidisciplinary approach to study these processes, integrating geological and geomorphological surveys and geotechnical tests along with detailed compositional characterization of the sediments and a careful definition of the type and intensity of weathering processes [1,2].

This study focused on a large landslide which occurred after intense and continuous rainfall in Montescaglioso (Basilicata, Southern Italy) on 3rd December 2013. The landslide affected a deep ancient slope failure and caused significant damage to buildings and infrastructures in an urbanized zone of the village. The prevailing slip mechanism is translational with a rotational component [3].

The study consisted of the compositional characterization of landslide sediments, belonging to the Subapennine Clay Formation of the Bradanic Foredeep, consisting of a hemipelagic succession of grey-blue marly and silty clays with lenticular sandy and silty bodies [4,5].

The stratigraphic characterization of the sediments from the landslide provided a distinction between debris cover and autochthonous silty-clayey component of the altered bedrock up to a depth of 25 m. Detailed sampling was performed at several depths in order to collect samples representative of all macroscopic lithological, structural and textural changes.

Grain size, mineralogical and chemical characterization of sediments was carried out and Atterberg limits and activity were determined. A new weathering index was used for these sediments and its depth trend was compared to the compositional characters.

Some correlations between compositional characters of sediments and their physical behaviour were detected (e.g. between <8 μm fraction and plasticity). A zone showing an increase in the <8 μm fraction and larger amounts of phyllosilicates was found between 15 and 20 m below ground level, where higher plasticity and liquidity were also detected. The weathering index also showed anomalous values, indicative of an increased alteration in sediments at the same depth. Furthermore, kaolinite also occurs in increased amounts in this zone, and previous studies have already indicated it as a possible risk factor in relation to the triggering of slip in landslides affecting analogous Plio-Pleistocene sediments [1,2]. As such, this depth range could be identified as a possible weakness zone, according to the increased alteration of sediments compared to the surrounding zone in the stratigraphic column. Further studies will be performed to characterize deeper sediments and assess the effectiveness of the latterly discussed compositional characters as predicting factors for the depth of the slope failure and/or as diagnostic elements of an already active slide.

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CHROMIUM AND NICKEL BEARING MINERAL PHASES IN SERPENTINE SOILS FROM THE SOUTHERN APENNINES

Vito Summa (1), Salvatore Margiotta (1), Achille Palma (2), Pietro Pasquale Ragone (1)*

(1) IMAA, Istituto di Metodologie per l'Analisi Ambientale, CNR, C.da S. Loja, Z.I. 85050 Tito Scalo, Potenza, Italy, (2) Centro Ricerche Metaponto, ARPAB, Strada Statale Jonica 106 - Km 448,2 - Località Metaponto 75012 Bernalda, Matera, Italy

The presence of heavy metals in shallow groundwaterand soils, usually related to anthropogenic causes, can also belinked to geogenic factors, in particular geo-environmental contexts characterized by rocks naturally containing these elements. The northern sector of the Pollino Massif (Southern Italy) is a very important pilot case as it is characterized by the presence of ultramafic and crystalline rocks, such as metabasites, serpentinites and gneiss, which are potential natural "tanks" of several heavy metals, including chromium and nickel, enriching the soil and ground water significantly [1,2]. This study investigates the mobility of chromium and nickel inserpentine soils in a cultivated pilot area, through the compositional characterization of soils, parent rocks and the groundwater used for irrigation. Multiple chemical extractions using the BCR scheme were performed and metal concentration data was validated usingcertified reference material BCR-701 (lake sediment).

Samples studied showed the mineralogical paragenesis typical in serpentine soils, together with allogenic contributions mainly consisting of quartz, micas and K-feldspars, in this order of abundance. Dominant minerals were serpentine in chrysotile form and iron chlorite, according tohigh iron concentrations detected in chemical analyses. Diffractometer peaks also showed significant amounts of spinels (chromite and Cr-magnetite) and Cr-chlorite. Olivine and pyroxenes also occur in smaller quantities. Nickel can be released from these primary minerals by weathering and substitute for magnesium in clay minerals during the early stages of serpentine soil development [3,4,5]. Clay minerals were mainly represented by vermiculite and interstratified vermiculite/chlorite. The <2 µm fraction analysis confirmed the prevalence of serpentine, chlorite and amphibole and highlighted the presence of vermiculite/oxide and hydroxideinterstratifiedphases. No significant differences were observed along the stratigraphic profile.

Sequential extraction (BCR scheme) results were consistent with mineralogical analyses. Nickel was distributed among the soluble/extractable, reducible, organic and residual fractions. The latter contains more Ni (67% on average) than the other fractions, whichis typical of the occurrence of Ni-bearing phases such as serpentine, olivine, pyroxenes [5,6], according to mineralogical observations.

Chromium dominates in the residual fraction (89% on average), in line with the presence of spinels and other Cr-rich minerals which are less susceptible to weathering and were dissolved during the fourth step of extraction. However chromite chemical modificationscould increase the potential labile chromium and favour chromite weathering [5,7,8]. This could partially explainthe very high concentrations of chromium detected in the spring watersin the area, together with theintense rock mass fracturing that enhances the rock-water interaction surfaces, favouring the weathering processes.

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MONITORING THE Ar RETENTIVITY OF K/Ar ILLITE FINE FRACTION AGES IN THE CONTACT METAMORPHIC AUREOLE OF THE TORRES DEL PAINE INTRUSION (CHILE)

Annette Süssenberger (1)*, Klaus Wemmer (2), Susanne Th. Schmidt (1)

(1) Department of Earth Sciences, University of Geneva, Geneva, Switzerland, (2) Geoscience Centre, University of Göttingen, Göttingen, Germany

The K/Ar illite closing temperature for illite fine fractions (<0.2 µm, <2 µm) is so far poorly constrained. Early studies reported a closure temperature interval (end of significant diffusion of Ar) for mica fractions (<2 µm) of 260 ± 30 C [1]. Other authors found indications that fine-grained white micas (sericite <2 µm) did not behave as open systems, even at temperatures of 275 °C [2].

This study aims to monitor the Ar retentivity behaviour in a contact aureole setting to set new constraints for the closing temperature of the <0.2 µm and <2 µm illite fractions. The contact metamorphic aureole of the Torres del Paine intrusion in southern Chile (51°S) provides the possibility of studying profiles related to temperature as a function of the distance to the intrusive body and their respective K/Ar ages. The temperature conditions of the regional metamorphosed pelitic host rock and the contact metamorphic pelite is monitored by chlorite thermometry, illite and chlorite crystallinities and by temperatures obtained from Raman spectroscopy on carbonaceous material.

The Torres del Paine intrusive complex is located in the Magallanes foreland basin. The regional thermal evolution in the Magallanes Basin is characterized by a complex interaction of burial under diagenetic conditions, deformation during fold-and-thrust belt formation under anchizonal to epizonal conditions, and contact metamorphism. The thrusting and associated uplift is dated at around 60 Ma and anchizonal metamorphism with temperatures between 240 and 270 °C. The Miocene Torres del Paine intrusive complex was emplaced between 12.59 and 12.43 Ma into the folded Cretaceous Cerro Toro and Punta Barrosa formations [3,4]. The somewhat earlier Paso Gardner intrusion is dated at 16.24 Ma [5].

The metapelites were sampled in three profiles starting from the cordierite-in isograde of the contact aureole to the regional anchizonal host rock unaffected by the intrusion. K-Ar ages were obtained for nine samples in their <0.2 and <2 µm fractions.

First promising results constrain the beginning Ar-degassing of illites in the <2 µm fraction to temperatures of 287±32 °C. A gradually increasing amount of Ar loss towards the intrusion is observed up to a temperature of 300 °C. A complete reset occurs at a distance of 400 m to the early Paso Gardner gabbro diorite intrusion located in the western part of the Torres del Paine intrusive complex. This sample yields an age of 15.1±0.5 Ma and first temperature estimations indicate a temperature of 370±7.2 °C.

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PROPERTIES AND PROCESSING OF CLAY-POLYMER NANOCOMPOSITES MODELLED USING A MULTISCALE APPROACH

James L. Suter, Peter V. Coveney

University College London, London, United Kingdom

With ever increasing computing power, one can envisage developing novel materials *in-silico* through bottom-up design, where chemical specificity and molecular self-assembly is used as a fabrication tool. To model these processes, we have to simulate the behaviour of the materials at the mesoscale. Modelling the very small length and timescales (atomistic) and the very large (continuum) is commonplace, but the intermediate regime (0.01—100 micrometers), where collective behaviour becomes important, is much rarer, due to the complexity resulting from interactions occurring over many length and time scales.

Here we will present our findings from modelling chemically specific combinations of clay, polymers and organic surfactants using multiscale simulation to explore mesoscale properties [1,2]. The aim of our study is to predict the chemical and physical conditions required to disperse aggregated layered nano clay tactoids into their individual separated layers. We have considered two general factors:

1. Equilibrium conditions (such as the chemical composition and grafting density of surfactants on the layer surface);

2. Processing conditions (such as the mechanical force required to shear off a layer from a stack of aggregated layers, found in melt-extrusion processing conditions).

We have firstly calculated by computer simulation, using high fidelity coarse-grained molecular dynamics, the free energy required to separate clay sheets in organically modified clay-polymer nano-composites. To achieve this, we constrained the separation of surfactant-treated clay sheets while immersed in a polymer melt. The chemically specific polymer molecules can, therefore, move into the nanoscale interlayer region as the layer separation increases. Our simulations and associated calculations assess the many competing factors that determine the equilibrium separation of the clay tactoids, including the enthalpic attraction of the polymer to the clay surface, compared to the surfactant molecules, and various entropic changes, such as the increase in entropy of the surfactant chains when the sheets are separated and the associated reduction in entropy due to the confinement of the intercalating polymer molecules.

Secondly, with such layer separations known, we can estimate the force required to “shear off” one of the separated sheets at these configurations by adding a force to a clay sheet in the lateral directions, and observing whether this is sufficient to separate the tactoid. Finally, we have simulated a large tactoid of many clay sheets experiencing shear forces transmitted through the molten polymer molecules, on which we impose a shear flow, reflecting the situation found in melt-extrusion processing conditions. These simulations have now been performed for a variety of chemically distinct polymers and surfactants (both hydrophobic and hydrophilic), along with varying surfactant grafting densities, to produce chemically specific predictions for these clay-polymer nano composite systems.

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STUDY OF THE FORMATION OF SODIUM-TYPE SYNTHETIC MICA AND ITS CESIUM ADSORPTION CHARACTERISTICS

Noriko Suzuki*, Kaori Suzuki

Showa Pharmaceutical University, Tokyo, 194-8543, JAPAN
*n-suzuki@ac.shoyaku.ac.jp

Although six years have passed since the accident at Fukushima Daiichi Nuclear Power Station, little news has been heard about its decontamination. Moreover, the problems arising from the presence of radioactive materials in environmental water and contaminated water are still far from being resolved. According to recent information, the cooling device of the frozen soil wall has been stopped. Apart from this, several other problems need to be addressed in order to not increase the amount of contaminated water. To this end, our laboratory reported certain methods for the adsorptive removal of cesium (Cs) using clay minerals. In one of these methods, an adsorbent obtained by transforming sodium taeniolite into a sponge-like state was found to be efficient for the removal of Cs from pure water and artificial seawater. Sodium taeniolite is an artificial form of mica containing lithium but is unsuitable in terms of cost-efficiency for large-scale use. In this context, although the rate of recovery of Cs in a powder experiment was slightly lower than that obtained using sodium taeniolite, similar studies were conducted using lithium-free, sodium-type synthetic mica (hereinafter referred to as Na-TSM) as an ion exchanger. However, various difficulties were encountered under the same conditions as those used for sodium taeniolite, a spongy form of Na-TSM was shrunk during drying and Na-TSM leached out from the sponge at the time of the adsorption experiment.

The purpose of this report is to establish a method for preparing a spongy form of Na-TSM with suppressed leaching as well as elastic properties and then conduct basic studies on the Cs adsorption characteristics of the spongy form of Na-TSM.

The formation of a spongy form of Na-TSM was achieved according to a previous report [1] by changing the ratio of Na-TSM, polyvinylidene fluoride (PVF), and the solvent dimethylacetamide (DMA) as components of the structure. Both adsorption and desorption experiments were performed using a batch method. An aqueous solution of cesium chloride adjusted to a predetermined concentration was placed in a 20-cm^3 plastic tube, into which the prepared spongy forms of Na-TSM were introduced. The tube was then placed on a rotary shaker and continuously stirred for 24 h. The reaction was performed at room temperature. After the reaction, the supernatant was filtered through a filter (pore size = 45 μm), and the Cs concentration was measured using an atomic absorption spectrophotometer.

The ratio of PVF: Na-TSM (g) in the obtained spongy form of Na-TSM was 0.1:0.1 in Sponge α, 0.2:0.2 in Sponge β, and 0.1:0.2 in the existing form. In the case of sodium teniolite, sponge formation occurred when the mass ratio of the binder to the adsorbent was 1:2; however, with Na-TSM, sponge could be formed at a ratio of 1:1. Swelling clay minerals tend to absorb moisture even in the atmosphere and retain it as interlayer water. Thus, it can be assumed that more moisture can be held between the layers of Na-TSM, which has stronger swelling properties than sodium teniolite. It was expected that the removal of this interlayer water would occur during the drying process and that the sponge would shrink accordingly. We were able to partially confirm this phenomenon via suppression of the contraction of the sponge by decreasing the ratio of Na-TSM.

The results of an investigation of the adsorption rate by changing the initial concentration of the reactants indicate the higher the concentration, the lower the adsorption rate for both spongy forms of Na-TSM; however, large differences were observed in the extent of the decrease. Because the amount of Na-TSM, *i.e.,* the amount of the ion exchanger, was doubled in Sponge α and Sponge β, it could be anticipated that the adsorption rate would also double; however, the adsorption rate observed was even higher. To increase the amount of the ion exchanger, the amount of PVF must also be increased. Upon doing this, the size of the sponge becomes larger and the contact between the reactant and the spongy form of Na-TSM increases; this may be one of the factors responsible for the increase in the adsorption rate. This tendency is more noticeable as the concentration of the reactant increases; it can be assumed that depending on the design of the sponge, Cs may be recovered even from contaminated water at relatively high concentrations. However, considering its generally admitted cation exchange abilities, the adsorption rate of the reactant at concentrations of 5.0 mmol dm^{-3} and 10 mmol dm^{-3} is low. Other factors, *e.g.,* ionic strength are also conceivably involved, and the task for the future is to establish and develop a system that recovers Cs more effectively, including the elucidation thereof.

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CATIONIC BIPHENYL DERIVATIVE INTERCALATED IN SMECTITES

Yasutaka Suzuki, Makoto Tominaga, Yukihiro Nishioka*, Seiji Tani, Jun Kawamata

Graduate School of Science and Technology for Inovation, Yamaguchi University, Yamaguchi, Japan

A high pressure field alters the stereostructure of molecules in a solution. For example, the dihedral angle of biphenyl around the central bond connecting the phenyl rings decreases from 45° to 20° when the hydrostatic pressure increases to 1.2 GPa from ordinary pressure. Such a stereochemical change produces various interesting features, including enhanced reactivity due to shortening of the bond length, the expansion of the π-electron system due to an improvement of the molecular planarity and the generation of radical species through bond cleavage. It is reported that tetrakis (1-methylpyridinium-4-yl) porphyrin is flattened in the interlayer space of a smectite although the pyridinium ring is twisted with respect to the plane of the porphyrin ring in a solution due to the steric hindrance [2]. The interlayer space imposes molecules similar flattened conformation that in a high-pressure field.

The principle force that makes a cationic organic molecule flattened in the interlayer space of a smectite is the electrostatic one between the exchangeable inorganic cations and/or intercalated organic cations and the anionic sites of a smectite layer. The uniaxial force exerted on molecules in the interlayer space can be controlled by varying the charge density of the layer and/or the loading level of organic cations. Consequently, the intercalated organic molecules should experience a tunable pseudo high-pressure field by varying the charge density or the loading level.

In this study, we investigated the applied pseudo pressure to a biphenyl derivative confined in the interlayer space of smectites. The pressure was calculated by using the reported equation, which relates the dihedral angle of biphenyl to pressure. The averaged dihedral angle about the central bond of a biphenyl moiety in a biphenyl derivative confined in the interlayer spaces of smectites was estimated from the molecular thickness corresponding to the gallery height estimated by X-ray diffraction (XRD) measurements. As a guest organic molecule, we designed a cationic biphenyl derivative with strong electronic absorption at visible wavelength (BP).

The averaged dihedral angle of a BP in the interlayer space of synthetic saponite (SSA) at a loading level of 27% versus cation exchange capacity was ca. 26.3°, which leads to conclusion that the pseudo pressure corresponded to 0.99 GPa was applied to a BP in the interlayer space of SSA. Such a high pseudo pressure field in the interlayer space of SSA was also confirmed from the result of absorption measurements. Absorption peak of SSA-BP hybrid film was remarkably red shifted compared with that in a solution. It was deduced that the dihedral angle around the central bond of biphenyl moiety decreased to enhance its planarity due mainly to the electrostatic force operating between negatively charged SSA layer and interlayer cation. The pseudo pressure operating on a BP in the interlayer space of a smectite could be controlled by varying the charge density of a smectite layer and/or the loading level of BPs. By using this methodology, controllable pseudo high-pressure properties of organic molecules were conveniently obtained under ordinary temperature and pressure.

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EVOLUTION OF CLAY MINERALS STRUCTURE DURING THEIR INTERACTIONS WITH ORGANIC MOLECULES

Ariane Suzzoni (1,2)*, Eric Kohler (1), Loïc Barre (1), Laurent Michot (2), Pierre Levitz (2)

(1) IFP Energies Nouvelles (IFPEN), Rueil Malmaison, 92500, FRANCE, (2) Laboratoire Physicochimie des Electrolytes et Nanosystèmes interfaciaux (PHENIX), UMR 8234, Université Pierre et Marie Curie, 75005 Paris, France
*ariane.suzzoni@ifpen.fr

Interactions between clay minerals and organic molecules are important in numerous industrial processes and particularly, in the oil industry. For instance, one of the methods used for improving hydrocarbon recovery is to inject chemicals, such as polymers and surfactants in the well. Often, these techniques are based on the use of anionic surfactants as these molecules are only weakly adsorbed on reservoir rocks. This maintains a constant composition of the injected solutions and minimizes losses associated to adsorption. Still, especially in the presence of clay minerals, some reactions (adsorption, aggregation, deflocculation…) can occur between the surfactants and the rocks, which can, in turn, significantly impact oil recovery. It is then essential to reach a better understanding of the interaction between anionic surfactants and various clay minerals, which is the main objective of our present work.

This presentation will focus on the results obtained with kaolinite.

Reference kaolinite was purified and suspensions of this mineral were contacted with a typical anionic surfactant bis (2-ethylexyl) sulfosuccinate sodium (AOT). In agreement, with previous studies (Lagaly, 1989; Welzen *et al.*, 1981) significant stabilization of kaolinite suspensions can be observed in the presence of AOT. The effect of various chemical conditions (pH, ionic strength) and the role of adsorption on the observed phenomena will be analyzed in this presentation together with spectroscopic studies that can yield information about the conformation of adsorbed species and structural studies by scattering techniques (SAXS mainly) that provides data about the organization of particles in suspension.

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HYDROPHOBICITY OF SMECTITE SURFACES PROBED BY MOLECULAR DYNAMICS SIMULATIONS

Marek Szczerba (1)*, Andrey G. Kalinichev (2)

(1) Institute of Geological Sciences, Polish Academy of Sciences, Kraków, Poland, (2) Laboratoire SUBATECH, Institut Mines-Télécom Atlantique, Nantes, France

The siloxane surface of uncharged clays is known to be hydrophobic, as strongly supported by numerous experimental and theoretical evidence. For the siloxane surfaces of charged clays, like smectites, the picture is not as clear. Based on aromatic hydrocarbon adsorption experiments, the smectite surface was characterized as mostly hydrophobic [1]. On the other hand, neutron scattering experiments provided evidence that the surfaces of smectite clays with tetrahedral substitutions are hydrophilic [2]. The present study is aimed at advancing the aforementioned discussion by bringing new quantitative arguments based of molecular simulations. Theoretical calculations provide an unique opportunity to separate in the analysis the effects resulting from different structural and compositional features, and can be effectively used to assess the degree of hydrophobicity of smectite surfaces within a wide range of structural charges from which all charge-balancing cations are artificially removed.

In order to explore systematically the effects of smectite composition, a series of MD simulations were performed for six models of dioctahedral smectites with a total layer charge of 0.2, 0.3, 0.4, 0.5, 0.6 and 1.0 per half unit cell (phuc) with octahedral (montmorillonitic) charge localization. MD simulations for a neutral pyrophyllite surface were also performed for comparison. Partial atomic charges and other interatomic interaction parameters of smectite layers were described using the ClayFF force field [3] with structural OH groups modified by introducing a more accurate Morse potential [4,5].

The largest difference between the results of MD simulations performed for smectite surfaces covered with counterions and devoid of the ions is in the shape of the water film coverage. For smectite surfaces with charge balancing counterions the interface is quite uniform: a relatively flat water film is forming. Its irregularity is related to the total number of ions (Na^+ in our simulations) on the surface: the larger their number, the less rugged is the interface between the water film and the surrounding gas. In all cases for smectite surfaces devoid of ions a water droplet is formed. Its contact angle is very similar to that formed on the uncharged pyrophyllite surface and is in range from 90^o to 78^o, with the lowest being observed for the charge of 0.4 phuc. It was also found that the angle is dependent on the distribution of atoms in the octahedral clay sheet.

The angular distributions of the interfacial H_2O dipole vectors with respect to the direction normal to the surface and as a function of the distance z from the surface clearly show two preferred surface-bound types of water molecules for the clay models with surface ions present. For the smectite surfaces devoid of counterions there is practically no difference between smectites with different structural charges.

All presently obtained MD simulation results clearly indicate that the siloxane smectite surface itself is definitely hydrophobic. Its experimentally observed hydrophilicity is only emerging due to the presence of charge balancing counterions on the surface.

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HYDROXIDE ION CONDUCTION IN LAYERED DOUBLE HYDROXIDES AND THEIR APPLICATION TO ELECTROCHEMICAL DEVICES

Kiyoharu Tadanaga*, Kohei Igarashi, Takashi Kubota, Akira Miura, Nataly Carolina Rosero Navarro, Mikio Higuchi

Faculty of Engineering, Hokkaido University, Sapporo, Hokkaido 060-8628, Japan

In recent years, electrochemical devices using alkaline electrolytes such as alkaline fuel cell and zinc-air battery have received much attention. In these electrochemical devices, KOH solution is often used as the alkaline electrolyte, but the formation of solid state K_2CO_3 in electrolyte or electrode-electrolyte interface with the reaction with CO_2 in the air is a serious problem. Thus, to avoid the reaction, the use of an anion exchange membrane as a separator has been proposed. In the air electrodes used with a solid electrolyte separator, a hydroxide ion conducting ionomer to form favorable triple-phase boundary regions is necessary to transport OH^- ions effectively.

We have focused attention on layered double hydroxides (LDH) as an ion conducting material. We found that the ionic conductivity of LDHs were closely related to the species of intercalated anions, and LDHs intercalated with CO_3^{2-} showed high hydroxide ion conductivity of the order of 10^{-3} S cm^{-1} under 80% relative humidity [1-3]. We also reported that LDHs can be applied to the solid electrolyte of alkaline direct ethanol fuel cell (DEFC) [1,3].

In a fuel cell, the formation of good triple phase boundary (TPB) in the electrodes is very important. We reported the effects of LDH addition to a catalyst layer of an alkaline DEFC. The addition of LDHs increased the oxygen reduction reaction (ORR) activity in the cathode, indicating that hydroxide-ion conducting LDHs construct favorable TPB regions in the catalyst layer [4,5]. In the catalyst layer, a material with higher electronic conductivity along with ionic conductivity should be desirable.

In this presentation, the ionic conductivity of M-Al LDHs (M=Ni, Mg, (Ni, Mn)) and M-Fe LDHs (M=Ni, (Ni, Mn)) intercalated with CO_3^{2-} will be presented. Application of LDHs to the electrolyte or catalyst layer of the fuel cells will also be reported.

LDHs studied in the present study are found to show high ionic conductivity of the order of 10^{-3} S cm^{-1} under the rerative humidity 80%. The results in electromotive force measurements for a water vapor concentration cell showed that these LDHs are a hydroxide ion conductor under the humidified condition. The conductivity of (Ni, Mn)-Al LDH and (Ni, Mn)-Fe LDH was found to be higher than that of Ni-Al LDH or Ni-Fe LDH.

H_2-O_2 fuel cells with Mg-Al and Ni-Al LDHs as an electrolyte and MnO_2 as the cathode catalyst were confirmed to be operated. Alkaline-type DEFC using anion exchange membrane as an electrolyte and the electrodes with LDH as “ionomer” was also fabricated [4]. The DEFCs using catalyst layers with Ni-Al, Mg-Al, Ni-Fe, and (Ni, Mn)-Fe LDHs showed higher cell performance than the DEFC using catalyst layer without LDH. The addition of (Ni, Mn)-Fe LDH to the catalyst layer more effectively increased the reduction current for ORR than the addition of (Ni, Mn)-Al LDHs or Ni-Fe LDH.

We have confirmed that the air electrodes containing LDHs as a hydroxide ion conducting ionomer can also be applied to rechargeable Zn-Air batteries [5], and electrochemical oxygen separating cells [6].

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GEOLOGY AND FEATURES OF GREEN SAPROLITE, SETO DISTRICT, CENTRAL JAPAN

TETSUICHI TAKAGI (1)*, YUKI TSUNAZAWA (1), SADAHISA SUDO (1), MAYUMI JIGE (2)

(1) Geological Survey of Japan, AIST, Tsukuba, 305-8567 Japan, (2) Osaka-Ohtani University, Faculty of Education, Tondabayashi, 584-8540 Japan
*takagi-t@aist.go.jp

Seto-Tono district is the largest pottery and porcelain industrial region in Japan, and the history of their manufacturing is longer than 1,000 years. The raw materials of the industry have been supplied from sedimentary kaolin clay deposits (mines) in the district. However, ore reserve of the kaolin clay mines has rapidly been exhausted in the recent decade due to longtime exploitation, urbanization, and environmental problems. To extend the lifetime of the mines, local mining associations plan to exploit “green saprolite” underlying the kaolin clay deposits. Green saprolite is low-grade clayey rocks; it has been regarded as unsuitable raw materials for traditional pottery and porcelain so far due to its high iron contents. We have studied geology and mineralogy of green saprolite to develop its utilization technology.

In the Seto district (southern half of the Seto-Tono district), kaolin clay deposits occur as fluvial and lacustrine sediments of late Miocene to Pliocene, which were subjected to intense kaolinization [1,2]. Green saprolite is unconsolidated weathering crusts of granite beneath the sedimentary kaolin clay deposits, showing greenish gray to dark green color. Green saprolite appears to be unsorted and viscous sandstone, but original granitic texture ambiguously survives. The upper most portions were partly reworked by surface water, and include pegmatitic mineral fragments in places. The constituent minerals are medium- to coarse-grained quartz, feldspars with minor amount of biotite and clays. No chlorite and vermiculite are detected. The fraction of clays accounts for about 10 wt. percent; this is a distinctive feature of green saprolite. The clay fraction consists mostly of kaolinite with subordinate halloysite; we may regard that kaolin clay deposits and green saprolite were formed by a sequence of kaolinization. Exploration drillings indicate that the thickness of green saprolite beneath kaolin clay deposits ranges from 8.5 to 24 meters, while the thickness beneath silica sand deposits is only several meters.

The basement rocks beneath the kaolin clay deposits are late Cretaceous Naegi-Agematsu (NA) granite [3]. Green saprolite has intermediate values between the NA granite and kaolin clay ores with respect to Ca+Na+K, while Fe of them are plotted in the same compositional ranges. Though, biotite content of green saprolite was evidently reduced from that of the NA granite during kaolinization, Fe appears to remain mostly in green saprolite. Our preliminary study suggests that kaolinite of green saprolite contains small amount of Fe, and the Fe-bearing kaolinite would cause its greenish gray to dark green color. To utilize green saprolite as raw materials of pottery and porcelain, the main technical issue should be the separation and reduction of Fe by mineral processing.

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STRUCTURE AND PROPERTIES (IMOGOLITE/BIOPOLYMER) HYBRIDS

Atsushi Takahara (1,2,3), Yuji Higaki (1,2,3), Kyung-Lynne Park (1)

(1) Graduate School of Engineering, (2) International Institute for Carbon-Neutral Energy Research (WPI-I2CNER), (3) Institute for Materials Chemistry and Engineering, Kyushu University, 744 Motooka, Nishi-ku, Fukuoka, 819-0395, Japan

Imogolite is a naturally occurring aluminosilicate nanotube. It consists of a single-wall nanotube with a composition of $(OH)_3Al_2O_3SiOH$ with Al-OH and Si-OH groups distributed on the external and internal surfaces of the tube wall, respectively. The Al-OH groups at the outer surface of imogolite can interact specifically with phosphate ions and alkyl phosphonyl/phosphoryl groups [1,2]. In this study, (imogolite(IG)/biopolymer) hybrids were prepared by a specific interaction hydrophilic groups of biopolymer with OH groups at the surface of imogolite.

The hybrid hydrogel composed of tubular “imogolite” and pepsin was prepared in a simple manner of pepsin and imogolite solutions [3]. We confirmed the formation of a network structure of imogolite in hydrogel by FE-SEM observations. Pepsin immobilized onto imogolite showed enzymatic activity even after repeated reactions.

The novel hybrid hydrogels were prepared from imogolite nanofibers and DNA by a strong interaction between the Al-OH groups on imogolite surface and phosphate groups of DNA [4]. The hybrid hydrogels of imogolite and DNA were prepared in various blend ratios, and their physicochemical properties and molecular aggregation states were investigated in both dispersion and gel states. The maximum DNA content in the hybrid gels was equivalent molar ratio of imogolite and DNA. The physical properties of the hybrid gels were controlled by varying DNA blend ratios. In the dispersion state, the hybrid gels showed a fibrous structure of imogolite, whereas a continuous network structure was observed in pure imogolite, indicating that the hybrid with DNA enhanced the dispersion of imogolite. In the gel state, DNA and imogolite nanofibers formed a 3D network structure.

Hybrid hydrogels composed of imogolite fibrous nanotube and hyaluronic acid (HA) were prepared. Hexamethylenediamine (HMDA) was used as a non-toxic chemical cross-linker. The homogeneous dispersion of imogolite in the HA solution was accomplished by careful pH control, and subsequent chemical cross-linking provided mechanically stable self-standing hybrid hydrogels. The imogolite /HA hybrid hydrogels were characterized by FT-IR, SEM, swelling test, compression test, oscillatory rheological analysis, and enzymatic degradation test. The imogolite/HA hybrid hydrogels showed better mechanical properties and lower degradation rate than native HA-based hydrogels without imogolite hybridization because the cross-linking density increases by incorporation of additional imogolite network into chemically cross-linked HA network [5].

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HALLOYSITE NANOTUBES AS A FINE GRAINED MATERIAL FOR HEAVY METAL REMOVAL IN TROPICAL BIOFILTRATION SYSTEMS

Andreas Aditya Hermawan (1), Chang Jia Wie (1), Amin Talei (1)*, Pooria Pasbakhsh (2), Sherwin Ng (1)

(1) Discipline of Civil Engineering, School of Engineering, Monash University Malaysia, Bandar Sunway, Selangor Darul Ehsan 47500, Malaysia, (2) Discipline of Mechnical Engineering, School of Engineering, Monash University Malaysia, Bandar Sunway, Selangor Darul Ehsan 47500, Malaysia
*amin.talei@monash.edu

Biofiltration systems are landscape depressions or shallow basins used to slow and treat on-site stormwater runoff and are considered as one of the important components of a sustainable drainage system. Biofilters generally consist of two components: a filtration media which is sand-dominant and a top vegetated soil layer [1]. The efficiency of a biofiltration system is normally assessed by two key parameters namely hydraulic conductivity and percentage removal of pollutants [2]. In tropical areas like Malaysia where rainfall intensity is normally high, hydraulic conductivity of the biofiltration systems needs to be high enough to prevent ponding and possible flooding of the system. To date, several studies have been done on development and maintenance of such systems; however, few have studied such systems under tropical climates with heavy and intense rainfall which needs high hydraulic conductivity. The present study aims to identify proper soil filter media that not only can remove heavy metals efficiently but also has reasonably high hydraulic conductivity. For this, a soil column experimental set up were developed and the effectiveness of adding different fine grained materials such as fly ash, halloysite nanotubes (HNTs) from two different origins (Imerys from NZ and HalloPure from i-Minerals, Idaho), and zeolite in sand-based soil media were assessed. To assure the validity of the results for each proposed filter media three replicates were prepared. The performance in removing heavy metals Fe, Mn, Cu, Zn, Ni, and Pb was then evaluated for each soil composition using Inductively Coupled Plasma -Optical Emission Spectroscopy (ICP-OES) test. Synthesized stormwater was used to provide consistency of pollutant concentration in experiments. The watering dosage was calculated based on hydrological data of a Malaysian catchment. Hydraulic conductivity of each soil composition was also measured for further comparison. Results showed that increasing the percentage of fine materials can improve the heavy metals removal; however, the drawback would be significant decrease in hydraulic conductivity. In general, HNTs were found to fulfill both requirement of high percentage removal and high hydraulic conductivity compared to zeolite and fly ash. Moreover two different types of HNTs used in this study have been compared with each other as well. For this, the effect of aspect ratio, surface area, particle size and chemical composition on their efficiency in heavy metal removal and hydraulic conductivity have been studied.

Keywords: halloysite nanotubes; tropical biofilter; heavy metals removal; sotrmwater treatment.

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PURIFICATION AND DEFIBERING OF A CHINESE SEPIOLITE

Jianjie Tan*, Hongqi Zhou, Cheng Weiquan

National Technical Committee 54 on Foundry of Standardization Administration of China, Shenyang 110022, China
*qilinc1990@hotmail.com (Jianjie Tan), clk6203@163.com (Hongqi Zhou), 290482108@qq.com (Weiquan Cheng)

To extend the utilization of the low-grade Hu'nan (China) sepiolite, the purification of the ore is the prerequisite for all applications. Sepiolite accompanied by quartz and calcitewas effectively purified via sedimentation method and the microwave assisted acid treatment. The influence of treatment time on sepiolite purity and structure was qualitatively studied based on XRD and FESEM. Sepiolite had been successfully purified and the content was elevated from 42 wt.% to more than 90 wt.%. Microwave assisted acid treatment demonstrated to be an effective purification process by removing carbonates without affecting sepiolite length. Furthermore, both physical method of lyophilization and chemical method of surface modification were proposed as simple alternatives to defibering acid-treated sepiolite crystal bundles. The effects of freezing time and surfactant chain length on the disaggregation state, micro-structure and properties of treated sepiolite were analyzed comparatively using FESEM, TEM and BET. Results of FESEM and TEM indicated that the crystal structure of sepiolite was not changed after freezing at −50 °C for 12h or modification with hexadecyl trimethyl ammonium bromide (HDTMA), but the aggregates were effectively disaggregated. The BET specific surface areas of the dispersed sepiolite rods obtained by these two methods increased to 144.3 and 93.1 m^2/g, respectively, showing good agreement with the perfect dispersion of sepiolite fibers.

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ALKALI ACTIVATION OF SULFATE-BEARING KAOLIN

Roberta Occhipinti (1), Serena Chiara Tarantino (1,2)*, Maria Pia Riccardi (1), Michela Sturini (3), Andrea Speltini (3), Federica Maraschi (3), AgnèsElmaleh (4), Michele Zema (1,2)

(1) Dipartimento di Scienze della Terra e dell'Ambiente, Università degli Studi di Pavia, via A. Ferrata 9, I-27100 Pavia, Italy, (2) CNR-IGG, Sezione di Pavia, via A. Ferrata 9, I-27100 Pavia, Italy, (3) Dipartimento di Chimica, Università degli Studi di Pavia, via T. Taramelli 12, I-27100 Pavia, Italy, (4) Institut de Minéralogie et de Physique des Milieux Condensés, UPMC/CNRS, 4 Place Jussieu, Case 115, F-75252 Paris CEDEX 5, France
*serenachiara.tarantino@unipv.it

In a recent work from our group [1], the feasibility of using volcanogenic sulfate-bearing kaolin for alkali activation has been assessed. Alunite, $KAl_3(SO_4)_2(OH)_6$, which is present in kaolin deposits deriving from trachyte, rhyolite, and similar potassium-rich volcanic rocks, normally hinders the use of these clays in the ceramic industry due to the release of SO_x at high temperature. It can be, however, a source of potassium and aluminium in alkali activation. Results are promising, as evidenced by high thermal stability and high compressive strength (ca. 80 MPa) of the AAMs obtained from this material. However, the presence of the nardite, Na_2SO_4, deriving from the dissolution of alunite, was observed in the final products.

Aims of the present work are: to study the effect of the presence of SO_4^{2-} on the nature and chemical composition of the resulting N-A-S-H gel; to identify the non-soluble sulfate-bearing phases; and finally, to evaluate the possibility of sulfate uptake by the gel itself.

To this end, an alunite-bearing kaolin (alunite 13% wt.)derived from rhyolite and preliminarily heated at T = 550 °C was activated with different alkaline solutions. In parallel, alkali activation was carried out on synthetic mixtures of alunite and high-grade kaolin for comparison. The pastes were cured at 50 °C for 20 h. All samples have been characterized by X-ray powder diffraction, infrared spectroscopy and scanning electron microscopy. The synthesized samples revealed to be composed mainly by an amorphous gel and characterized by high thermal stability, no new crystalline phases apart from the nardite have been formed. Leaching tests have been carried out, and chemical analyses performed on leached solution as well as on the resulting leached materials revealed that sulfates are still present in the samples. In the conditions of our experiments, the presence of sulfate seems not to promote crystallization of zeolites, differently from what observed in literature for alkali activation of fly-ash [2]. However, we cannot exclude the uptake of sulfate ions by the gel. In particular, chemical microanalyses have revealed the presence of sulfur-rich particles containing Si and Al in all the samples, likely amorphous or nanosized zeolites phases.

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NANOSTRUCTURE OF LDH INTERCALATED WITH DIFFERENT THERAPEUTIC AGENTS

Christine Taviot-Gueho (1), Michele A. Rocha (3), Vanessa R. R. Cunha (1), Kamil Lang (2), Fabrice Leroux (1), Vera R. L. Constantino (3)

(1) Departamento de Química Fundamental, Instituto de Química, Universidade de São Paulo, C. P. 26077, SãoPaulo, BRAZIL, (2) Institute of Inorganic Chemistry of the ASCR, v.v.i., Husinec-Rez 1001, 250 68 Rez, CZECH REPUBLIC, (3) Université Clermont Auvergne, CNRS, Institut de Chimie de Clermont-Ferrand, F-63000 Clermont-Ferrand, France
christine.taviot-gueho@uca.fr

Layered double hydroxide LDH have recently emerged as an attractive candidate for delivery of various therapeutic agents into their targets. Small drug molecules or large biomolecules like proteins, DNA can be intercalated into LDH host. LDH could also possibly be employed in delivery of diatomic therapeutic agents, like singlet oxygen.

LDH nanocontainers display interesting chemical and physical properties for transporting and unloading pharmaceuticals agents. First, they provide non-toxic carriers. A second advantage is their ease of synthesis. Furthermore, the wide range of composition and the variable charge density of LDH layers allow a fine tuning of the structures and the stability of LDH-drug assemblies, providing effective and selective means of controlling subsequent intracellular release.

In this oral presentation, first, we will be discussing the intercalation of Sulindac [1], a non-steroidal anti-inflammatory of the indene acetic acid class, and Pravastatin [2], a member of the drug class of Statins in Mg_2Al and Zn_2Al layered double hydroxide nanovessels through one pot reactions. The resulting materials were characterized by chemical elemental analysis, X-ray diffraction (one dimensional electron distribution along the c-stacking axis, pair distribution function analysis), scanning and transmission electron microscopies, mass coupled thermal analyses, vibrational infrared and Raman spectroscopies, and solid state ^{13}C NMR. We found that the spatial organization of interleaved Sulindac molecules is similar to that reported for the pristine polymorph II crystal structure. In the case of Pravastatin, a bilayer arrangement is observed with intermolecular hydrogen bonding between adjacent organic species and chloride ion cointercalation is required. In both case, the features indicate that the intercalation preserves the drug structural integrity.

The intercalation of porphyrin-based photosensitizers will also be presented [3,4]. LDH host prevents the aggregation of porphyrins and increases the thermal stability of porphyrins. Moreover, the photophysical properties of porphyrins are maintained, namely the formation of singlet oxygen under visible light irradiation.

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INVESTIGATION OF SUPERPLASTICIZER-LAYERED CALCIUM ALUMINATE HYDRATE INTERFACE INTERACTIONS

QIRONG WANG, GUILLAUME RENAUDIN, CLEMENCE BIGOT, KARINE BALLERAT, FABRICE LEROUX, CHRISTINE TAVIOT-GUEHO*

Université Clermont Auvergne, CNRS, Institut de Chimie de Clermont-Ferrand, F-63000 Clermont-Ferrand, France
*christine.taviot-gueho@uca.fr

The AFm phase of Portland cements refers to a family of hydrated calcium aluminates based on the hydrocalumite LDH (Layered Double Hydroxide) structure$Ca_2Al(OH)_6$,1/nX^{-n}·yH_2O (X: anion of negative charge -n) [1-3]. Ten organic model molecules simulating the chemical functions of superplasticizers used in concrete formulations were intercalated into this lamellar cement hydrates resulting in hybrid AFm phases. The interfaces between the organic and inorganic networks of these hybrid compounds have been studied to characterize the interactions between AFm cementitious hydrate and organic additives in concrete.

We would like to present this work as a poster in session MISC-01.

The affinities of these molecules toward the mineral layers have been compared and display the following tendencies: $-PO_3^{2-} > -SO_3^{-} > -CO_2^{-}$for the hydrophilic parts and C_7-R> Φ-R> C_5-R> C_2-Rfor the hydrophobic parts. The organic-inorganic interface ie the connection mode and orientation of the organic molecule were characterized by powder XRD, NMR and infrared spectroscopies. Organic molecules are oriented either perpendicular or parallel to the sheets resulting from different connection modes, intercalation and grafting. The various hydration levels of these hybrid AFm phases were then determined, and a structural resolution was attempted on $C_6H_5SO_3^-$ containing AFmallowing a description of its interlayer structure.

Finally, a study on the intercalation of some commercial superplasticizers highlighted the exfoliation phenomenon for these lamellar hydrates. The present study on model molecules leads to a better understanding of the interactions occurring in complex fresh concrete environment.

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COLLECTION OF WATER-SOLUBLE POLYMER FROM AQUEOUS SOLUTION BY THE ADSORPTION ONTO BENTONITE

Aranee (Pleng) Teepakakorn (1)*, Makoto Ogawa (2)

(1) School of molecular science and engineering, (2) School of energy science and engineering, Vidyasirimedhi Institute of Science and Technology, Rayong, 21210, Thailand
makoto.ogawa@vistec.ac.th

Water-soluble polymers such as poly(vinylpyrrolidone) (PVP), poly(ethylene glycol) (PEG), poly(vinyl alcohol) and poly(acrylamide) have been widely used in industry (including daily life products, for example, toothpaste and shampoo dispersant, skin cream, paper coating, and adhesive in glue stick, and also drug delivery carriers and tissue engineering scaffolds in medical applications [1]. The contamination of the soils and water by the polymers will be an environmental concern. Hence, the method for the removal of the polymers (the collection and/or the decomposition) from the environment is worth developing. As an example, Tagawa and co-worker [2] reported the decomposition of various polymers using wet-ozone. Although this technique showed high performance for polymer removal, it is an energy consuming and not environmentally friendly (acid as by-product).

In this work, the adsorption of water-soluble polymers onto natural bentonite was investigated as a green method for the collection from aqueous environments. A Ca-bentonite from china (abbreviated as Ca-BT) was used as an adsorbent and PVP (with the molecular weight of 10,000 and 160,000) was used as the adsorbate. The adsorption isotherms, which is the relationship between the amount of PVP remaining in the aqueous phase (equilibrium concentration) and the immobilized amount of PVP, was used to clarify the interactions between adsorbent and adsorbate. The isotherm was type-L, showing the high affinity between the Ca-BT and PVP. At present, the highest amount of adsorbed PVP is 0.17 mg/mg of Ca-BT.

The amount of the adsorbed PVP was higher for higher molecular weight PVP. The interlayer space of Ca-BT expanded (from 1.5 to 1.6 nm) after the adsorption of PVP, confirming the interactions with Ca-BT. Because the expansion was not enough to explain the adsorbed amount of PVP, it was thought that a certain porsion of PVP was adsorbed on the external surface. A synthetic saponite (Sumecton SA, Kunimine Ind. Co., finite particles of several tens of nm size) was used after the ion exchange with calcium (Ca-SA) as an adsorbent. Ca-SA adsorbed larger amount of PVP than Ca-BT, supporting the idea that the PVP was adsorbed on the external surface in addition to the intercalation. These results suggested that the removal of PVP from water by the adsorption onto Ca-BT is a possible way for purification of water contaminated with water-soluble polymer.

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NUMERICAL ANALYSIS OF REACTIVE SURFACE AREA IN COMPACTED CLAY STRUCTURES

Kenichi Terada (1)*, Shusaku Harada (1), Hisao Satoh (2), Daisuke Hayashi (3)

(1) Faculty of Engineering, Hokkaido University, N13W8, Sapporo, 060-8628, Japan, (2) Mitsubishi Materials Corporation, 1002-14, Mukohyama, Naka, Ibaraki, 311-0102, Japan, (3) Radioactive Waste Management Funding and Research Center, 1-15-7, Tsukishima, Tokyo, 104-0052, Japan
*terada@eng.hokudai.ac.jp

It was experimentally found that the dissolution rate of montmorillonite drastically decreases with the increase of the density [1]. It is important for long term prediction of bentonite alteration in TRU waste geological disposal engineered barrier system. One of the primary reasons of the dissolution rate reduction is that the edge of montmorillonite particles is covered with the other particles and consequently the reactive surface area is reduced (physical masking) [2]. Therefore understanding of the equilibrium structure of montmorillonite particles is essentially important for predicting the dissolution rate quantitatively.

We investigated numerically the equilibrium structure of disk-shaped particles which models montmorillonite particles by Monte Carlo method. In a dispersion system at low density, the quadrupole potential is used for the model of particle-particle interaction [3]. The potential includes the effect of the charge of each particle and the surrounding electric double layer and expresses the anisotropic interaction of disk-shaped particles. However, the quadrupole potential is available only for low density conditions due to the limitation of the model. Therefore we used the rigid body potential for the calculation of high-density structures of particles.

The numerical results indicated that the disk-shaped particles make aggregates with “house of cards” structures in the dispersion system at low density, which is typically observed in clay sols. On the other hand, the equilibrium structure of particles at high density shows qualitatively similar to the drawing of microstructure of bentonite given in the previous study [4]. We calculated the Effective Edge Surface Area (Effective ESA) from the equilibrium structure of particles obtained by Monte Carlo method. We propose a masking model in which the edge surface masked by the other particle is calculated from edge-to-surface distance of particles. From the model analysis, the reduction of the reactive surface area at high density can be explained qualitatively. Moreover, the numerical results of the Effective ESA are quantitatively in good agreement with those obtained from the experimental measurement of the dissolution rate of montmorillonite particles using atomic force microscopy in a wide range of density condition.

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ENHANCEMENT OF CO EVOLUTION BY LAYERED DOUBLE HYDROXIDE CO_2 CAPTURE AND STORAGE MATERIALS FOR THE PHOTOCATALYTIC CONVERSION OF CO_2 BY H_2O

Kentaro Teramura (1,2)*, Yudai Hasegawa (1), Shoji Iguchi (1), Hiroyuki Asakura (1,2), Saburo Hosokawa (1,2), Tsunehiro Tanaka (1,2)

(1) Department of Molecular Engineering, Graduate School of Engineering, Kyoto University, Kyotodaigaku Katsura, Nishikyo-ku, Kyoto 615-8510, Japan, (2) Elements Strategy Initiative for Catalysts & Batteries (ESICB), Kyoto University, 1-30 Goryo-Ohara, Nishikyo-ku, Kyoto 615-8245, Japan
*teramura@moleng.kyoto-u.ac.jp

The reduction in human-induced emissions of CO_2 from automobiles, factories, power stations, etc., over the next 15 years is currently one of the most important issues facing the planet. The Intergovernmental Panel on Climate Change (ICPP) warned that temperature change has to be controlled lower than 2 degrees Celsius relative to average temperature before the Industrial Revolution by the end of century. It has also warned that if no action is taken to deal with the rate of CO_2 emissions, this will result in grave consequences for the planet, leading to sea surface elevation and desertification. We should therefore attempt to develop industrial processes using CO_2 as a feedstock in order to build a sustainable society in the near future. Linear CO_2 molecules adsorbed on the surface of the solid bases are converted into unique structures, such as bicarbonate and carbonate species possessing lattice oxygen atoms. We believe that the process involves the capture and distortion of CO_2 upon adsorption on a solid base through activation by photoirradiation. Unstable CO_2 species adsorbed onto the surface can then be reduced by electrons with protons derived from H_2O ($CO_2 + 2e^- + 2H^+ \rightarrow CO + H_2O$). These days, we found that $ZnGa_2O_4$/Ga_2O_3, [1,2] $La_2Ti_2O_7$,[3] SrO/Ta_2O_5,[4] $ZnGa_2O_4$,[5] $ZnTa_2O_6$,[6] and $Sr_2KTa_5O_{15}$[7] with the modification of Ag cocatalyst exhibit good conversion of CO_2 and high selectivity toward CO evolution for the photocatalytic conversion of CO_2 by H_2O as an electron donor. An isotope experiment using $^{13}CO_2$ and mass spectrometry clarified that the carbon source of the evolved CO is not the residual carbon species on the photocatalyst surface, but the CO_2 introduced in the gas phase. In addition, stoichiometric amounts of O_2 evolved were generated together with CO. Modification of the surface of Ga_2O_3 with layered double hydroxide (LDH) enhanced the evolution of CO as a reduction product in the photocatalytic conversion of CO_2 using H_2O as an electron donor under UV irradiation in aqueous $NaHCO_3$ as a pH buffer, with the LDH functioning as a CO_2 capture and storage material. Consequently, Ag-loaded Mg−Al LDH-modified Ga_2O_3 exhibits much higher photocatalytic activity (245.6 μmol h^{-1} of CO) and better selectivity (59.8%) than the pristine Ag-loaded Ga_2O_3 when 1.0 g of Mg−Al LDH-Ga_2O_3 composite photocatalyst was used in the presence of 0.25 wt.% of Ag cocatalyst. Moreover, the turn over number (TON) of electrons, which are utilized to reduce CO_2 into CO, was 88.6 per Ag atom for 5 h of the photoirradiation. To the best of our knowledge, this is the highest CO evolution rate for the photocatalytic conversion of CO_2 in an aqueous system ever reported.

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EFFECT OF PARTICLE SIZE AND POROSITY ON THE MACROSCOPIC DIFFUSION OF WATER IN COMPACTED SWELLING CLAY MINERALS

Emmanuel Tertre (1)*, Fabien Hubert (1), Sebastien Savoye (2), Dimitri Prêt (1), Thomas Dabat (1), Alfred Delville (3), Eric Ferrage (1)

(1) IC2MP, Equipe HydrASA, UMR 7285 CNRS/ Université de Poitiers, 86073 Poitiers, France, (2) DEN-SECR, CEA, Université Paris-Saclay, 91191 Gif-sur-Yvette, France, (3) ICMN, UMR 7374 CNRS/Université d'Orléans, 45071 Orléans, France

In the last decade or so, different models have been developed to predict water and solute diffusion in clayey matrices within the specific framework of radioactive nuclear wastes storage [1]. Up to now, the most sophisticated models were those developed for pure Na-smectite materials and accounting for two different types of porosities: (i) interparticle porosity and (ii) interlayer porosity. However, smectite displays osmotic swelling in water-saturated conditions leading to an ill-defined interlayer volume. Such osmotic swelling for smectite clay minerals makes then impossible to correctly account for (i) the distribution of different types of porosities in the sample and for (ii) the role played by the anisotropic particle organization on the overall diffusion of water and solutes in the sample.

In order to constrain macroscopic models predicting diffusion in dual porous media rich in swelling clays, diffusion experiments were carried out with vermiculite, a mineral that does not present any osmotic swelling under water-saturated conditions. Water (HDO) diffusion experiments were performed using a through-diffusion setup adapted from previous studies [2]. Samples were prepared from 0.1-0.2, 1-2 and 10-20 µm size fractions of vermiculite with well-known particle morphologies[3], representative of the different sizes of clay minerals present in complex and natural clayey samples. For each size fraction, through-diffusion experiments were performed at different degrees of compaction (*i.e.*, porosity) in order to vary the proportion of interparticle porosity over total porosity (interlayer + interparticle).

Effective diffusion coefficients of water (HDO)interpreting experimental data are compared with values found in literature for diffusion in smectite samples to assess effect of osmotic swelling on water diffusion in swelling clay minerals. Moreover, data are also compared to effective diffusion coefficients simulated by Brownian dynamics using representative virtual porous media [4] of our vermiculite samples, and for which porosity and organization of clay particles (anisotropic degree) can be controlled. Comparison between experimental and numerical data display consistent trends concerning evolution of effective HDO diffusion coefficients with porosities. Such a comparison helps at deciphering on the role played by different geometrical parameter (particle size, anisotropy, porosity distribution, presence of osmotic swelling) on the overall diffusional process of water tracer in compacted swelling clays. Then, such results will bring significant inputs in the perspective to better constrain models relative to the transport of solute in engineered clay barriers.

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IMOGOLITE AND IMOGOLITE-LIKE TUBULAR NANOCRYSTALS. FORMATION MECHANISM, PROPERTIES AND APPLICATIONS

Antoine Thill

CEA Saclay, UMR 3685 CEA/CNRS, DSM/IRAMIS/NIMBE/LIONS, 91191 Gif-sur-Yvette, France

Imogolites are aluminosilicate nanotubes naturally occurring in volcanic soils (Yoshinaga and Aomine, 1962) and even found on Mars recently (Bishop and Rampe, 2016). Getting inspiration from this natural clay, it is possible to prepare synthetic aluminosilicate or aluminogermanate nanotubes of formula $(OH)_3Al_2O_3SixGe_{(1-x)}(OH)$ which are perfectly monodisperse in diameter (from 2 to 4 nm depending on composition) and polydisperse in length from several tens of nanometers up to several microns (Thill et al. 2012, Amara et al, 2013). The formation mechanism of these nanotubes has been the subject of recent discoveries especially for the aluminogermanate nanotubes. The existence of Double-walled nanotubes has been discovered and their formation mechanism has been explained. A better understanding of the imogolite precursors (proto-imogolite) has been achieved and the growth kinetic of the nanotubes has been studied *in situ* and modelled. It has recently been discovered that it is possible to prepare hybrid nanotubes having coexisting hydrophobic and hydrophilic surfaces (Bottero et al. 2011, Bac et al. 2009). These hybrids inside/out janus nanotubes can be prepared in two symmetric configurations. Through the grafting of phosphonic acids bearing an aliphatic carbon chain on the outside aluminol surface, nanotubes dispersed in apolar solvents, are obtained. Alternatively, by replacing the tetraethoxysilane precursor by methyltriethoxysilane, nanotubes possess a hydrophobic nanocavity covered with Si- CH_3 groups instead of Si-OH (Figure 1A, B). These nanotubes are easily dispersed in aqueous solutions and are able to trap poorly soluble organic molecules (Figure 1C) (Amara et al. 2015).

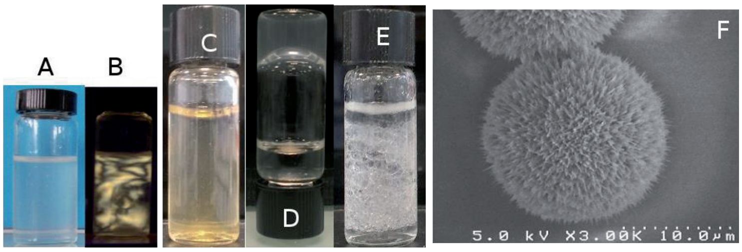

Fig. 1. A) Water suspension of hybrid imogolite nanotubes with internal hydrophobic nanocavity, B) A observed between cross-polarizers, C) encapsulation of pyrene in water through hybrid imogolite, D) oil-triggered hydrogel formation, E) stabilization of an oil-in- water emulsion, F) electronic microscopy image of a dried water-in-oil emulsion droplet.

We believe that their very original structure brings new and fascinating properties to these nanoparticles. In particular, we are currently studying the behaviour of such hybrid inside/out janus nanotubes at oil/water interfaces (Picot et al., 2016). Addition of oil to water containing hydrophilic/hydrophobic nanotubes or water addition to oil containing hydrophobic/hydrophilic nanotubes without mixing led into the formation of a gel (Figure 1D). When water and oil are mixed in the presence of the nanotubes, stable emulsions are obtained whose size is controlled by the concentration of particles (Figure 1E). After drying, a very original hedgehog-like structure is observed with electronic microscopy, (Figure 1F). Therefore, such an oil/water-triggered gel formation signs for a very specific and original behaviour of these hybrid nanotubes originating from their inside/out janus functionality.

In this mini-lecture, a review of the recent discoveries on imogolite formation mechanism will be made. We will also present the synthesis of the hybrid janus nanotubes. These hybrid nanotubes have promising properties. We will illustrate their behavior in contact with an oil/water interface.

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RECENT PROGRESS IN THE SYNTHESIS OF IMOGOLITE AND IMOGOLITE-LIKE CLAY MINERALS. A FOCUS ON THE SPHERE/TUBE TRANSITION

Pierre Picot (1), Yuanyuan Liao (1), Sophie Le Caër (1), Thibaud Coradin (2), Antoine Thill (1)*

(1) LIONS, NIMBE, CEA, CNRS, Université Paris-Saclay, 91191 Gif sur Yvette, France, (2) Sorbonne Universités, UPMC Univ. Paris 06, CNRS, Collège de France, Paris 75005, France

Imogolite has been discovered more than 50 years ago in the weathering products of volcanic soils in Japan [1]. It has been quickly realized that imogolite is a ubiquitous clay mineral which can be readily synthesized in the laboratory using rather simple co-precipitation receipts [2].

From this initial discovery researchers have started to explore the possible modifications of the imogolite nanotubes. Many successful examples are now available [3,4]. Some of these chemical modifications were shown to be coupled with important structural modifications. The discovery of double walled germanium based imogolite or the larger hybrid imogolite with a hydrophobic internal surface are good examples [5,6]. This growing number of new materials derived from imogolite and sharing the same imogolite local structure (ILS) is now making a new whole family of nanoclays.

The study of the synthesis of these new ILS materials has triggered much progress in the understanding of their formation mechanism. In this presentation, we will go through the recent discoveries about the formation mechanism of imogolite-like nanoclay. We will focus on recent investigations of the early constitution stage of imogolite. We will show that from the same starting conditions, it is possible to produce imogolite, allophane or mixture of both shapes.

These results demonstrate that imogolite and at least some allophanes can be considered as polymorphs of the ILS material. The control of the spherical or tubular shapes has barely been investigated. Bac et al. showed that in the case of germanium based imogolite, it is possible to go from mainly spherical to mainly tubular shape by changing the pH and salinity [7]. Abidin et al. using DFT simulations proposed that it is due to local properties of the Si-OH internal groups [8]. As sphere/tube transitions are also observed for hybrid ILS with the internal surface covered by Si-CH_3 groups an extension of this work as to be considered.

We propose a new hypothesis related to the mechanical properties of proto-imogolite. Using a simplified model accounting for border stress on small proto-imogolite, we show that it exits a size threshold for the sphere/tube transition. We suppose that this transition can at least in part explain the control in shape between ILS tube (imogolite) and sphere (proto-imogolite/allophane). We believe this mechanism to be very general and may be of interest for other clay minerals for which a spontaneous curvature exists and a coexistence of spherical and tubular shapes has been described (for example halloysite).

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ORIGIN, DISTRIBUTION AND FATE OF PHOSPHORUS AND POTENTIALLY TOXIC ELEMENTS IN THE SEDIMENTS OF INLE LAKE (SOUTHERN SHAN STATE, MYANMAR)

Myat Mon Thin (1), Elisa Sacchi (2), Massimo Setti (2)*, Viviana Re (2), Sergio Comizzoli (3)

(1) Department of Physics, University of Mandalay, Myanmar, (2) Department of Earth and Environmental Sciences, University of Pavia, Italy, (3) Centro di Ricerca sulle Acque, University of Pavia, Italy

Inle Lake is the second largest lake in Myanmar and the most important, for its economic, touristic, agricultural and environmental value. Previous studies report that Inle lake is seriously threatened by anthropic activities on the lake sides and in its drainage basin. One of the main problems is related to the decrease in the open water surface, attributed to an increase in sedimentation caused by accelerated soil erosion, as a consequence of deforestation in the watershed, and to the expansion of agriculture in the form of floating gardens [1].

A detailed sediment sample collection including 10 sediment cores ranging from 40 to 85 cm in length, and 16 dredged samples, was carried out in March 2014 (hot dry season). Dredged sediments and cores, cut in 5 cm slices, were wrapped in polythene foil to prevent oxidation, and were transported to the Department of Earth and Environment Sciences, University of Pavia (Italy). In the laboratory, sediment samples were dried at room temperature for 2-3 days in order to maintain the crystal structures, weighted and described for their colour using the colour chart. Major shells were eliminated by manual picking and dried sediment was ground to fine powder in agate mortar. Total P and trace metal concentrations in sediment samples were analysed by Total Digestion ICP/MS. In addition the acid soluble-P content and P fractions were investigated using a sequential extraction procedure according to the SMT protocol [2].

Results indicate a good correlation of P with U, Cd, Mo and Sb concentrations, but no correlation with the mineralogical composition of the samples. This correlation can be considered as the “P pollution factor”, due to the association of this element and to other trace elements commonly found in P fertilizers. The more enriched Tot-P content was found in the floating gardens area, due to the use of chemical fertilizers and to other anthropogenic sources such as domestic and sewage effluents. High amounts were also detected at the inflow stream, and at the centre of the lake, where the P content derives from to soil erosion and detrital inputs by the streams. The highest Tot-P concentrations were detected in the top layers of the sediment cores, which are affected by anthropogenic activities, whereas low values were observed in the deep sediment, which can be attributed to the natural level of phosphorus. Ca-bound P, accounting for an average of 35%, was the main inorganic-P pool. This is a relatively stable and non-bioavailable P form. Another important form was organic-P, accounting for about 30% of the total. This P pool is considered the more bioavailable since, during organic matter degradation, it can be released to the water column, thus contributing to the lake eutrophication. The rank order of P fractions allowed classifying Inle lake as mesotrophic, potentially shifting to eutrophic. In conclusion, the study provides useful information of anthropogenic impact on the lake ecosystem as a premise for the correct management of this valuable water body.

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THE SEDIMENTS OF INLE LAKE (SOUTHERN SHAN STATE, MYANMAR): MINERALOGICAL AND GEOCHEMICAL CHARACTERISATION TO TACKLE ORIGIN AND DEPOSITIONAL PROCESSES

Myat Mon Thin (1), Massimo Setti (2)*, Elisa Sacchi (2), Maria Pia Riccardi (2), Enrico Allais (3)

(1) Department of Physics, University of Mandalay, Myanmar, (2) Department of Earth and Environmental Sciences, University of Pavia, Italy, (3) ISO4 s.n.c., Torino, Italy

Inle Lake is the second largest lake in Myanmar and the most important, for its economic, touristic, agricultural and environmental value. Previous studies report that Inle lake is seriously threatened by anthropic activities on the lake sides and in its drainage basin, leading to a decrease in the open water surface, estimated to as much as 32.4% between 1935 and 2000. This is attributed to an increase in sedimentation caused by accelerated soil erosion, as a consequence of deforestation in the watershed, and to the expansion of agriculture in the form of floating gardens. [1]

Ten sediment cores, ranging from 40 to 85 cm in length, were collected in March 2014 (hot dry season). Cores were cut in 5 cm slices, wrapped in polythene foil to prevent oxidation, and transported to the Department of Earth and Environment Sciences in Pavia (Italy). In the laboratory, sediment samples were dried at room temperature for 2-3 days in order to maintain the crystal structures, and ground to fine powder in an agate mortar. The mineralogical composition was determined by X-ray powder diffraction (XRPD), while the topography of some crystal structures and the elemental composition were analysed using scanning electron microscopy (SEM). Major and trace element contents were determined by Total Digestion ICP/MS.

In the bulk sediment, the most abundant mineral is calcite (27 to 100%), followed by quartz (0 to 54%). Other less abundant minerals are: mica/illite (0 to 33%), kaolinite (0 to 14%), aragonite (0 to 15%) and hematite (0 to 9%). The clay fraction is mostly composed by kaolinite with lower mica/illite and chlorite, and traces of smectite. Calcite is not evenly distributed in the lake area: samples collected at or near the main inflow and at the outflow show an abundance of about 50%, generally increasing with depth, whereas within the lake calcite rises up to more than 90%. Endogenic calcite precipitation is known to occur in the warmer months, triggered by photosynthetic activity and evaporation of the water body [2], but detrital calcite is also likely present in the sediments.

SEM observations showed a variety of grain morphologies and surface textures. Grains are medium to coarse in size (4-500 µm), and are commonly constituted by calcite and quartz. Sediments collected near the inflow show the abundance of detrital minerals such as feldspar, calcite and quartz, which can be attributed to soil erosion. In addition, coarse grains are dominated by mineral aggregates, also probably formed in the soil, in which calcite is associated with organic matter. Sediments from the centre of the lake, accounting for 90% of calcite, show both detrital and endogenic calcite grains, characterized by a rounded shape and by superposed layers, respectively. An apatite grain was detected in sediments from the agricultural zone, and attributed to the use of phosphate fertilizers in the floating gardens.

Chemical analyses indicate that Ca is the most abundant element, in agreement with the abundance of calcite, followed by Al, Na and K, all elements contained in detrital minerals and associated heavy metals. The comparison between the elemental compositions of lake sediment with that of the rocks outcropping in the watershed confirmed that accelerated soil erosion, and the consequent detrital input to the lake, constituted a major source of potentially toxic elements to the lake.

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CLAY MINERALS AS THERMAL HISTORY INDICATORS OF INNER DINARIDES LITHOLOGIES FROM THE SURROUNDINGS OF HRVATSKA KOSTAJNICA (CROATIA)

Darko Tibljaš (1)*, Ena Topalović (1), Dražen Balen (2)

(1) Faculty of Science, University of Zagreb, HR-10000 Zagreb, Croatia

In the Eocene clastic rocks, represented by conglomerates, sandstones and shales, which crop out as a part of Inner Dinarides in the vicinity of Hrvatska Kostajnica (Croatia), zeolite minerals have been described earlier [1]. Zeolites, represented by stilbite and laumontite, occur mainly as cement but sometimes they are present in veinlets. Exact conditions of their formation are not defined yet. Cretaceous clastic and metasedimentary rocks are also present in the area, and it is difficult to distinguish them from Eocene ones due to absence of fossils and clear geological relations.

In order to decipher thermal conditions resposible for zeolite formation clay mineralogy of the rocks was studied. In addition clay mineralogy was also used to distinguish petrographically similar rocks of different ages. Investigations comprised standard X-ray powder diffraction determination of clay minerals including Kubler (KI) and Árkai indices (AI) measurements.

Preliminary results showed that clay minerals in Eocene rocks are represented mainly by smectite and illite having KI values characteristic for diagenetic zone. On the contrary Cretaceous rocks contain different varieties of chlorite-smectite interstratifications and illite with KI values typical for the anchizone.

Obtained results of thermal history based on clay mineralogy and Kubler and Árkai indices confirm existence of so far vaguely defined/poorly known very-low grade metamorphic event in the period from Cretaceous to pre-Eocene in the northwestern most part of the Inner Dinarides realm.

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SYNTHETIC AND NATURAL MATERIALS WITH THE BRUCITE-LIKE LAYERS AS CATALYSTS FOR THE SYNTHESIS OF PROPYLENE GLYCOL METHYL ETHERS

Maria N. Timofeeva (1)*, Aleksey E. Kapustin (2), Eleonora O. Butenko (2), Valentina N. Panchenko (1), Antonio Gil (3), Miguel A. Vicente (4)

(1) Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia, (2) Azov State Technical University, Mariupol, Ukraine, (3) Public University of Navarra, Pamplona, Spain, (4) University of Salamanca, Salamanca, Spain
*timofeeva@catalysis.ru

It is well-known that materials with the brucite-like layers, such as layered double hydroxides (LDHs) are widely used in catalytic reactions due to their unique structural and physicochemical properties. Unfortunately, information on catalytic applications of natural materials with the hydrotalcite-type structure is rather limited in literature.

In the present work, natural brucite (Kuldur deposit, Russia) and Mg,Al-layered double hydroxides (Mg,Al-LDHs) with various Mg/Al atomic ratios were investigated as catalysts for the reaction of propylene oxide (PO) with methanol to propylene glycol methyl ether (PGME) which is used as pollution-free solvent in fine chemicals synthesis in pharmaceutical, chemical and cosmetic industry.

The acid-base properties of Mg,Al-LDHs were analyzed by Hammett acidity titration with n-butylamine and benzoic acid, finding that the amount of acid and base sites can be tailored by the Al-content in the solids. The decrease in Al content led to the simultaneous increase in the amount of basic sites and the decrease in acid sites. The basic properties of the anionic clays were investigated by FT-IR spectroscopy using $CDCl_3$ as probe molecule. The increasing of the heating temperature of brucite from 90 to 150 ºC increased its basicity, but the further increasing of the heating temperature did not affect the strength of the basic sites. Basicity rose with the increase in the heating temperature of brucite, while the decrease in Al content favored the increase in basicity of the LDHs. This result was in agreement with the data of optical basicity estimated by a semiempirical method.

Special attention was focused on the investigation of correlations between basic and catalytic properties of these materials. It was found that the activity of brucite correlated well with the basicity, which depended on the activating temperature of brucite. In Mg,Al-LDHs, the decrease in Al content led to the increase in the selectivity towards PGME and the conversion of PO. The activity of Mg, Al-LDHs was lower than that of brucite, while selectivities towards PGME were close. In the presence of Brucite (150 ºC) and Mg,Al-LDH (Mg/Al = 3.89) conversions of PO were 42 and 28%, respectively, at 140 °C, 4.1 wt.% of catalyst, MeOH/PO molar ratio of 12 and time of reaction 7.5 h. The higher activity of Brucite (150) compared with Mg,Al-LDH (Mg/Al = 3.89) is related to the difference in the surface basicities.

The stability of the most active sample, namely Brucite (150 ºC), was investigated by means of recycling tests. It was demonstrated that Brucite (150 ºC) can be used repeatedly without significant loss of catalytic activity during at least four catalytic cycles.

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EFFECT OF ACID MODIFICATION OF CLAYS ON THE TEXTURAL, PHYSICOCHEMICAL AND CATALYTIC PROPERTIES

Maria N. Timofeeva (1)*, Valentina N. Panchenko (1), Kristina N. Makarova (1), Antonio Gil (2), Miguel A. Vicente (3)

(1) Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia, timofeeva@catalysis.ru, (2) Public University of Navarra, Pamplona, Spain, (3) University of Salamanca, Salamanca, Spain

Nowadays, acid-activated clays, mainly montmorillonites, have received much attention in organic synthesis due to their unique structural and physicochemical properties, and low cost. The acid activation of clays leads to the formation of Brønsted acid sites, which are important for carrying out various organic transformations. Acid-activated clays are widely used in reactions of isomerization, alkylation, acylation, among others. It is well-known that the type and concentration of the acids used in the chemical activation should affect the strength and the number of acid sites on the surface of the clay that should change the catalytic properties of the solids. However, this effect has received weak consideration to investigation in the open literature.

Our investigation is devoted to the exploration of the effects of concentration (0.125-3.0M) and type of acid (HCl, HNO_3, H_2SO_4 and CH_3COOH) on (a) the chemical composition of clays (natural montmorillonite (MM), natural kaolin (K) and metakaolin (MK)), (b) structural and textural properties of clays, (c) acid-base properties of clays, and (d) catalytic properties of clays in the synthesis of oxygen- and nitrogen-containing heterocyclic compounds.

Combination of physicochemical methods points that the chemical composition of the samples obtained by acid-activation of MM depends on the acid concentration. Substitution of the exchangeable cations by H^+ is observed when concentration of acid (HCl and HNO_3) is less than 0.5 M. The increase in acid concentration leads to the leaching of Al^{3+} cations from the octahedral sheets. The changes of chemical and phase compositions affect the textural properties of the activated samples. According to IR spectroscopy using pyridine as probe molecule, the amount of Brønsted acid sites in MMs rises with increasing the acid concentration up to 0.5 M and then slightly decreases. The strength of Brønsted acid sites varied negligible in acid-activated MMs. Using HCl for acid activation we demonstrated that the amount and strength of Brønsted acid sites depend on the type of clay and decreases in the order:

$$\text{HCl-MM} > \text{HCl-K} > \text{HCl-MK}$$

Correlations between the Brønsted acidity, the porous structure of the acid-activated clays and their catalytic performance were revealed in (a) the Prins cyclization reaction of (-)-isopulegol with vanillin to octahydro-2*H*-chromen-4-ol, (b) cyclocondensation of glycerol with acetone to solketal, (c) cyclocondensation of o-phenylenediamine with acetone to 1,5-benzodiazepine. According to the experimental results, the Brønsted acidity, the microporosity and the structure of the catalysts are key factors for the control of the reaction rate and the selectivity towards the main products.

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EFFECT OF SILICA-BEARING PHASES IN DREDGED SOIL ON THE STRENGTH DEVELOPMENT OF STEEL SLAG-DREDGED SOIL MIXTURES

Kanako Toda (1)*, Yu Arai (1), Tsubasa Otake (2), Tsutomu Sato (2), Haruna Sato (1), Nilan Weerakoon (1), Satoshi Nishimura (2)

(1) Graduate School of Engineering, Hokkaido University, Sapporo 060-8628, Japan, (2) Faculty of Engineering, Hokkaido University, Sapporo 060-8628, Japan
*knktd@eis.hokudai.ac.jp

Both steel slag from ironworks and dredged soil extracted beneath the ports are by-products from industrial activities. While the most of steel slags have been reutilized as construction materials, significant volume of dredged soils have been disposed as wastes. Dredged soils have soft physical properties and therefore are difficult to be utilized for construction materials. They are land filled or dumped in other sea floor. However, Japan faces the problem of land filling site shortage, increasing the need to utilize dredged soil as a constant resource supply. Dredged soils are mainly composed of minerals including clays, organic debris and seawater. Indeed, its characteristics differ greatly depending on the sampling areas due to the variation of its composition. Recently, it is discovered that mixtures of steel slag with dredged soil are hardened. This discovery may expand their application into building materials for undersea construction such as refilling, reclamation and constructing tideland. Nonetheless, different combinations of a type of steel slag and dredged soil from various areas show gaps in the strength development even under an identical mixing condition. The relationship between mixing condition and strength development is not yet clarified, making the mixture difficult to be utilized for the above application.

Understanding of the hardening mechanism of the steel slag-dredged soil mixture will enable the prediction of the strength with a particular combination of steel slag and dredged soil. To achieve it, clarifying the secondary mineral formation that contributes to hardening is essential. Previous studies suggested that the strength development was related to the pozzolanic reaction, which results in cementation by the formation of calcium silicate hydrates (C-S-H). Key factors in the pozzolanic reaction are the increase in pH of the pore water and the supply of calcium and silica ions to pore water. Steel slag contains $Ca(OH)_2$, which supplies calcium and increases pH of the mixture. From the dredged soil, silica will be supplied but it is not clarified what component is being the silica supply.

Focusing on the variation of dredged soil affecting the strength development, the objective of this study is to understand the effects of silica-bearing phases in dredged soil on the strength development of steel slag-dredged soil mixture.

In this study, dredged soils from various sampling locations (A, B, C and D) and a steel slag from ironworks 1 were mixed for the investigation. The unconfined compressive strength showed mixtures with soil A exhibits the highest strength, followed by those with B, C and D. Through 3-day cured sample's cross-sectional area observation, formation of C-S-H in mixture A was found to be denser than mixture D, filling up pores in the mixture. In addition, the measurement of mixtures' pore water pH transition showed decreasing trend in pH from 12.5 in only mixtures A and B but not C and D during 0day-91days curing time. This suggests stronger mixtures' (A and B) pore water's pH was dominated by formed secondary minerals, such as C-S-H which expels H^+ when the reaction goes forward for the formation of it, indicating that the secondary mineral formation was notably greater in stronger mixture. Firstly, the effect of humic acid, that is a kind of organic substance, which may limit the supply of soluble calcium is quantified to see the effect on strength development of the mixtures. Further, the silica ion was most likely supplied from dredged soils so the biogenic silica contents is also clarified by the dissolution experiment. Inorganic amorphous silica such as volcanic glass content is also discussed. XRD analysis showed no significant difference between the mineralogical compositions of all the dredged soils before mixing, all containing Fe-chlorite, kaolinite, 2-8mica and smectite in terms of clay minerals. The consumption of clay minerals through multiple curing times is traced using XRD. Through geochemical modeling for estimation of C-S-H formed from above silica supply, we suggest that the silica supply from each silica-bearing phase of dredged soils may be the driving force for the pozzolanic reaction during strength development.

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HIERARCHICALLY POROUS LAYERED DOUBLE HYDROXIDE THROUGH PSEUDOMORPHIC REPLICATION FROM AMORPHOUS HYDROXIDE

Yasuaki Tokudome (1)*, Masanori Takemoto (1), Vanessa Prevot (2,3), Claude Forano (2,3), Masahide Takahashi (1)

(1) Graduate School of Engineering, Osaka Prefecture University, Sakai, Osaka 599-8531, Japan, (2) Institut de Chimie de Clermont-Ferrand (ICCF), Université Clermont Auvergne, Université Blaise Pascal, BP 10448, F-63000, Clermont-Ferrand, France, (3) Institut de Chimie de Clermont-Ferrand (ICCF), UMR 6296, Centre National de la Recherche Scientifique (CNRS), F-63171, Aubiere, France
*tokudome@mtr.osakafu-u.ac.jp

Layered double hydroxides (LDHs) are a family of lamellar compounds with a general formula of $[M_{1-x}^{z+}M_{x}^{3+}(OH)_2]^{a+}[A^{n-}]_{a/n}\cdot mH_2O$, where M^{z+} and M^{3+} are cations, and A^{n-} is a charge compensating anion. Various combinations of cations and anions have been adopted to synthesize LDHs depending on targeted functionalities, such as optical, electrochemical, surface basicity, and anion-exchange properties. As well as the chemical tuning, structuration has been employed to optimize and enhance inherent characteristics of LDHs [1-3]. Most of LDHs with various morphologies reported so far rely on textural porosity where aggregated LDH platelets form pores that are not finely tunable by synthetic parameters. Alternatively, topochemical conversion of lamellar host materials into LDHs is a promising approach to yield pure LDHs with well-defined morphologies. Previous reports demonstrated that treatments of gibbsite, bayerite, and nordstrandite (polymorphs of $Al(OH)_3$) with aqueous lithium salts LiX ($X = Cl, Br, NO_3$) lead to simultaneous intercalation of Li^+ and X^- into the host structures to form Li/Al LDH with different intercalated anions [4,5]. To this end, a key issue is the preparation of crystalline aluminum hydroxide with a controllable morphology.

On the other hand, crystalline aluminum hydroxide with a predesigned structure is hard to prepare especially when its size is in nanometer size scale, where inhomogeneous agglomeration and Ostwald ripening are reported to occur to yield sedimentations of aggregated crystalline particles. Developing a pathway to prepare nano precursory hydroxides and transcribe them into LDH via a pseudomorphic manner is highly demanded.

Herein, for the preparation of Li/Al LDH, characteristics of nanoparticulate amorphous aluminum hydroxide, *i.e.* high reactivity and feasibility toward nano/macrostructuration were fully employed. We demonstrate the fabrication of hierarchically porous pure Li-Al LDH though a pseudomorphic replication from a hierarchically porous monolith composed of amorphous aluminum hydroxide nanoparticles. The highly soluble amorphous nanoparticles reacted with LiOH aq with a diffusion limited manner, allowing the pseudomorphic replication into Li/Al LDH. As well as the hierarchically porous monolith, aqueous suspension of Li/Al LDH nanocrystals was successfully obtained through the same replication strategy from corresponding suspension of aluminium hydroxide. These replicated Li/Al LDHs exhibited catalytic activity toward a transesterification of soybean oil, confirming considerable surface basicity derived from high specific surface area and intrinsic LDH nature. The discussion will be mainly dedicated to the mechanism of LDH crystallization thorough the replication process.

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SYNTHESIS OF AQUEOUS COLLOIDAL LDH NANOCRYSTALS: ALKALIZATION REACTION ACCOMPANIED WITH GELATION-DEFLOCULATION TRANSITION

Yasuaki Tokudome*, Masanori Takemoto, Masahide Takahashi

Graduate School of Engineering, Osaka Prefecture University, Sakai, Osaka 599-8531, Japan
tokudome@mtr.osakafu-u.ac.jp

Nanostructuration is a promising way to improve inherent properties of layered double hydroxide (LDHs), such as anion exchangeability, surface basicity, and adsorption characteristics. Synthesizing LDH nanoparticles has been in great demand and widely explored to this end. Despite its importance, the aqueous synthesis of LDH materials with a single-nm-size is hard to achieve expect a very few cases [1,2]. Most of LDHs nanomaterials reported so far are composed of primary particles with a size a few tens nm and more, and additionally, they are strongly aggregated to form sedimentations. Alternative route to access LDH nanomaterials is delamination of bulky LDH crystals. Recent studies reported that the delaminated LDH powders exhibit a high surface area (>260 m^2/g) by employing a special drying step called as AMOST [3]. On the other hand, isolating delaminated LDH nanosheets in polar solvents is still a considerable challenge because of aggregation and restacking of the nanosheets. Developing stable and concentrated aqueous suspensions of LDH nanocrystals will provide benefits for various applications taking advantage of features derived from nanometric LDH materials.

Herein, we demonstrate a synthesis pathway towards aqueous suspension of LDH nanocrystals with a size of 5 nm. Two different families of LDHs, M(II)/M(III) and M(I)/M(III) LDH, were nanocrystalized and simultaneously stabilized as a highly concentrated aqueous suspensions through a simple one-pot process. As a typical example, the synthesis of Ni/Al LDH was performed at a considerably-high supersaturation with using a starting mixture 80 times more concentrated than those for standard LDHs. Nevertheless, stable suspension without aggregation was successfully achieved by taking advantage of the spontaneous gelation−deflocculation transition of nanocrystalline LDH gels [4]. As a result, suspension of LDH nanocrystals (isotropic shape with the size of 4.5 nm), which are concentrated (100 g/L in water/alcohol solvent), stably dispersed (transparent sol for >2 weeks), and catalytically active have been successfully obtained. The synthesis strategy is versatile and can be extended to prepare various LDHs with chemical compositions, Zn/Al, Ni/Al, Co/Al, and Li/Al LDH.

Proof of concept applications revealed that the LDH nanocrystals work as solid basic catalysts and allows easy separation from solvents of catalytic reactions, confirming the nature of nanocatalysts. LDH nanocrystals thus obtained with a single-nm-size work as nanobuilding blocks (NBBs) to form mesoporous and macroporous materials, allowing to enhanced diffusion and accessibility of guest molecules/ions. The formation mechanism of LDH NC as well as the capability of their use as crystalline NBBs will be closely addressed.

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SUSTAINABLE HAZARDOUS WASTE TREATMENT WITH NATIVE CLAY AND ZEOLITE

Dragana Tomasevic Pilipovic (1)*, Aleksandara Dosic (2), Djurdja Kerkez (1),
Milena Becelic-Tomin (1), Natasa Slijepcevic (1), Bozo Dalmacija (1), Dejan Krcmar (1)

(1) University of Novi Sad, Faculty of Sciences and Mathematics, Department for Chemistry, Biochemistry and Environmental Protection, 21000 Novi Sad, Serbia, (2) University of East Sarajevo, Faculty of Technology, Zvornik, Republic of Srpska
*dragana.tomasevic@dh.uns.ac.rs

Disposal of mine tailingswhich appears during the mining activity from “Bor” mine (Serbia), represents an enormously large environmental problem, because mine tailings is highly polluted with toxic heavy metals. This waste material is characterised as hazardous due to its high contents and leachabilities of toxic metals and constitutes a severe risk to the environment, especially ground water. Therefore it is necessary to expose mine talling to certain treatments of remediation. Stabilization/solidification (S/S) technology has been widely applied to immobilize toxic metals in different types of sludge with various additives [1]. Quantifying the environmental impact of S/S materials in real environment scenarios is crucial for selecting proper disposal and reuse alternatives and for certification of immobilization technologies.

This work investigate the possibilities of immobilizing heavy metals in waste sludge from mine tailings, using different low-cost effective sorbents (native clay and zeolite) and determines their effectiveness depending on numerous factors. The performance of the immobilizing procedures was examined using several leaching tests: one long-term diffusion test (ANS 16.1 [2]) and three batch leaching tests (DIN 38414-4 [3], TCLP [4], MWLP [5]). Each test uses a different leaching fluid to mimic field conditions and give realistic access into the actual environmental scenario.

Overall, the test results indicated that solidification/stabilisation treatment was effective for immobilization toxic metals in the mine tailing, and can be considered acceptable for “controlled utilization”. Also, the results indicated that all S/S samples can be considered as non-hazardous waste, as all leached metal concentrations met the set criteria.

These results will further enable the modelling of metals behaviour during long-term leaching from treated mine tailing and assess the most effective agents for the immobilization. The data are invaluable in terms of economically and environmentally sound management of mine tailing.

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RADIATION PRESSURE INDUCED ORIENTATION OF COLLOIDAL OXIDE NANOSHEETS

Makoto Tominaga (1,2)*, Takashi Nagashita (3), Yuki Higashi (4), Takuya Kumamoto (5), Teruyuki Nakato (5), Yasutaka Suzuki (1,3,4), Jun Kawamata (1,3,4)

(1) Graduated School of Medicine, Yamaguchi University, Yamaguchi 753-8512, Japan, (2) Research Fellow of Japan Society for the Promotion of Science, Tokyo 102-0083, Japan, (3) Graduated School of Sciences and Technology for Innovation, Yamaguchi University, Yamaguchi 753-8512, Japan, (4) Faculty of Science, Yamaguchi University, Yamaguchi 753-8512, Japan, (5) Department of Applied Chemistry, Kyusyu Institute of Technology, Fukuoka 804-8550, Japan
j_kawa@yamaguchi-u.ac.jp

A photon carries not only energy but also momentum. When photons collide to an object, momenta of photons change by scattering. At the same time, a force called radiation pressure is applied to the object. By taking advantage of the radiation pressure of a tightly focused laser beam, an object can be trapped selectively at the focal point [1]. For example, particles such as a protein and a droplet with a diameter of 3 to 12 μm have been trapped [2-4].

In this study, we applied radiation pressure of a tightly focused laser beam to liquid crystalline oxide nanosheets. Nanosheet liquid crystals, which are lyotropic liquid crystals, consist of colloidally dispersed oxide nanosheets with a thickness of 1 nm and a lateral size of several μm. Orientation of the oxide nanosheets can be changed at macroscopic scales by applying an electric field, similar to organic liquid crystal [5]. However, the orientational change of oxide nanosheet at a microscopic scale has not been realized. Thus, we attempted to realize the orientation of oxide nanosheets at a microscopic scale by the radiation pressure of a focused laser beam.

Oxide nanosheet colloids consisting of niobate nanosheets with a particle size of ca. 1.6 μm were prepared at concentrations of 0.05, 5 and 50 g/L. The colloids exhibited isotropic, mixture of isotropic and liquid crystal and liquid crystal phases, respectively. The niobate nanosheet colloids were sandwiched by a glass slide and a cover glass with a spacer of 100 μm. A linearly polarized laser beam ($\lambda = 532$ nm, 100 mW) was irradiated to the sample mounted on a polarizing microscope through an objective lens (x25, N.A. = 0.4). The spot size of the laser beam at the focal point was estimated to be 0.8 μm. The orientation of niobate nanosheets was observed with crossed polarizers.

For the niobate nanosheet colloid prepared at 0.05 g/L, the polarized microscope image was dark before and after the laser irradiation. On the other hand, bright area appeared upon the irradiation for the niobate nanosheet colloid prepared at 5 g/L around a focal point. An optical texture similar to Schlieren texture was observed during the laser irradiation, although the image before irradiation was dark. For the niobate nanosheet colloid prepared at 50 g/L, bright area was observed even before the laser irradiation and the texture was not changed during laser irradiation.

A dark area in the polarized microscope image indicates homogeneous orientation of the niobate nanosheets with their in-plane direction parallel to a cell surface. On the other hand, a bright area indicates the presence of niobate nanosheets with their out-of-plane orientation to a cell surface [5]. Therefore, it was concluded that, in the niobate nanosheet colloid prepared at 5 g/L which exhibited the mixture of isotropic and liquid crystal phases, orientation of the niobate nanosheets at a microscopic scale was changed by radiation pressure of a focused laser beam.

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STUDY OF THE Fe/BENTONITE INTERFACE AT DIFFERENT TEMPORAL AND SPATIAL SCALES: SIGNIFICANCE FOR UP-SCALING

Elena Torres (1)*, M. Jesús Turrero (1), Raúl Fernández (2), Ana Ruiz (2), Jaime Cuevas (2)

(1) Applied Environmental Geology. CIEMAT. Madrid, Spain, (2) Department of Geology and Geochemistry, Faculty of Science, Madrid, Spain

The FEBEX experimental program was planned regarding the up-scaling effect when research on long-term evolution of deep geological repositories (DGR) is addressed. Results provided by different experimental concepts and using different scales and test durations feed models but it is necessary to evaluate the representativeness of the results in terms of performance assessment of the DGR. Having this in mind, this work presents and compares the results obtained from both laboratory and *in situ* experiments designed with the aim of further interpretation of the up-scaling effect. The experimental plan and the duration of the experiments were prepared to make up an added value to previous works, since both imply a quite realistic approach to the conditions expected in a repository during the re-saturation process.

The FEBEX in situ test was a full-scale demonstration of the Spanish DGR concept in granite, in which the waste canisters are emplaced horizontally in drifts, surrounded by a barrier of high density compacted bentonite blocks [1]. Two metallic heaters simulating the thermal load of the metallic waste packages were switched on to a temperature of 100 °C, while the bentonite buffer was slowly hydrating in a natural way with groundwater coming from the granite. The heater closer to the gallery entrance was switched off and dismantled after 5 years. The gallery was sealed with a sprayed concrete plug and a second operational phase started (*www.grimsel.com/gts-phase-vi/FEBEX-dp*). The experiment was dismantled in 2015, after 18 years of operation and the post-mortem characterization of aged samples of bentonite that have been in contact with metallic components (e.g. heater and liner) has been made.

A series of six scale-model experiments was designed to simulate as close as possible the evolution of the geochemical environment in the carbon steel/bentonite interface of a DGR. The six column experiments were assembled and sequentially dismantled to evaluate the evolution of the system from transient to full-saturation state [2]. These column experiments started running simultaneously in August'06. Up to now, four of them have been dismantled sequentially after 6, 15, 52 (4.3 years) and 82 months (7 years) of operation. Characterization of the bentonite in contact with iron was accomplished in the six tests.

Common geochemical processes were observed in the two scales. Due to simultaneous heating and hydration of bentonite, thermal and hydraulic gradients were generated along the bentonite blocks. These gradients are responsible for the accumulation of salts observed in the proximity of the heaters and the redistribution of exchangeable cations. Magnesium is the major cation in hotter areas whereas it tends to decrease in low-temperature saturated zones. On the other hand, precipitation of carbonates such as calcite (aragonite) and siderite (ankerite) have been detected in bentonite in contact with the heater or the liner.

Deliquescence of salts, especially chloride, seems to play a relevant role on the initialization of corrosion since chlorine traces were detected in corrosion products. Low relative humidity and oxygen fugacity in the proximity of the canister has favoured low corrosion rates. An overall Fe enrichment has been observed in all the analyzed interfaces, mainly related to the precipitation of FeOOH. EDS analyses revealed that the alteration zone do not exceed 100-µm in any case. The altered area consisted basically of a mixture of corrosion products and compacted bentonite enriched in chloride and sulfate. Fe-rich newly-formed clay phases could not be detected in any of the Fe/bentonite interfaces.

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CLAY MINERALS AND THEIR DIAGENETIC EVOLUTION: EXAMPLE OF THE MIDDLE MISSISSIPPIAN DEPOSIT OF JBEL BOUKHMIS, CENTRAL MOROCCO

Hafsa Tourab*, Mostafa Berkhli, Hassan Mounach, Amal Hachimi

University of Moulay Ismail, Faculty of sciences, Department of geology. PO. Box 11201 Zitoune, Meknès - Maroc
m.berkhli@fs-umi.ac.ma

The Jbel Boukhmis Formation outcrops in the East of central Morocco. It's located at the North of Mrirt city, less than two kilometers from the national road R712 connecting Meknes to Mrirt. It lies in angular unconformity on Devonian series. The overthrust structure shows a verging towards the NW. The biostratigraphic dating of this Formation gives it a Brigantian age. This Formation, about 100m thick, is composed essentially of very diverse carbonate facies ramp. The analysis of carbonates microfacies indicates an internal, medial and external environments ramp. These facies show lateral and vertical variations indicating a translation on time and space of depositional environments [1]. The aim of this paper is to determine the clay minerals of the Jbel Boukhmis Formation and to determine their diagenetic evolution.

The qualitative and semi-quantitative analysis of the different diffractograms reveals that the clay minerals of the Jbel Boukhmis Formation are composed essentially of simple minerals such as kaolinite (0-44%), illite (41-100%), chlorite (0-31%), vermiculite (0-28%) and mixed layer clay minerals such as illite-chlorite and illite-vermiculite type (<21%). The vertical evolution of these minerals shows the dominance of inherited minerals (kaolinite, illite, chlorite) towards the top of this Formation. The kaolinite of the Jbel Boukhmis Formation has a detrital origin. Its predominance along this Formation shows a shallow depth of burial and testifies to a warm and humid climate that prevailed in Morocco during the Brigantien. The distribution model of kaolinite can inform us about changes in the accommodation space. Indeed, its distribution along this Formation shows its dependence on lithology. The percentages of kaolinite show a significant increase towards the coastal facies and a decrease towards the sea. Chlorite, detritic with a badly formed 14 A° peak, is transformed into vermiculite by degradation process, by washing of Mg^{2+} cations that exists between the interlayer spaces of the chlorites. The increase of the diagenetic processes (pressure and/or temperature) towards the depth favors the increase of the illite crystallinity and the disappearance of the kaolinite, which becomes sensitive under the effect of these new conditions. They favor also the appearance of mixed layer clay minerals (illite-chlorite or illite-vermiculite) from simple minerals and/or the transformation into illite and chlorite more or less stable under these conditions. This is called the burial diagenesis. The distribution of clay minerals (C, I-C, I, I-V and V) along the Jbel Boukhmis Formation also shows a visible cyclicity. This cyclicity is related to variations in sea level, thus asserting the relationship between sedimentary facies and clay minerals. These data indicate rather the major effect of the detrital contribution and the intense effect of the meteorization in the study area during the Brigantian.

The ratio I002 / I001 of the illite is superior than 0.3, which testifies to an aluminous character of the illites. The representation of the illite crystallinity (Kübler's index) as a function of the I002/I001 ratio of the illites on the Esquevin diagram shows diagenetic to anchizonal domains.

Clay minerals are excellent diagenetic and climatic indicators. The distribution of clay minerals proves that the carbonate platform of Jbel Boukhmis evolved under the influence of a tropical climate during the Brigantian. The origin of these alumina silicates is mainly the alteration, in a hot and humid climate, of the silicate minerals of a hinterland that feeds this carbonate platform. The covering of the sedimentary series does not exceed about 4km. The degree of metamorphism that affected the Jbel Boukhmis area is very low and the effect of the hercynian deformations is negligible.

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CLAY MINERALS AND THEIR TECTONIC SIGNATURE: A CASE OF THE MIDDLE MISSISSIPPIAN OUTCROPS OF AGARAD-N-AZDAÏT AREA, CENTRAL MOROCCO

Hafsa Tourab*, Mostafa Berkhli, Hassan Mounach, Amal Hachimi

University of Moulay Ismail, Faculty of sciences, Department of geology. PO. Box 11201 Zitoune, Meknès - Maroc
m.berkhli@fs-umi.ac.ma

The Middle Mississippian series of the Agarad-n-Azdaït area crop out at North of the Mrirt city (East of central Morocco). At less than two kilometers to the East of national road R712 connecting Meknes to Mrirt, two Brigantian Formations, Boukhmis and Aoujgal Formations, crop out in this area. The Boukhmis Formation lies in abnormal contact on Devonian series. The Aoujgal Formation lies in angular unconformity on Namurian series and overlapped by a Devonian series. This overthrust structure shows a verging towards the NW. These two Formations are composed of very diversified carbonate ramp facies which show lateral and vertical variations indicating a translation of the deposit environment in space and time [1,2]. The aim of this piper is to identify the clay minerals of Agarad-n-Azdaït area and show their tectonic signatures.

The qualitative and semi-quantitative analyzes of the clay fraction of the Boukhmis and Aoujgal Formations show a clay mineral assemblage composed of simple minerals such as illite, kaolinite, chlorite and vermiculite and mixed layer clay minerals such as illite-Chlorite and illite-vermiculite. The persistence of kaolinite and vermiculite along these Formations confirms a total recovery of less than 4000m. Five samples were taken near the thrust fault, separating the Boukhmis Formation from the Devonian substratum. Those samples are composed of 47 to 100% of illite and 0 to 53% of chlorite. Five other samples were taken from the proximity of lystric faults which subdivide the Aoujgal Formation to three unites. Those samples are composed of 65.22 to 100% of illites and 0 to 53% of chlorites. On the whole, we remark that the samples taken in the brecciation zones are composed only of illite. The mineralogical data delivered by these samples show a disappearance of kaolinite and an increase in the illite crystallinity. The other clay minerals (vermiculites and mixed-layers clays) are transformed to chlorites and/or illites more or less stables under these conditions, indicating a strong increase in temperature and pressure. The disappearance of vermiculate in favor of illites and chlorite and the increase of illite crystallinity attest the tectonic effect. The disappearance of kaolinite proves thermal effect of tectonic.

The representation of the illite crystallinity as a function of the illite I002/I001 ratio on the Esquevin diagram of Agarad-n-Azdaït shows that all the samples taken in the faults zones, are located in the epizona domain. In this domain all clay minerals are transformed by recrystallization into illites and/or chlorites under the thermal effect of tectonics. Also, a sensitive kaolinite was disappeared under these conditions, so as the increasing of the illite crystallinity. Moreover, the other samples taken along the Aoujgal and Boulhmis Formations are located in diagenitic and anchizonal domains. These results prove that a posterior tectonic affecting the Agarad-n-Azdaït area.

These new mineralogical data call into question the theory of intra-viséan synsedimentary sheet evoked by the previous works and proves that their establishment would be rather post-Namurian.

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PYRENEAN OSCILLATORY-ZONED CHLORITE: FROM FIELD TO GEOCHEMICAL SOLID-SOLUTION MODEL

Trincal Vincent (1)*, Buatier Martine (2), Charpentier Delphine (2), Lanari Pierre (3), Lacroix Brice (4), Labaume Pierre (5), Muñoz Manuel (6)

(1) IMT Lille Douai, Laboratoire GCE Ecole des Mines de Douai, France, (2) Université de Franche-Comte, Laboratoire Chrono-Environnement, Besançon, France, (3) Institute of Earth Sciences, University of Bern, Bern, Switzerland, (4) Department of Earth and Environmental Sciences, University of Michigan, Ann Arbor, United States, (5) Géosciences Montpellier, UMR 5243, Montpellier, France, (6) Laboratoire ISTerre, Université Joseph Fourier, Grenoble, France
*vincenttrincal@gmail.com

Oscillatory-zoned chlorites were sampled in hydrothermal quartz-chlorite shear veins from the Pic-de-Port-Vieux thrust, a second-order thrust related to Gavarnie thrust in the Axial Zone of the Pyrenees (Spain). They occur as pseudo-uniaxial plates arranged in rosette-shaped aggregates which appear to have been developed as a result of radial growth of the chlorite platelets. Chemical zoning is common in solid solution minerals (e.g. garnet), it is commonly attributed to changing chemical or physical conditions during crystal growth, and however it has been rarely reported in phyllosilicates. In order to filling this gap, oscillatory-zoned chlorite have been imaged by microscopy (Figure 1) and analysed coupling X-ray quantitative micro-mapping and μ XANES spot analyses collected at the Fe-K edge. Results suggest that zoning corresponds to alternating iron-rich and magnesium-rich bands; could be interpreted to a cyclic change in temperature from about 310 to 400±50 °C throughout the chlorite crystallization. Its chemical composition ranges from:

Fe rich pole ($[Si_{2.59}Al_{1.41}](Al_{1.37}Fe^{3+}_{0.74}Fe^{2+}_{1.04}Mg_{2.48}\square_{0.35})O_{10}(OH)_{8}$) to

Mg rich pole ($[Si_{2.63}Al_{1.37}](Al_{1.35}Fe^{3+}0._{38}Fe^{2+}_{1.13}Mg_{2.95}\square_{0.18})O_{10}(OH)_{8}$).

In situ measurements of XFe^{3+} ($Fe^{3+}/Fe^{2+} + Fe^{3+}$) performed in this study suggest an Al-free di-trioctahedral substitution $2Fe^{3+} + \square = 3(Mg,Fe^{2+})$ in chlorite; and a ferri-sudoite end-member $(Si_{3}Al)[(Fe^{2+},Mg)_{2}Fe^{3+}_{2}\square Al]O_{10}(OH)_{8}$ within the chlorite solid-solution domain. These unexpected observations in heterogeneous chlorites must be confirmed by further studies to precise the crystallographic position of Fe^{3+} and refine ferri-sudoite thermodynamic properties.

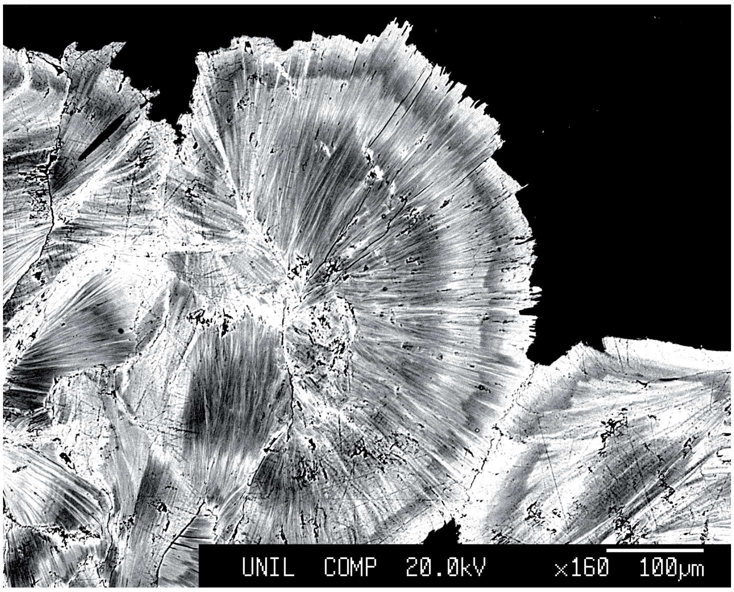

Fig. 1. Oscillatory-zoned chlorite from the Pic-de-Port-Vieux thrust

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LAYERED DOUBLE HYDROXIDES: MATRICES FOR STORAGE AND SOURCE OF BORON FOR PLANT GROWING

Jader Alves Ferreira (1), Gustavo Franco de Castro (2), Gustavo Nogueira Guedes Pereira Rosa (2), Denise Eulálio (1), Silas Junior de Souza (1), Roberto Ferreira Novais (1), Frederico Garcia Pinto (1), Jairo Tronto (1)*

(1) Universidade Federal de Viçosa, Instituto de Ciências Exatas e Tecnológicas, Campus de Rio Paranaíba, Rodovia MG-230 km 08, Rio Paranaíba - MG, 38810-000, Brazil, (2) Departamento de Solos, Universidade Federal de Viçosa, Viçosa - MG, 36570-900, Brazil
*jairotronto@ufv.br

Boron (B) is a micronutrient essential for plant growth and development. Part of the B that is added to soil as a fertilizer remains soluble and may be easily leached into the soil profile. To increase plant adsorption efficiency, it is essential to increase crop productivity. It is therefore necessary to search for alternative ways of making B available for plants. Incorporating B into two-dimensional inorganic host matrices, i.e. Layered Double Hydroxides (LDHs), provides an interesting alternative for evaluating how these materials can make B available for the plants. The objectives of this work were: (*i*) synthesis and characterization of LDH intercalated with B (LDH-B); (*ii*) to evaluate B availability in soils as a function of different contact times between the B sources (LDH-B and H_3BO_3) and the soils; (*iii*) the application of LDH-B as a B source for plant growth.

LDH-B was prepared by the coprecipitation method at constant pH [1]. The synthesized material was characterized by DRXP, FTIR/ATR, TG-DSC, specific surface area (BET method), pore volume, pore size, SEM and elemental analysis. To evaluate applicability of LDH-B in agriculture, we conducted an experiment to evaluate available B in the soil. In this experiment, 0, 10 and 20 mg·dm^{-3} doses of total B, in the forms of H_3BO_3 and of LDH-B, were applied to two different soils (clayey and medium texture). Available B in the soil was evaluated after 40, 20, 10, 5, 3, 2 and 1 days of contact between the B sources and the soils [2]. A bioassay, conducted in a greenhouse with appropriate statistical analysis, was done to verify the B supply for plants from the two sources, H_3BO_3 and LDH-B. Sunflower plants (*Helianthus annus*) were cultivated in pots. After 45 days of cultivation the aerial part of the plants was harvested. Plants were dried to determine dry material (DM) production.

The diffractogram profile was characteristic of hydrotalcite-like compounds, and the basal plane spacing value calculated with the Bragg equation was 12.0 Å. This is coincident with values reported in the literature for the intercalation of tetraborate anions [$B_4O_5(OH)_4^{2-}$] among LDH layers [1]. The spectrum of FTIR/ATR presented bands in 1600 to 500 cm^{-1} region, which are attributed to various vibrational modes because of the presence of tetraborate anions [1]. The specific surface area, pore volume and pore size values for LDH-B were 89.85 m^2·g^{-1}, 3.65x10^{-2} cc·g^{-1}, and 1.98 Å. The results of B available in the soil as a function of the different contact times demonstrated that LDH-B presented better performance for B release in clayey soils than H_3BO_3. The quantities of B available in the soil were lower for LDH-B than H_3BO_3, suggesting LDH-B presents higher stability compared to H_3BO_3. For medium texture soil however, behavior was similar between the two sources, which suggest that LDH-B would not be stable in this soil. In the bioassay, for both soils and both sources studied, DM production in the aerial part of the plants increased compared to the treatments that did not receive B. DM production, obtained in the clayey soil using H_3BO_3 and LDH-B, presented very similar values, 15.8 g·dm^{-3} and 15.4 g·dm^{-3}. For the medium texture soil, DM production was much lower than values found for clayey soils. In this soil, values were also close to DM production for both sources, 11.8 g·dm^{-3} for H_3BO_3 and 10.1 g·dm^{-3} for LDH-B. To evaluate the behavior of the LDH-B compared to H_3BO_3, DM production results between the two sources, suggests that LDH-B may be potentially used as a B source for plants. Successive sunflower crops in these soils, without the replacing the B sources, are being done by our research group, with the end goal of evaluating LDH-B as a slow release B matrix for plants.

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SMECTITE IN BENTONITE: CHEMOMETRIC PREDICTION OF LAYER-CHARGE BY NIR SPECTROSCOPY

Constantinos Tsiantos, Vassilis Gionis, Georgios D. Chryssikos*

Theoretical and Physical Chemistry Institute, National Hellenic Research Foundations, Athens, 11635, Greece

NIR spectroscopy offers a convenient tool for the non-invasive and accurate study of interlayer H_2O and structural O-H in clays, without interference from commonly present non-hydrous mineral admixtures. For example, a recent survey of ~1000 natural bentonite samples has indicated that the smectite in them (montmorillonite or beidellite) exhibits a range of frequencies of the sharp Al_2O-H and H_2O ($\nu+\delta$) combination modes (4537-4512=20 cm^{-1} and 5258-5242=16 cm^{-1}, respectively [1]). The positions of the two bands are linearly correlated. Moreover, the locus of reference samples (SAz-1, STx-1, SWy-2) suggested a tentative relationship between increasing Al_2O-H and H_2O ($\nu+\delta$) frequencies and decreasing layer charge.

The sharp H_2O ($\nu+\delta$) combination band at ~5250 cm^{-1} involves the high-frequency stretching component (ν) of interlayer H_2O in smectite, assigned to dangling HO-H bonds which are pointing towards the siloxane surface [2,3] and proposed as an indirect quantitative probe of layer charge [4]. Unfortunately, the MIR-based layer charge prediction tool cannot be directly transferred to the NIR. This is because the contribution of the bending mode δ in the ($\nu+\delta$) combination introduces a dependence of peak position on the nature of the interlayer cation [2].

In order to explore the possibility of developing NIR-based tools for the prediction of layer charge we have studied a set of 65 raw bentonite powders, each in its natural (Ca-, Mg-) and Na-exchanged form. Layer-charge measurements on both series of samples by the D_2O method of Kuligiewicz et al. [4] indicated that Na-activation has no effect on the value of the charge determined. Each series of NIR spectra from natural and activated samples can then be modeled by PLS chemometrics [5] to yield a direct and accurate NIR tool for charge prediction applicable to both laboratory and field measurements: Layer charge in the 0.4-0.55 range can be predicted on the basis of derivative spectra (6000-4200 cm^{-1}) by a 3-dimensional PLS model with $R^2 \approx 0.95$ and an RMS error of cross-validation of the order of 0.01. The overall time for measurement and analysis is ~90s or less. The method is expected to enable the high-throughput layer charge determination of smectite in natural samples with a spatial resolution of <1 cm^2.

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CRYO-NIR SPECTROSCOPIC INVESTIGATION OF MONTMORILLONITE

Constantinos Tsiantos, Vassilis Gionis*, Georgios D. Chryssikos

Theoretical and Physical Chemistry Institute, National Hellenic Research Foundations, Athens, 11635, Greece

NIR spectroscopy is an exceptional tool for the non-invasive structural characterization of H_2O and OH in clays. In the present context NIR is employed to map the temperature dependence of spectra obtained at various levels of smectite hydration. Emphasis is placed on the systematics of the sharp features associated with interfacial interlayer H_2O, in weak interaction with the charged siloxane surface of the smectite [1,2].

A homemade cell [3,4] was modified to enable for the variable temperature (-180 - 150 °C) NIR spectroscopic measurement of powder samples by a diffuse reflectance fiber probe. The cell offers contact-less, real-time measurements of ~10 mg samples subjected to heating and cooling schemes with the accuracy and precision of typical DSC or TGA furnaces and is employed to study the montmorillonite SAz-1. The samples have been studied upon cycling between ambient and -180 °C, to study the effect of temperature on the spectra at nearly constant clay hydration, as well as upon heating up to 150 °C (with concomitant dehydration) and subsequent quenching to -180 °C.

Within the range of these measurements, temperature is found to have little effect on the layer structure of montmorillonite up to ~100 °C, evidenced by the stability of the characteristic M_2O-H ($\nu+\delta$) combination band(s). Above this temperature, the combination bands undergo changes suggesting the onset of structural distortions or a drastic change of the layer-interlayer interactions.

The sharp H_2O ($\nu+\delta$) combination mode of smectite at ~5250 cm^{-1}, which is specifically assigned to the dangling O-H bonds of interlayer H_2O that are pointing to the negatively charged siloxane layer, exhibits rich temperature dependence. It blue-shifts by ~6 cm^{-1} upon heating (resulting in dehydration) to ~90 °C and then collapses to a number of sharp components in the 5300-5200 cm^{-1} range, best seen upon quenching to -180 °C. On the other hand, the cooling of ambient samples to -180 °C without dehydration is also causing a blue-shift of the same band by ~6 cm^{-1}. Opposite to the heating branch, the trend is now sigmoidal (inflection at ~-90 °C) and reversible upon temperature cycling.

Finally, the low-temperature spectroscopic data allow for the observation and identification of the hitherto elusive 2ν stretching overtone of interfacial H_2O at 7127 cm^{-1} (νO-H= ~3630 cm^{-1}, νO-D= 2686 cm^{-1}, [1]), next to the Al_2OH overtone at ~7050 cm^{-1}. The observation of the weak 7127 cm^{-1} band is made possible by its narrowing upon cooling which results in enhanced amplitude in the 2nd derivative mode.

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ENGINEERING PROPERTIES OF SAND STABILIZED COMPACTED MARLY CLAYS FROM THE GUADALQUIVIR BASIN (SOUTHERN SPAIN)

Carlota Gómez De Santos*, Meaza Tsige, Svetlana Melentijevich, Luis Fernández Almiñana

Dept. Geodinámica, UCM, Madrid, Spain
*meaza@ucm.es, carlotagomezdesantos@ucm.es, svmelent@ucm.es

This paper presents the results of the first laboratory-based study on the viability of using sand additive to improve the geotechnical behaviour of compacted high plastic clay soils. The studied soil belongs to the known Guadalquivir Blue Marly Clay (GBMC), thick marine deposits of Miocene age, which are widely distributed in the whole basin. The general engineering properties of the GBMC are described as, cohesive, over consolidated and stiff clays. They are predominantly fine grained with an average percentage of clay fraction between 50 and 60%, and are classified as Highly plastic clay (CH). Mineralogical composition of the formation is fairly homogenous, and is mainly composed of phyllosilicates, with smectite (beidelite) and illite being the dominant phases, and kaolinite and some amount of I/S interstratified mineral being present in small amounts. Calcite and quartz constituted the main rock minerals, together with small quantities of gypsum. A significant portion of the calcite belongs to microfossils, which are distributed through the clay mass (Tsige, 1999). These soils are classified as marginal-inadequate for use in engineering works because of their high plasticity and swelling behaviour. However, they are increasingly being used in construction in most earthworks in southern Spain, and more recently in environmental engineering, despite having a limited understanding of their mechanical behaviour. It is known that in most of engineering earth works lime or other chemical additives are recommended to address some of the engineering problems based on the principle of rapid ion exchange reactions and slower soil-lime pozzolanic reactions. However, the effectiveness of this treatment for some type of clays is limited to the reduction of Liquid Limit (LL) and so Plastic (PL), and is insignificant for calcium rich clay soils. The low success rate of these methods has been attributed to the low interaction of the active clay with the additives (Elerta et al, 2016). This research was aimed to study the use of granular soil mixture to improve the geotechnical properties of the GBC as a valuable alternative for civil infrastructure construction involving general earthworks, road embankments and earth dams. The use of this inert material provides an environmentally friendly option over the chemical additives, in improving geotechnical properties of these soils while still being cost-effective to the costumer. For the purpose a natural GBMC was mixed in different proportion with a well graded silica sand (SP) (clay-sand mixture). The compaction, strength and swelling properties (% and swelling pressure) of clay-sand mixtures were measured at optimum moisture content and maximum dry density of Standard Proctor. The results of this study showed that, beside there is no change in the index properties of the investigated materials, a significant increase was observed in the compressive strength, stiffness and damping ratio while deformability decreased as the granular material content increased. Samples with only 10% sand content got an important reduction in deformability (90% swelling pressure and 80% swelling per cent) compared to the pure compacted clay and making the mixture acceptable for any earthwork. These improvements are explained by the changed microstructure of the mixed and compacted soil, which is formed by a framework of large clay aggregates and sand grains arranged in a “grain (clay aggregate) to grain (sand)” framework with relatively medium size pores. The reduction in volume change and swelling pressure is probably due to strain (volume) accommodation by sand grains. Other interesting point to note is the marginal increase in deformability of the samples containing 20% sand, which is associated with an increased material heterogeneity.

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MICROFABRIC, MINERALOGICAL AND GEOMECHANICAL CHARACTERIZATION OF CLAY RICH FAULT GOUGE FROM AMF (MURCIA, SOUTHEAST SPAIN)

Meaza Tsige (1)*, J. Miguel Insua Arrevalo (1), Jose J. Martinez Diaz (1,2),
Emilio Rodriguez-Escudero (3), Pablo Rodriguez Soto (1), Elena Crespo (4)

(1) Dpto. de Geodinámica, UCM, Madrid, Spain, (2) Instituto de Geociencias, IGEO (CSIC-UCM) Madrid, Spain, (3) Dpto. Geología y Geoquímica UAM, Madrid, Spain, (3) Dpto. de mineralogía y cristalografía, UCM Madrid, Spain
*meaza@ucm.es, insuarev@ucm.es, jmdiaz@ucm.es, escudero@uam.es, ecrespo@ucm.es

In this work we present the results of the microfabric and mineralogical study of natural clay rich fault-rock (clay gouge) from one of the most active faults in the Iberian Peninsula, Alhama de Murcia Fault (AMF) [1]. AMF shows segments partially formed by exhumed fine grained fault gouge (FG) with a thickness of more than 50 m (Lorca-Totana section) developed mainly in a brittle regime. In outcrops the shear zone has a marked tectonic fabric with different small and large shear planes with a general pseudo-ductile texture [2]. A systematic sampling of FG materials was undertaken from an observatory borehole (174 m) drilled near Lorca, FAM-1. The main objective of the study is to characterize the mineralogy and micro fabric of the clay gauge at depth and see the influence of these on the mechanical behavior of the fault zone. The study has been performed using X-ray diffraction (XRD), SEM and laser diffraction technique for particle size distribution analysis. The stress-strain tests were performed under low confining pressures using a conventional triaxial and direct shear tests.

The results of the study shows that the FG reflects mainly the original mineral composition of the hanging wall rock (phyllite and schists), with a small variation in mineral assemblages. The FG is mainly represented by fine grained materials with more than 30-48 wt% 2 µm and 20-30 wt% <5 µm, indicating a very important grain reduction produced by fragmentation and mechanical crushing under low pressure and temperature conditions. The mineral assemblage is represented by mica minerals (muscovite and paragonite), quartz and traces of chlorite and carbonates (calcite, dolomite and ankerite) and some graphite. The predominant clay mineral is illite followed by paragonite, and small amounts of kaolinite. The amount of kaolinite varies from one sample to another but always in very low proportions. A small illite crystallinity variation was observed between the FG and the protolithic rock which could have been developed by lattice distortion during intense deformation of the FG. One of the relevant aspects of the mineralogical results is that, in two of the studied samples (135- 140 m depth) it has been observed (SEM) a trace amount of smectite minerals (a low friction material) with a cornflake-like micro-fabric filling the small size pores which was not identified in the wall rock. Regarding to the microstructure, the SEM study reveals that the overall microfabric of the gouge matrix is characterized by a random oriented microfabric, however, there is a remarkable alignment of the platy clay minerals along small shear planes. In general they appear to form an anastomosing texture (turbostatic microfabric) and/or surrounding the large quartz grains. This strong local orientation of the platy minerals is probably produced by intense, slow, creep-like deformation in the shear planes with high local stain concentration.

The stress-strain laboratory test results show a great variation of mechanical property; uniaxial compression and shear strength in the FG. This variation is clearly shown for the Coefficient of friction (μ) where it has been observed from very low (μ= 0.28) to very high (μ = 1.19) values. These large differences in the mechanical behavior of the FG found in this study (with homogenous mineralogy assemblage), is mainly attributed to the direction of the applied stress with the shard plane [3]. However, we suggest that this large difference in the strength and mechanical weakening behavior of the fault rock (especially the very low μ) can also be related to the orientation of the clay microfabric (preferred orientation along shear zones) and the presence of low friction minerals (smectite and graphite) seen in the studied samples.

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SEPIOLITE- AND HALLOYSITE-TIO2 NANOCOMPOSITES: SYNTHESIS, CHARACTERIZATION AND PHOTOCATALYTIC ACTIVITIES

Panagiota Tsigrou (1)*, Dimitrios Papoulis (1), Dionisios Panagiotaras (2), Konstantinos Christoforidis (3), Elias Stathatos (4)

(1) Department of Geology, University of Patras, Rio 26 504, Patras, Greece, (2) Department of Mechanical Engineering, Technological Educational Institute of Western Greece, M. Alexandrou 1, 26 334, Patras, Greece, (3) Department of Chemical Engineering, Imperial College London, South Kensington Campus, London SW7 2AZ, UK, (4) Department of Electrical Engineering, Technological Educational Institute of Western Greece, M. Alexandrou 1, 26 334, Patras, Greece

Sepiolite from Greece and Halloysite from Utah were combined with nanophase anatase for the synthesis of three nanocomposites. The samples were Sepiolite-TiO_2 (STi), Halloysite-TiO_2 (HTi) and the three phase nanocomposite Sepiolite+Halloysite-TiO_2 (SHTi). In all samples the weight ratios are clay mineral/TiO_2: 30/70, while the sample that contains two clay minerals there are in equal amounts (TiO_2 amount remains the same). The nanocomposites were synthesized by depositing anatase on the clay mineral surfaces using titanium isopropoxide as a precursor under hydrothermal treatment at 180 ^{o}C. The characterization of the nanocomposites was performed by using various techniques (XRD, ATR-FTIR, SEM, TEM, UV-Vis, BET). The photocatalytic activity of the prepared materials was evaluated for the degradation of two significant as well as completely different pollutants and specifically paracetamol and rhodamin B (RhB) in aqueous solutions.

The characterization proved that TiO_2 nanoparticles are well dispersed on clay mineral surfaces, while TiO_2 nanoparticles are in the form of anatase. The photocatalytic activities in decomposing paracetamol for nanocomposite STi based on TiO_2 content is higher than standard titania while the other two nanocomposites showed lower activities. The photocatalytic activities in decomposing RhB of all nanocomposites are significantly higher than standard photocatalyst (P25). The highest photocatalytic activities in both pollutants were measured for nanocomposite STi. This is due to sepiolite's properties and especially SSA and crystal size, shape and morphology.

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MONTMORILLONITE AS A HIGHLY EFFICIENT ANION CONDUCTIVITY ENHANCER IN ALKALI DOPED POLYBENZIMIDAZOLE BASED MEMBRANES FOR PEM ELECTROLYZERS

Filip Ublekov (1), Hristo Penchev (1), Vasil Georgiev (1), Ivan Radev (2), Vesselin Sinigersky (1)

(1) Institute of polymers, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria, (2) Zentrum für Brennstoffzellen Technik, ZBT GmbH, Carl-Benz-Str.201, D-47057, Duisburg, Germany

Polymer electrolyte membrane (PEM) fuel cells generate electricity from an electrochemical reaction in which oxygen (air) and a fuel (e.g. hydrogen) combine to form water and heat. In PEM electrolysers water is split into hydrogen and oxygen. In both devices, the polymer electrolyte membrane is a crucial component. Polybenzimidazoles (PBI) are a class of thermostable polymers, containing benzimidazole rings. The most popular ones, used for preparation of membranes for fuel cells and electrolysers, are denoted as p- and m-PBI. When treated with acids or bases (a process denoted as doping), PBI becomes solid ion conductor. If doped with phosphoric acid (PA) it becomes a proton (H^+) conductor, when alkali bases like potassium hydroxide (KOH) are used, an anion (OH^-) conducting material is obtained. For attaining high ion conductivity, high doping levels are required. Unfortunately, very high dopant content results in deterioration of the mechanical properties. A possible way for stabilization is introduction of reinforcing inorganic fillers. In a previous work we showed that protonated montmorillonite (MMT-H) can be applied as highly effective proton-conductivity enhancer in p-PBI/PA membranes [1]. Drastic increase of proton conductivity - over 100% higher than the PA doped pristine p-PBI membrane was observed. The mechanical properties are also improved - E modulus goes up by 133%.

As anion conductive polymer membranes can be used in water electrolysers, working with catalysts, containing no precious metals like Pt. The interest in such materials is steadily increasing during the last years. Here we report the preparation and characterization of composite KOH doped PBI membranes, containing MMT. MMT-H was prepared by treating montmorillonite-Na^+ with diluted HCl. It was mixed with the polymer solution, a film was cast on a glass support, after washing with water it was treated with 50% water solution of KOH. In this way p-PBI membranes with PBI:MMT weight rations up to 1:1 were prepared. Very high doping levels (molecules KOH per PBI repeating unit) were achieved thanks to the MMT, incorporated in the PBI matrix. The highest doping level - 42, was calculated for the p-PBI membrane with weight ratio 1:1. Anion conductivity measurements were performed at 110 °C and relative humidity (RH) 10-100% using the *EasyTest Cell* method [2]. Conductivities over 1300 $mS.cm^{-1}$ were measured - value not very far from that of 50% KOH solution (1600 $mS.cm^{-1}$). The mechanical properties of these membranes are also very good. The highest conductivity, reported in the literature (for m-PBI membranes, doped with KOH) is 130 $mS.cm^{-1}$[3]. This phenomenon - drastic improvement of properties - has to be attributed to the water and KOH trapped in the MMT- channels. MMT obviously acts as “reservoir”, which keeps the water and KOH contents in the membrane higher than the one provided by the RH. This behavior is clearly observed with increasing the MMT contents in the composite membranes.

For proving concept, KOH doped m-PBI membranes, containing MMT were also prepared. For the membrane with weight ratio PBI:MMT = 10:1 conductivity of 380 $mS.cm^{-1}$ was measured. Obviously just a small amount of MMT is sufficient for achieving higher doping levels and higher conductivity, compared to the KOH doped, non MMT containing m-PBI - 130 $mS.sm^{-1}$ [3].

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ION-EXCHANGED PHILIPPINES BENTONITES: PREPARATION, CHARACTERIZATION, AND PHENOL ADSORPTION PROPERTY

Camille Mendoza (1), Mel Bryan L. Espenilla (1), Xandr Neal B. Uboan (2)*,
Carlo A. Arcilla (2), Marlon T. Conato (1,3)

(1) Institute of Chemistry, University of the Philippines, Diliman, Quezon City, Philippines, (2) National Institute of Geological Sciences, University of the Philippines, Diliman, Quezon City, Philippines, (3) Natural Sciences Research Institute, University of the Philippines, Diliman, Quezon City, Philippines
marlon.conato@upd.edu.ph

Modified Philippine bentonites were prepared by ion-exchange with sodium chloride, a surfactant cetyltrimethylammonium bromide (CTAB), a pillaring agent (aluminum hydroxypolycation), and a hybrid inorganicorganic bentonite derived from the combination of CTAB and the metal polycation. The presence of intercalated modifiers and structural variations on the modified clay materials are monitored by spectroscopic techniques. Thermal analysis and in-situ high temperature XRD investigation of Philippine bentonites provide initial data of the structure-adsorption property. Adsorption properties in the removal of organic pollutants such as phenol from aqueous solutions were assessed through batch adsorption tests. The modified bentonites were all shown to have enhanced physical and chemical properties compared to the native bentonite. The results also showed that Philippine bentonites modified with CTAB and the CTAB/Al-combination were the most efficient towards sorption of phenol as compared to the other bentonite materials. As the sorbent concentration increased, the removal percentages of phenol were shown to be increasing for the two organo-modified Philippine bentonites. Also, XRD results showed that the increased interlayer spacing of the bentonites modified with CTAB are one of the factors for high uptake of phenol. The results of the study showed that the enhancement of the physicochemical properties of bentonite makes them an attractive alternative adsorbents of organic pollutants for wastewater treatment.

Keywords: Philippine bentonite, natural clays, ion-exchange, structure transformation, phenol adsorption.

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WATER AND POROSITY IN PERLITE

Peter Uhlik (1)*, Peter Varga (1), Jaroslav Lexa (2), Valeria Bizovska (3), Rastislav Milovsky (4), Juraj Surka (4), Peter Kodera (1), Zlatomir Saravolac (5), Helena Palkova (3)

(1) Department of Economic Geology, Faculty of Natural Sciences, Comenius University in Bratislava Slovakia, (2) Earth Science Institute of the Slovak Academy of Sciences, Bratislava, Slovakia, (3) Institute of Inorganic Chemistry, Slovak Academy of Sciences, Bratislava, Slovakia, (4) Earth Science Institute of the Slovak Academy of Sciences, Banská Bystrica, Slovakia (5) Termika, Zrenjanin, Serbia
*uhlik@fns.uniba.sk

Perlite is an acid volcanic glass with water content between 2-5 wt%. The water is one of the most important factors allowing production of expanded perlite - the main commercial perlite product. The most important deposits in Slovak Republic - Jastrabá and Lehôtka pod Brehmi - are related to rhyolite volcanism of the Jastrabá formation of the Upper Sarmatian age. The purpose of this study is to compare raw and expanded perlite properties from these deposits as well as from other deposits and occurrences of volcanic glass.

At the Lehôtka pod Brehmi deposit exploited perlite occurs as coarse breccia with fragments of pale and dark grey color. The ratio of matrix and fragments is variable. Based on macro and micro observations and water content (loss on ignition, thermal analyses - TA) two types of perlite fragments have been confirmed: pale perlite with significant porosity, and dark perlite with low porosity. Pale perlite has average water content about 4 wt%, dark-colored perlite contains about 3.5 wt% of water. Light, fine sand matrix has higher water content ~5.5 wt%. Higher water content is caused by water adsorbed at the surface of grains, because 35% of total water was lost after drying at 105 °C, while adsorbed water content was only 9% in dark perlite and 13% in light perlite. Perlites from the Jastrabá deposit (glassy lava flow) comprise two types of pores - oval in micrometrics scale (~1 μm) and elongated (~100 μm long). The amount of total water is approximately 5.1 wt% with 14% of adsorbed water. A significant predominance of open porosity was determined for studied perlite from both deposits by X-ray computed tomography.

In addition to TA, the infrared (IR) spectroscopy in the near IR region is also a useful method for observation of water present in perlite because the area of combination vibration band of water (~5240 cm^{-1}) reflects the amount of water. This band was normalized on the combination vibration band of Si-OH groups (~4500 cm^{-1}) and also to the ratio of stretching vibration bands of OH groups (~3600 cm^{-1}) and Si-O (~1050 cm^{-1}) in the middle IR region. Both methods, TA and IR spectroscopy, demonstrated that the molecular water dominates in studied perlites and the content of hydroxyl water is only a few tenths of percent.

Process of water release from perlite glass was investigated in a broad range of temperatures (from 150 to 900 °C), at different durations of treatments, on three different grain fractions. The highest loss of molecular water was observed between 150 and 250 °C. Almost entire molecular water was released after 15 hours of treatments at 550 °C. The studied perlites were also expanded at 850 - 935 °C in a laboratory furnace. Expansion ratio (bulk density of raw perlite to bulk density of expanded perlite) is between 17 and 20.

A source of water in perlite is also an important phenomenon that can help to clarify its genesis. The preliminary results of hydrogen isotope study of perlite form Lehôtka pod Brehmi and Jastrabá indicate that perlitization was governed by meteoric water with a distinct isotopic composition for each locality. For comparison, obsidian sample from Streda nad Bodrogom was also analysed, while its composition was slightly heavier compared to all perlite samples. Obsidian isotope composition corresponds to the expected source of hydrogen in residual magmatic water affected by open-system degassing.

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FABRICATION OF 3-LAYER-COMPONENT ORGANO-CLAY HYBRID FILMS WITH REVERSE DEPOSITION ORDERS BY A MODIFIED LANGMUIR-SCHAEFER TECHNIQUE AND THEIR PYROELECTRIC CURRENTS MEASURED BY A NON-CONTACT METHOD

Yasushi Umemura*, Masanari Hirahara

Department of Applied Chemistry, National Defense Academy of Japan, Yokosuka, Kanagawa 239-8686, Japan
*umemura@nda.ac.jp

We have studied organo-clay hybrid films prepared by a modified Langmuir-Schaefer method [1]. In an aqueous clay mineral (montmorillonite) dispersion at a low concentration, isolated clay nanosheets with negative charges were suspended. When a solution of amphiphilic octadecylammonium chloride ($ODAH^+Cl^-$) was spread on an air-dispersion interface, the clay nanosheets were adsorbed on the $ODAH^+$ cations at the interface to form a stable ultrathin floating film [2]. The floating film was transferred onto a substrate by the Schaefer method (horizontal dipping), and then the film was immersed in a $[Ru(dpp)_3]Cl_2$ (dpp=4,7-diphenyl-1,10-phenanthroline) solution. The Ru(II) complex cations were adsorbed on the film surface because the film surface possessed a cation-exchange ability. The layers of $ODAH^+$, clay nanosheets, and $[Ru(dpp)_3]^{2+}$ were deposited in this order. By repeating these procedures, 3-layer-component films were fabricated (OCR films). In a similar way, 3-layer-component films in which the layers of $[Ru(dpp)_3]^{2+}$, clay nanosheets, and $ODAH^+$ were deposited in the reverse order (RCO films) were prepared by spreading a $[Ru(dpp)_3](ClO_4)_2$ solution and immersing the films in a $ODAH^+Cl^-$ solution. Both OCR and RCO films were characterized by surface pressure-molecular area (π-A) curve measurements, IR and visible spectroscopies, and XRD method. The OCR and RCO film systems possessed nearly the same properties in the densities of $ODAH^+$ and $[Ru(dpp)_3]^{2+}$ and the tilt angle of the Ru(II) complex cation, while the layer distance for the RCO film was a little longer than that for the OCR film and the layered structure for the RCO film was less ordered than that for the OCR film. Pyroelectric currents for the films were measured by a non-contact method using an ^{241}Am radioactive electrode. When the films were heated, the pyroelectric currents were observed and the current directions for the OCR and RCO films were different. This was clear evidence that the layer order in the OCR film was reverse to that in the RCO film [3].

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PROBLEMS OF CLAY FILLING AT THE KARSTIC LIMESTONE AND DAM WATER SEEPAGES

Bunyamin Unal

5. Regional Directorate of State Hydraulic Works, Ankara, Turkey
bunyaminunal@dsi.gov.tr

Carbonate rocks are observed in a wide range because of Turkey's geological features. An important part of carbonate rocks are in the the karstic feature. Water seepages are one of the most important problems for dam engineering. If some cautions are not taken to prevent this, with the increasing volume of seepage, some problems can occur in the dam construction and these problems can lead the life, economic and time loss.

The gaps in the karstic limestone rocks are usually filled with clay. A research carried out during drilling shows that water pressure tests (WPT) has a very low permeability values. Moreover, due to the compact clays in the karstic limestone grouting clays, the grouting studies have not been successful. Therefore, an effective and efficient grouting curtain does not occur. After the construction of the dam with water retention due to washing of clays, water leaks occur around the grouting curtain. Washing of the karstic clays increases, the water leaks are also increasing. In order not to damage the safety of the dam, it is necessary to empty the reservoir and regrouting has to take place. This incident occurs repeatedly, causing economical and time losses.

In this study, the Ataturk and Armağan Dams in Turkey, which have been built on karstic limestone rock bases, and the manufacturing of grouting curtain water seepage measurements with changes over time have been investigated.

Ataturk Dam (Southeastern Turkey) was built on Upper Cretaceous karst characteristics of plaquetted-clay limestone on Sayındere formations. Grouting curtain was built about 10 km long, 4 m wide and three rows. Grouting curtain created by the surface area of 1.2 km², the world's largest grouting curtain was built until today. Karstic limestone constructed on the foundation of the depth of the grouting curtain dam is 180 m, 250-300 m in some places. Ataturk dam water seepage was measured as 10 units between the years 1991-2005. The end of measurements of seepage at Ataturk Dam, the grouting curtain were efficient and effective.

Armağan Dam (Nortwestern Turkey) was built on the Dolapdere Formation which is composed of crystalline metamorphic limestone and calcschist. Metamorphic limestone which will be under the dam embankment has been fractured and highly karstic. Cracks and other discontinuous layers have been filled with clay. Karstic structures are seen in the foundation of the dam, diversion tunnel and the cut-off followed during the excavation. Grouting curtain which was done in the Armağan dam is washed by the effect of the reservuar and is powered by doing extra groutins. The effectiveness of the dam is observed by doing colour experiments, piezometre and downstream flow measurements.

Keywords: water seepage, grouting curtain, Ataturk Dam, Armagan Dam, karstic limestone, clay filling.

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STARCH-CLAY BASED COMPOSITES FOR WATER PURIFICATION BY FILTRATION

Tomás Undabeytia (1)*, Shlomo Nir (2), Leonila Laiz-Trobajo (1), Esmeralda Morillo (1), Ido Gardi (2), Virginia Lozano (1)

(1) Institute of Natural Resources and Agrobiology (IRNAS-CSIC), Seville 41012, Spain, (2) The Hebrew University of Jerusalem, Rehovot 76100, Israel
*undabeyt@irnase.csic.es

Significant concerns have been raised due to increasing pollution of surface and ground waters. In the vast majority of water treatment plants, depth filtration is incorporated through the use of non-compressible filters made of granular activated carbon (GAC), but the efficiency of GAC for removal of pathogens is very poor. In addition, the removal of small organic polar molecules is not usually satisfactory. Therefore, there is a growing interest in the development of composites that improve the performance of GAC or even can be an alternative to its use. The current research describes the synthesis, characterization and potential use of clay-polymer composites for their use in water purification by filtration. The advantages of these clay-polymer composites are that they can be easily scaled for production at industrial levels; and they were formed by inexpensive materials, a clay mineral (bentonite), and cationic starches which are widely used as additives in paper-making, textile and cosmetic industry. These starches are derivatized by the introduction of the cationic functional moiety 2-hydroxypropyltrimethylammonium.

The interactions of three polymers with different degree of substitution with the surface of a commercial bentonite were examined. Sorption of the polymers and analysis of the surface charge of the complexes formed showed that charge neutralization at the external surface was observed at loadings lower than the CEC of this clay. The lower values for the point of zero charge than the CEC of the clay can be explained by the high screening of the clay surface by non-charged segments of the polycation after sorption. The loading of polymer on the clay was highest for the polymer with the lowest charge density adopting a loop-and-train conformation on the clay surface, whereas a planar conformation was elucidated for the other two higher charged polymers.

Several polymer-clay complexes were synthesized and tested for the inactivation and killing of the enteroindicator *Escherichia coli* as a function of the polymer loading and surface charges. The critical parameters affecting the bactericidal activity were the surface potential and the concentration of cationic monomers in excess over that needed for neutralization of the clay surface. The clay-polymer composite with higher bactericidal activity was also tested for the removal of the emerging contaminants diclofenac and sulfamethoxazole. This study showed that the introduction of functional moieties that are capable to create a network of H-bonds with the pollutants promoted their sorption in addition to electrostatic interactions.

Filtration experiments showed a better performance of the columns including clay-polymer composites over that of GAC for the removal of *E. coli*, diclofenac and sulfamethoxazole. The performance of filters based on the composites under different constructive and operational parameters, such as the flow rate, and concentration of bacteria, or pharmaceuticals added, was investigated and modeled. The success in the modeling of these filtration processes by using an adsorption-convection model enabled predictions under different operational conditions, and economic projections based on the estimated capacity. Since regeneration of the filters was achieved by the use of dilute and inexpensive HCl or NaOCl solutions, implication is that the effective capacity of the filters is larger than that preliminary determined and consequently the price for successive water treatments will be significantly reduced.

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UNDERSTANDING WETTABILITY ALTERATION THROUGH MOLECULAR DYNAMIC SIMULATIONS: THE PHENOMENON OF LOW-SALINITY ENHANCED OIL RECOVERY

Thomas Underwood*, H. Chris Greenwell

Department of Earth Sciences, Durham University, Durham, DH1 3LE, UK
*thomas.underwood@durham.ac.uk, chris.greenwell@durham.ac.uk

This research aims to bring clarity to the fundamental mechanisms of clay-oil-brine interfaces that underpin low-salinity enhanced oil recovery (EOR), a technique whereby sea water, partially desalinated, is used to push increasing amounts of crude oil from existing, and future, oil reservoirs, boosting the reservoir lifetime and overall production [1].

Previous research has examined the complex three-phase (clay-oil-brine) problem using large-scale molecular dynamic (MD) simulations [2,3]. Whilst such simulations have successfully elucidated the role of pH and divalent cations in a low-salinity water flood, the salinity dependence has remained elusive.

In the present work, we show how the complex three-phase system can be understood on the basis of simpler two-phase simulations. Using Young's equation, we decouple the three-phase problem into three separate two-phase problems. We show how one can calculate and understand the phenomenon of interfacial tension through MD simulations, and we validate a variety of force-fields based upon their accuracy to reproduce experimental surface tension values. Further, we calculate contact angles between clay minerals, brines and oils and compare simulated trends to recent experimental results [4].

The results presented highlight how we can understand wettability alteration at the molecular level, and ultimately presents the role that salinity plays in driving the phenomenon of low-salinity enhanced oil recovery.

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RIGID CLAY FOR REMOVING ORGANIC MOLECULES

Leslie Valdés (1)*, Asor María-Martínez (2), Martha Velázquez (2), Louis Charles de Ménorval (3), Aramis Rivera (4)

(1) Department of Pharmacy, Institute of Pharmacy and Food (IFAL), University of Havana, 10400 Havana, Cuba, (2) Research Center for Mining and Metallurgy Industry (CIPIMM), Boyeros 8067, Havana, Cuba, (3) Institut Charles Gerhardt Montpellier, Equipe Agrégats, Interface, et Materiaux pour l'Energie (AIME), Université Montpellier, 34095 Montpellier CEDEX 5, France, (4) Zeolites Engineering Laboratory, Institute of Materials Science and Technology (IMRE), University of Havana, 10400 Havana, Cuba

Among the many benefits offered by clays, there is safety for humans and for the environment, that is why these materials have been widely used by human since prehistoric times. Based on their properties as adsorbents and ion exchangers, the pharmaceutical industry exploits these porous materials not only as active drug carrier but also for the removal of organic contaminants [1]. With the increasing number of emerging contaminants, there is a need for environmentally-friendly and low-cost sorbent materials. The use of natural clays to capture organic waste from the pharmaceutical and biotechnological industries is especially important to avoid soil and water contamination with potential impact on human health. According to our knowledge, there are limited reports in the literature about palygorskite's use in the removal of drug wastes. Recently, a significant deposit of natural palygorskite was discovered in Cuba, which could be used for several potential applications in different areas.

Ciprofloxacin (Cipro) is a broad-spectrum antibiotic that is widely used because of its high efficiency. In the present study, we studied the adsorption of ciprofloxacin (Cipro) onto palygorskite). In a previous study [2], the intercalation of this model drug was evaluated on natural and synthetic clays, with promising results. Here, different chemical-physical parameters such as pH, initial concentration of ciprofloxacin, contact time and temperature were monitored to select the optimal adsorption conditions. Drug adsorbed palygorskite was characterized by XRD, IR and TG. The results showed a good incorporation of Cipro into the mineral, which suggests that this clay can be effectively used for the removal of pollutants from the pharmaceutical industry.

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LI-FLUOROHECTORITE AS DRUG DELIVERY SYSTEM: INCORPORATION OF SULFAMETHOXAZOLE AND TRIMETHOPRIM

Dayaris Hernández (1), Lismet Lazo (1), Leslie Váldez (2), Louis Charles de Ménorval (3), Zbigniew Rozinek (4), Ernesto Altshuler (5), Jon Otto Fossum (6), Aramis Rivera (1)*

(1) Zeolites Engineering Laboratory, Institute of Materials Science and Technology (IMRE), University of Havana, 10400 Havana, Cuba, (2) Department of Pharmacy, Institute of Pharmacy and Food (IFAL), University of Havana, 10400 Havana, Cuba, (3) Institut Charles Gerhardt Montpellier, Equipe Agrégats, Interface, et Materiaux pour l'Energie (AIME), Université Montpellier, 34095 Montpellier CEDEX 5, France, (4) Faculty of Physics, Adam Mickiewicz University, Umultowska 85, Poznań 61-614, Poland, (5) Group of Complex Systems and Statistical Physics, Physics Faculty, University of Havana, 10400 Havana, Cuba, (6) Norwegian University of Science and Technology (NTNU), NO-7491Trondheim, Norway

It is well known that conventional release dosage forms provide an immediate release of drugs, without much control of the release rate. In order to obtain therapeutically effective plasmatic concentrations, and to avoid significant fluctuations in the plasmatic drug levels, it is necessary to achieve dosage control. The lack of it can lead to drug levels in the organism below of minimum effective concentration (MEC), or above of minimum toxic concentration (MTC), resulting in undesirable side effects, or in the lack of therapeutic benefits for the patient. Therefore, employing materials to control the drugs release, contributes to revert the disadvantages of conventional drugs formulations, which turns into the well-being for the patient [1,2].

Clays and clay minerals are commonly used in the pharmaceutical industry like active principles and/or excipients. Among the many benefits offered by clays, is its safety for the human health, which makes them materials widely used by man since prehistoric times. The desirable physical and physiochemical properties of clay minerals-as adsorbents and ion exchangers-have led them to play a substantial role in pharmaceutical formulations [3]. In the last years, clays from the smectite family have been used as support material in the preparation of drug slow release systems. The use of synthetic clay minerals offers the possibility to optimize the work conditions regarding incorporation of model drugs, because this way the interference of spurious phases in the interpretation of the results is avoided. However, in the literature there are few reports on the use of fluorohectorites as support system for pharmaceutical applications [4,5].

Considering the facts above mentioned, in the present work the incorporation of two model drugs, sulfamethoxazole (SMX) and trimethoprim (TMP), into a Li-Fluorohectorite (LiFh) synthetic clay was evaluated. Understanding the interactions established between these two antibiotics, which are complementary from the pharmaceutical point of view, and the LiFh, allows us to develop new formulations of drug delivery. The quantification of both drugs was followed by UV spectroscopy. The resulting solids of the interaction drugs-clay were characterized by X ray diffraction (XRD), infrared spectroscopy (IR) and thermogravimetric analysis (TG). The results indicate that the adsorption of both drugs depends on the pH of the clay-drug suspension. It was demonstrated that the TMP was really intercalated into the clay, which was corroborated by XRD. However, SMX seem be adsorbed onto the clay surface. The IR spectra indicated interactions between clay-drug in the LiFh-TMP composite, via the amine groups of the TMP, which was evidenced by a shift in the characteristic bands of this organic molecule. The TG analysis allowed corroborating the thermal stability of the composites. The drug release profiles were obtained following the pharmaceutical standards, and they suggested the possibility to design formulations of drug delivery based on Li-Fh.

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EMULSIFICATION KINETICS OF MONTMORILLONITE STABILISED DROPLETS

William J. Ganley, Jeroen S. van Duijneveldt*

School of Chemistry, Cantock's Close, Bristol BS8 1TS, UK

Colloidal particles can be used to stabilise so-called Pickering emulsions. Solid stabilised emulsions are of interest due to the high adsorption energy of micro- or nanoparticles at the oil-water interface (many times kT) which results in long term coalescence stability under quiescent conditions. Smectite clay minerals would potentially be very effective emulsion stabilisers due to their high surface area. In practice however only a fraction of the clay particles are found to be adsorbed at the oil/water interface [1].

Here we investigate the emulsification kinetics in detail. Hexadecane-in-water emulsions were stabilised by montmorillonite platelets. In this system a large excess of platelets is required to drive droplet sizes down and the diameter was found to fall to a steady state that was dependent on the emulsion composition [2]. Under such harsh conditions the kinetic energy of the liquid exceeds the adsorption energy of a particle at the oil-water interface suggesting, perhaps counter-intuitively, that desorption of particles during mixing must be considered to correctly understand the formation process of these ultimately stable droplets.

A kinetic model based on a competition between droplet break-up and coalescence that is mediated by particle adsorption and desorption was able to reproduce experimental trends in droplet diameter. This model was numerically solved using known physical parameters and showed good agreement with experiment. Such a model therefore explains the need for an excess of stabilising particles in systems where droplet break-up and stabilisation processes are on similar time-scales and can be used to predict the most efficient formulation to minimise droplet diameters for given materials and mixing conditions.

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CONTROLLING THE RHEOLOGY OF MONTMORILLONITE STABILISED EMULSIONS

William J. Ganley, Jeroen S. van Duijneveldt*

School of Chemistry, Cantock's Close, Bristol BS8 1TS, UK

Suspensions of montmorillonite particles in water form gels around 3 wt% depending on salt concentration. Adsorption of polyetheramine surfactant to the particle faces is known to reduce the tendency to gel at low salt concentrations by neutralising surface charge, reducing electrostatic repulsion between platelets and therefore allowing them to come into closer proximity. This reduces the effective volume fraction of the clusters and reverses jamming in low ionic strength arrested phases [1,2]. Conversely, the adsorption of pyrophosphate introduces a high concentration of negative charge to the particle edge, resisting the formation of bonded percolating gels at high ionic strength [2].

Here it is shown that these surface modifications can be applied also to montmorillonite-stabilised oil-in-water emulsions, in which the majority of clay particles remains in the continuous water phase [3]. The emulsions were modified by the addition of NaCl and $Na_4P_2O_7$ to the continuous phase at varying concentrations. Remarkably, changes of up to 3 orders of magnitude in elastic modulus and yield stress of the emulsions were achieved. The droplets retained long-term coalescence stability after the addition of NaCl or $Na_4P_2O_7$ and even after the removal of the continuous phase network. The latter finding shows that the droplets are primarily stabilized by the formation of a solid barrier at the interface. These emulsions are therefore highly versatile formulation materials with an exceptional degree of stability and tunability.

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ALTERATION OF OLIVINE IN VOLCANIC ROCKS FROM TRINDADE ISLAND, SOUTH ATLANTIC

A. C. C. Mateus (1), A. F. D. C. Varajão (1)*, F. S. Oliveira (2)

(1) Departamento de Geologia, Universidade Federal de Ouro Preto, Ouro Preto, 35400-000, Brazil, (2) Instituto de Geosciências, Universidade Federal de Minas Gerais, Belo Horizonte, 31270-901, Brazil

Trindade Island is located in the South Atlantic, 1140 km from the Brazilian coast. The island is part of an extensive underwater volcanic chain of east-west orientation, named Victoria Trindade [1]. Trindade, an emerged island, has its genesis in the Cenozoic. It is associated with lava flow and sodium-alkaline intrusions, markedly sub saturated in silica and several pyroclastic rocks [1]. Over this diverse lithological framework, soils developed enriched in unusual minerals of tropical regions such as olivine that appears as fresh mineral remnant in the early stage of rock weathering. Until now little is known about the genesis and evolution of secondary mineral species and the relationship of these with the associated microsystems of alteration. In this paper we report on investigations of the weathering of olivine (forsterite) phenocrysts occurring in pyroclastic rocks from Trindade Island using optical microscopy, X-ray diffraction (XRD), electron probe microanalysis (EPMA) and scanning electron microscopy (SEM). Micromorphological analyses show very fractured phenocrysts of colorless olivines at plane polarized with high relief. They are irregular shaped crystals distributed in a dark reddish brown matrix constituted by small pyroxenes crystals of high interference color and subhedral magnetites and ilmenites. Pyroxenes are of the augite type and the ilmenites appear associated with the crystals of magnetite. The clay fraction of the matrix is composed of serpentine, kaolinite, hematite, magnetite and anatase. At crossed polarized light the fractured olivine crystals show high interference colors and a reddish brown material on the outer surface and along the inner fractures. This reddish brown material extinguishes parallel to the extinction direction of the olivine and appears to invade the crystal progressively until, in the most altered samples from the upper part of the soil profile, the original olivine is almost totally altered. The olivine was identified as a forsterite type and the reddish brown material in the fractures and in the edges has a chemical composition of Si, Fe, Mg, Al, Ca, Na, K, Mn and Ti, with predominant and variable of Si, Fe and Mg. This chemical composition and optical features are similar to that found in iddigsites [2,3,4] which may form through the incipient alteration of olivines due to the oxidation of ferrous iron to ferric iron and to the coordination of magnesium with hydroxyl groups.

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CLAY MINERALS ALTERATION IN AN OXISOL UNDER DIFFERENT GRAZING REGIMES IN A CROP-LIVESTOCK SYSTEM IN SOUTHERN BRAZIL

Vanessa Thoma Bertolazi (1), Alberto Vasconcellos Inda (1)*, Laurent Caner (2)

(1) Soil Department, Federal University of Rio Grande do Sul, Porto Alegre, Brazil, (2) HydrASA, Université de Poitiers, Poitiers, France
*alberto.inda@ufrgs.br

The state of Rio Grande do Sul (RS), in southern Brazil, is an important grain and beef cattle producer. To maintain and increase the current production levels, agricultural activities have been intensified. Production systems that alternate grain crops and grazing animals have been investigated. Integrated crop-livestock systems (ICLS) are well known and recommended because they optimize land use as both crops and pastures receive the same management level and will result in increased benefits to farmers [1]. In addition, the combined use of ICLS with no-tillage (NT) soil management may contribute to increase the soil organic matter content [2] and improve soil fertility levels and nutrient supplies [3]. Such pedoenvironmental changes will alter the existent natural conditions, producing a new dynamics in the soil surface layer, in which considerable alterations may take place.

Studies have been carried out to evaluate the effects of the ICLS onsoil chemical, physical and biological properties. These studies showed that soils under ICLS were less acidic and accumulated more organic carbon (OC) and N than those without pastures (grasses) [2,3]. In addition, it is possible that the pedoenvironment changes caused by ICLS can affect soil mineralogy, particularly 2:1 phyllosilicates [4,5]. However, studies directly focusing on alterations of the 2:1 clay minerals due to pedoenvironmental changes are scarce and there is no record of the effects of ICLS. In ICLS under NT, variable accumulation of plant residues, will occur compared to conventional systems of grain production. From that, one can infer that either the cumulative addition of animal manure to the soil or the variation in the grazing intensity will affect the 2:1 clay minerals, since they can significantly interfere in the dominant soil formation processes the soil surface. The aims of this studywere to evaluate the effects of grazing intensities (intensive grazing IG; moderate grazing MG; no grazing NG) on the mineralogy of an Oxisol, in an integrated soybean-cattle beef production system of southern Brazil.

The soil samples were taken from 0-5cm, 5-10cm, 10-20cm, and 20-40cm layers. The samples were air-dried, crumbled, and sieved (<2 mm) in order to separate the air-dried fine soil (ADFS) fraction. The clay fraction (<2 μm) of the 0-5cm and 20-40cm were obtained by sedimentation and separated into three sub-fractions (<0.05 μm; 0.05-0.1 μm; 0.1-2 μm) following the centrifugation procedures. The mineralogical analyses (XRD) of the clay fraction (<2 μm) show predominantly the presence of kaolinite and 2:1 clay minerals which are hydroxy-interlayered minerals (HIMs). The peaks of the 2:1 clay minerals of the IG treatment present better definition than those of the NG treatment. Also, the 2:1 clay minerals present expandable layers in the IG treatment. The sub-fractionation of the clay fraction <2 μm allowed the visualization and identification of important alterations in the soil clay fraction. Thus, under all treatments, the presence of hydroxyl-aluminum interlayered vermiculite (HIV-Al) has been highlighted. The peak corresponding to HIV-Al is more defined for IG and MG than for NG, which indicates greater aluminization of the interlayer space of the 2:1 clay minerals. The chemical analyses indicated a decrease in total organic carbon (TOC) with depth (0 to 40cm) in all treatments. However, this decrease is higher under NG because of the absence of livestock; thus there is a higher accumulation of plant-derived organic material. Soil pH_{water} is higher under IG due to the removal of aluminium from the soil solution linked to the higher aluminization of the 2:1 clay minerals. Low K values in solution under IG were observed, which are related to the formation of HIMs and/or swelling layers with exchangeable K; and under NG where there are no HIMs, high K values in solution were observed. Furthermore, it is assumed that the presence of animals induces K higher availability due to animal wastes, which may result in a competition between the exchangeable K and Al cations to form HIMs.

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INVESTIGATION OF PROCESSES PRODUCING DOLOMITE/CLAY MINERAL ASSOCIATIONS IN NATURAL ENVIRONMENTS AND CULTURE EXPERIMENTS

Crisogono Vasconcelos (1)*, Sylvia Anjos (2), Anelize Bahniuk (3), Gabriela Nascimento (1), Judith McKenzie (1), Francisca Martinez Ruiz (4)

(1) ETH Zurich, Geological Institute, Sonnegstrasse 5, 8092 CH-8092 Zurich, Switzerland, (2) Petrobras S.A, Rio de Janeiro, Brazil, (3) UFPR / LAMIR, Francisco H. dos Santos 100, 81531-980, Curitiba, Brazil, (4) Instituto Andaluz de Ciencias de laTierra (CSIC-UGR), 18100, Granada, Spain
*cris.vasconcelos@erdw.ethz.ch

The study of clay-mineral/dolomite associations within carbonate sequences has important consequences for the interpretation of scientific problems related with rock reservoirs, such as alteration of potential porosity and permeability. The genetic characteristics of clayey material, whether formed by allogenic or authigenic processes, affect the reservoir properties of rocks to a greater or lesser extent. In the case of carbonate reservoirs, the presence of clay can significantly affect the porosity and permeability of reservoir rocks. More specifically, when the clay minerals are randomly distributed within the carbonate matrix, it becomes difficult to predict the reservoir characteristics. This carbonate and clay mineral associationis commonly found in carbonate formations throughout the geological record, e.g., the Cretaceous Codó Formation, NE Brazil, (Bahniuk et al. 2015) and the Tertiary lacustrine sequence, JbelRhassoul, Morocco (Chahi et al. 1999). Some studies relatethis association to a diagenetic transformation of dolomite, but the formation processesremains a debatable matter.

In order to understand this association in the geological record, we have undertaken acomparative study of laboratory experiments and modern environments where clay minerals have been shown to precipitate together with dolomite. Two modern dolomite-forming environments, the Coorong lakes, South Australia and Brejo do Espinho Rio de Janeiro, Brazil, were selected for this investigation. In addition, enrichment microbial culture experiments, using natural pore water from Brejodo Espinhoas the growth mediumto promote mineral precipitation, were preformed. To establish the environmental parameters and biological processes facilitating the dual mineral association, the experimental samples have been compared with the natural mineralsusing HRTEM measurements. The results demonstrate that dolomite and clay apparently do not co-precipitate, but the precipitation of the different minerals in the same sample has probably occurred under different environmental conditions with variable chemistries, e.g., hypersalinity versus normal salinity resulting from the changing ratio of evaporation versus precipitation. Thus, the investigated mineral association is not a product of diagenetic processes.

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PREPARATION, CHARACTERIZATION AND APPLICATION OF A Pd-SUPPORTED Ti-Cu-PILLARED CLAY CATALYST FOR ULLMANN COUPLING REACTION

Kannan Vellayan (1), Beatriz González (2), Raquel Trujillano (2), Miguel A. Vicente (2)*, Antonio Gil (3)

(1) Department of Chemistry, Government College Kattappana, Kerala, India-685508, (2) Dep. Química Inorgánica, Univ. Salamanca, 37008 Salamanca, Spain, (3) Dep. Química Aplicada, Univ. Pública de Navarra, 31006-Pamplona, Spain

Formation of carbon-heteroatom bonds by means of Ullmann type coupling reaction between aryl halides and heteroaromatic compounds such as phenols, amines, etc. is very important in organic chemistry. The synthesis and characterization of clay supported catalysts and their application in the O, N, and S-arylation through Ullmann coupling reaction are presented in this communication. The catalyst consisted on a montmorillonite pillared with titanium polycations doped with copper, and then impregnated with a palladium precursor (MTiCuPd500). Usually, bi- and tri-metallic catalysts are reported to be more active than their monometallic counterpart in many organic reactions and clay supported catalysts are economic, reusable and have strong acidity for catalyzing many organic reactions. By these reasons, the use of MTiCuPd500 montmorillonite as catalyst in the Ullmann coupling reaction has been explored.

For the preparation of the catalyst, Ti-polycation solution was prepared by slow addition, under vigorous stirring, of $TiCl_4$ (doped with $Cu(NO_3)_2 \cdot 3H_2O$, Cu^{2+}/Ti^{4+} ratio 10:90) to absolute ethanol, until a homogeneous yellowish solution was obtained. This solution was added to a solution of glycerine in distilled water. The new mixture was maintained under stirring for 3 hours, and then was dropwise added to a previously prepared montmorillonite (Cheto, Arizona, USA) aqueous suspension (Ti/clay ratio 40 mmol/g), aging under magnetic stirring for 18 h. Then, the solid was separated by centrifugation, washed by dialysis for 2 days, dried overnight at 70 ºC and finally calcined at 500 ºC for 2 h at a heating of 1 ºC/min. This solid was impregnated with palladium (5% Pd), using Pd(II) acetate as precursor, dissolving in acetone, and impregnating the solid by the incipient wetness method. Then, the solid was dried, and calcined at 500 ºC for 2 hours, leading the final catalyst.

O-arylation between 4-nitrochlorobenzene and phenol was selected for screening the catalyst. MTiCuPd500 showed better activity than reported metal oxides catalysts [1]. Various substrates, such as phenol, naphtol, aniline, diethylamine, among others, were tested, finding that both the electron donating and electron withdrawing groups on phenol afforded good yield. Arylation involving oxygen gave better yield as compared to nitrogen and sulphur atoms. The catalyst was found to be effective and cheap as compared to other metal oxides catalysts, giving satisfactory yield. The catalyst was active over three cycles without appreciable loss in activity.

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OXYDATION OF A CALLOVO-OXFORDIAN CLAYSTONE (BURE, FRANCE) UNDER OXIDATIVE CONTROLLED ATMOSPHERE

Héloïse Verron (1)*, Jérôme Sterpenich (1), Franck Bourdelle (2), Régine Mosser-Ruck (1), Catherine Lorgeoux (1), Aurélien Randi (1), Nicolas Michau (3)

(1) GeoRessources UMR-CNRS 7359, Université de Lorraine, Vandoeuvre-lès-Nancy, 54506, France, (2) LGCgE, Université Lille 1, Villeneuve-d'Ascq, 59655, France, (3) ANDRA, Research & Development Division
Waste packages & materials Department, Châtenay-Malabry, 92298, France

The deep geological formation investigated for high-level nuclear waste repository in France is a Callovo-Oxfordian claystone (COx) comprising in weight percentage: 40% of clay minerals, 30% of carbonates, 25% of silicates and 5% of accessories minerals (including 3% of pyrite). The oxidation of claystone during the drilling of the galleries and the disposal cells is firstly controlled by the oxidation of pyrite, which releases Fe^{2+} and sulphuric acid in the interstitial water. As a consequence, the decrease of pH leads to the dissolution of the carbonate minerals fraction of the claystone, sulphate formation in solution and CO_2 release into the atmosphere of the repository. In disposal cell, which is not ventilated, CO_2 may be trapped and redissolved into the water when the claystone rehydrates, at the closing of the repository after the operating stage. This will induce transitory acidic conditions which increase the corrosion rate of the carbon steel components of the disposal cell. The use of a cementitious-bentonitic-material is provided to buffer the acid transient in the claystone. It will be injected between the oxidised COx and the carbon steel lining. In order to optimize the neutralization potential of this material and especially its composition, it is therefore essential to understand the mechanisms of the claystone oxidation and quantify the oxygen consumption, the CO_2 production and the mineral transformations.

Oxidation of pyrite has already been described in literature, where an oxidation rate was determined by sulphates concentration measurements [1] or by modelling [2]. Here, we propose an experimental approach of controlled oxidation. Three experiments were performed: the first one with pure pyrite, the second one with calcite and pyrite in the same proportion as in claystone, and the third one with a natural claystone sample preserved of atmosphere. Each of those preparations was crushed and put in a stainless steel autoclave linked to a micro gas-chromatograph system (micro-GC) allowing continuous in situ O_2 and CO_2 analysis. A starting oxygen pressure, higher than the one beforehand calculated to oxidize all the pyrite content, and 2 relatives humidity close to the ones observed in disposal cells were added into the reactor.

When the oxygen concentration is stabilized, the pyrite content exposed to the atmosphere is assumed to be oxidised. On the basis of the O_2 and CO_2 pressure measurements and the examination of the solid samples at the end of the experiment, it can be possible to calculate the molar fraction of iron sulphates and hydroxides produced, and the oxidation rate of pyrites as a function of relative humidity. The amount of O_2 consumed and CO_2 released enable a better control of parameters for further experiments with claystone samples. The data acquires during those oxidation experiments will be used into geochemical codes which model the behaviour of claystone [3] between the phase of drilling and the injection of the bentonitic-cement mixture. The results of those experiments enable a better understanding of claystone oxidation products and the quantification of the acidic front which has to be neutralised by the alkaline material.

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APPLICATION OF A SMECTITE-ILLITE FROM THE NORTH OF MOROCCO FOR THE TREATMENT OF POLLUTED WATER

Mohammadi Ahrouch (1,2), José Manuel Gatica (2), Khalid Draoui (1), Gustavo Aurelio Cifredo (2), Dolores Bellido (3), Hilario Vidal (2)*

(1) Laboratoire Matériaux et Systèmes Interfaciaux LMSI- Faculté des Sciences, Université Abdelmalek Essaadi,93002-Tétouan, Morocco, (2) Departamento C.M. I.M. y Química Inorgánica, Universidad de Cádiz, 11510-Puerto Real (Cádiz), Spain, (3) Departamento de Química Analítica, Universidad de Cádiz, 11510-Puerto Real (Cádiz), Spain

Clay materials play an important role in the treatment of wastewaters released by many different human activities. Many examples are directly related to domestic uses or agriculture, but the most problematic sources of pollution have to be with industrial processes as those involving construction and textile materials, drugs, mining, etc. The presence of both organic and inorganic toxic compounds represents a real danger to life and the environment. The elimination of these pollutants is often made through physical-chemical and biological treatments. Recently, the clay materials modified or not, have been proposed for the pollutant removal from aqueous solutions by means of adsorption [1-3].

The objective of our work is to study the potential use in this context of an interstratified smectite-illite which was collected from the north region of Morocco (Bab Berrad, Chefchaoun). This material was characterized by Fourier transform infrared spectroscopy, thermogravimetric analysis, scanning electron microscopy with EDS surface chemical analysis, X-Ray fluorescence, X-Ray diffraction and nitrogen physisorption. The adsorptive behavior of the clay mineral was tested by the adsorption of methylene blue taken as a model of cationic organic dyes [4]. We examined the influence of several parameters such as the contact time, pH, pHpzc, initial concentration of methylene blue and temperature. The adsorption equilibrium of methylene blue was analyzed based on Langmuir and Freundlich isotherm models. The maximum retention capacity obtained from the best fitting model (Langmuir isotherm) was about 93 and 100 mg/g at 25 and 45 ºC, respectively.

On the other hand, we also present in this work, preliminary results on the adsorption of heavy metals such as copper, lead and cadmium at the ppm and ppb levels. Besides studies performed under conventional experimental conditions using powdered samples, we took advantage of our previous experience in the manufacture of structured filters [5,6], using clay honeycomb-shaped monoliths obtained by extrusion. This kind of experiments allows approaching more realistic designs for the treatment of large volume of polluted effluents.

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HONEYCOMB MONOLITHIC DESIGN: RAISING THE POTENTIAL OF CLAYS FOR CO_2 CAPTURE

M. Pilar Yeste (1), José M. Gatica (1), Mohammadi Ahrouch (1,2), Hilario Vidal (1)*

(1) Departamento de C.M. I.M. Química Inorgánica, Universidad de Cádiz, 11510 Puerto Real, Spain, (2) Départemente de Chimie, Université Abdelmalek Essaadi, 93002 Tétouan, Morocco

Although CO_2 capture by clays has attracted increasing attention recently [1], their use in the form of honeycomb monoliths for this application, compared to other environmental uses, is still surprisingly missing [2]. However, if high volumes of gaseous effluents containing CO_2 had to be treated, such design would be necessary to ensure low pressure drop [3]. Moreover, honeycomb monolithic filters, being unitary structures, would facilitate both handling and replacement upon saturation. In this sense, many natural clays have ideal plastic properties to obtain pastes that can be extruded as honeycombs even without additives [4]. In fact, in previous studies we easily extruded honeycomb-shaped monoliths from natural clays for VOCs adsorption [5,6], methylene blue removal from aqueous streams [7] or biofuel combustion [8].

In this work clay honeycomb monoliths were manufactured from a kerolitic montmorillonite [9] and used for CO_2 adsorption, their performance being compared to that of the clay in the form of powder. Volumetric adsorption isotherms, thermogravimetric studies, TPD experiments and transient kinetic analysis, the two latter followed by mass spectrometry, were employed to investigate the interaction of the samples with CO_2, both under static and dynamic conditions.

This research showed that in general the honeycomb monoliths kept the adsorptive properties of the starting material exhibiting capture capacity (around 15 mg/g), Henry constant, heat of adsorption and activation energy values similar to those reported for other adsorbents in literature. Also remarkable most of retained CO_2 was weekly adsorbed, the temperature needed for its release being 130 ºC, an appropriate value which is sufficiently high to avoid undesirable desorption while low enough to minimize the costs derived from controlled regeneration if further CO_2 reutilization is wanted [12]. Furthermore, the kinetics of the CO_2 uptake over the monolith (though of second order like in the powder) was slightly different, allowing a wider operative window for a highly efficient CO_2 removal. All these results suggest the potential of the honeycomb monolithic design for an even more competitive use of clays as low cost CO_2 adsorbents.

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CRSYTAL-CHEMICAL TRANSFORMATIONS AND IRON REDUCTION IN CLAY MINERALS OF TWO BRAZILIAN MANGROVE SOILS

Gabriel R. P. Andrade (1), Javier Cuadros (2), Carmen S. M. Partiti (3), Renato Cohen (3), Pablo Vidal-Torrado (4)

(1) Universidade Estadual do Centro-Oeste, Departamento de Engenharia Florestal, Irati - PR, Brazil, (2) The Natural History Museum, Earth Sciences Department, London, United Kingdom, (3) Univiersidade de São Paulo, Instituto de Física, São Paulo - SP, Brazil, (4) Universidade de São Paulo, Escola Superior de Agricultura "Luiz de Queiroz", Piracicaba - SP, Brazil

Mangroves are important coastal ecosystems influenced by complex dynamics driven by redoximorphic features, tidal variation and constant deposition of continental and shelf sediments [1]. The formation of clay minerals in mangrove soils is an important key to understand pedogenic and biogeochemical processes in these environments [1,2]. Mangrove clay assemblages are usually composed by different minerals with high levels of octahedral Fe^{+2}, which indicates that microbial reduction may be involved in clay reactions [2,3]. To investigate the chemical transformations in clays and the role of Fe reduction in octahedral sites, samples from two Brazilian mangroves of different environmental settings were selected: the first in a humid tropical climate in the Amazonian coast (city of Bragança, Pará State), with predominance of kaolinite and pedogenic oxides as deposited minerals; and the second in the semiarid coast of northeastern Brazil (city of Acaraú, Ceará State), where 2:1 clays are sedimented in the mangroves together with kaolinite and Fe oxides. Samples of 2-0.2 μm and < 0.2 μm size fractions were studied using modeling of XRD patterns from oriented mounts (program ClaySIM®), TEM-EDS, X-ray fluorescence spectroscopy (XRF) and Mössbauer spectroscopy.

There is a complex mixture of end-member clay minerals and R0 mixed-layered phases in the two size fractions from the two mangroves. The phases are kaolinite-smectite (K-S) with a range of smectite layers (1%, 15-25%, 50% and 80% of S layers), illite-smectite (I-S, 10 to 90% of illite layers), Fe-rich illite and Al-rich illite. The best XRD-pattern fit indicated that most kaolinite, smectite and illite layers had high octahedral Fe contents. The 2-0.2 μm size fraction contained more kaolinite-rich K-S and Fe-rich illite minerals, with higher structural order, than the < 0.2 μm fraction, which had more smectite-rich K-S and I-S phases, and less Fe-rich illite. In the Acaraú samples, the Fe-illite content was higher than in Bragança samples. The chemical composition of individual crystals (TEM-EDS) confirmed the high Fe_2O_3 contents in illitic (~20% wt), smectitic (7-12% wt) and even in kaolinitic crystals (1-4% wt). Fe^{2+}/TotFe proportions, from the combination of XRF and Mössbauer spectroscopy data, is higher in samples of the 2-0.2 μm size fraction (10-16%) than in the < 0.2 μm size fraction (2-3%).

We interpret these results as a sequence of chemical transformations triggered by highly cation-saturated interstitial water. The deposited kaolinite is progressively transformed into smectite via K-S. This step includes the formation of a new tetrahedral sheet, gradual substitution of cations in tetrahedral (Al for Si) and octahedral sites (Fe+Mg for Al), and intercalation of cations (mainly K and Na) in the interlayer. These chemical modifications lead to an increase in layer charge, producing Fe-rich smectite layers. The second step is the illitization of smectite layers, which includes further Fe substitution for Al and and Fe reduction [3,4]. This is concluded because both total Fe and Fe^{2+}/TotFe proportion in the 2-0.2 μm size fraction correlated very well with Fe-illite contents from XRD. Of the two mangroves, the Acaraú samples have higher Fe-illite content because contitental 2:1 clays are deposited in the mangrove and they are transformed more quickly into Fe-illite than kaolinite. We conclude that Fe sequestration and reduction during illitization are important biogeochemical processes operating in mangrove soils, in addition to the usually reported Fe reduction/oxidation involving Fe oxides and sulfide [4].

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HARDENED STATE PROPERTIES OF PORTLAND CEMENT MORTAR USING RESIDUE OF VERMICULITE AS SUPPLEMENTARY CEMENTITIOUS MATERIAL

Roberto Antonio Rojas-Ramírez (1), Douglas Gouvea (1), Rafael Giuliano Pileggi (2), Marcel Hark Maciel (2), Valquíria de Fátima Justo (1), Antonio Carlos Vieira Coelho (1)*, Roberto Cesar de Oliveira Romano (2)

(1) Department of Civil Construction Engineering, (2) Department of Metallurgical and Materials Engineering
Escola Politécnica da Universidade de São Paulo, São Paulo, Brazil

Vermiculite is a hydrous mica-like phyllosilicate mineral. It is formed under natural conditions by hydrothermal or weathering alteration of biotite or phlogopite. It can be expanded to up 30 times its original volume when quickly heated between 650 °C and 950 °C, resulting in a low density product (called expanded vermiculite) that exhibits properties such as low thermal conductivity, low bulk density, chemical inertness and relatively high melting point [1-2]. Due to these peculiar properties, it is used in the civil construction sector in compositions of lightweight concretes as aggregates [3-4]. In the production of expanded vermiculite a by-product is generated, called, in this work, vermiculite residue (VR), a fine powder (<150 micron) which up to the moment does not have a suitable application, being disposed in dumps, resulting in a potential environmental problem. In order to find an application for this residue, this work evaluated its association with Portland cement in mortar, using VR both as received and after an additional calcination at 800 °C (cVR). Mortars were formulated with standardized sand, Portland cement and vermiculite (VR and cVR) as supplementary cementitious materials (SCM). The vermiculite content in the evaluation procedures varied from 5% to 20% in weight basis, in substitution to the Portland cement. In one previous work, it is reported that the use of this material affects the rheological properties of a cement composition [5]. In this work the water content was kept constant, independently of changes on the workability. This strategy was adopted to evaluate only the impact of vermiculite content on the properties of the hardening state. After moulding, proof samples were cured for 28 days at 25 °C and 98% relative humidity. Archimedes immersion method, tensile strength, dynamic elastic modulus and air-permeability by vacuum decay were used to evaluate the properties. The results show that there is a great possibility to find a large-scale application to this residue: there are no losses on the hardened properties up to 10% substitution of binder, meaning that the mechanical strength, elasticity and air-permeability of the samples with no vermiculite addition and with either 10% VR and cVR additions were statistically equivalent (Anova and t-test). This work was a first step to find a valuable application to this vermiculite residue although it is not yet possible to say that VR and cVR can be used in cementitious compositions, because is still necessary to evaluate durability aspects.

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INVESTIGATION OF EARLY MARS ENVIRONMENTS BY PERFORMING EXPERIEMENTS DEVOTED TO MINERALOGICAL COMPETITIONS

Viennet Jean-Christophe (1)*, Bultel Benjamin (1), Riu Lucie (2), Werner Stephanie (1)

(1) Centre for Earth Evolution and Dynamics, Department for Geosciences, University of Oslo, Postboks 1028 Blindern, 0316 Oslo, Norway, (2) Institut d’Astrophysique Spatiale, Université Paris-Sud, 91400 Orsay, France
*j.c.viennet@geo.uio.no

Widespread occurrence of tri-octahedral phyllosilicates (mainly Fe/Mg smectites) have been observed by remote sensing instruments (i.e. CRISM, OMEGA) on Noachian terrains (oldest Martian epoch, earlier than about 3.9 Ga) [1,2]. Their discovery was an exciting observation because it could imply an environment with a circum-neutral pH water activity where a prebiotic chemistry could have been developed. Therefore, a particular interest has been devoted by using geochemical simulations and laboratory experiments to the study of Fe/Mg smectites formation in order to characterize the early Martian environmental conditions [3,4]. In addition to the widespread occurrence of tri-octahedral phyllosilicates, di-octahedral phyllosilicates (kaolin and/or Al-smectite) stratigraphically above tri-octahedral phyllosilicates [5] are observed and could be linked to acidic environmental conditions [3]. Recently, widespread occurrence of carbonates during the early Noachian has been observed in association with the tri-octahedral phyllosilicates [6]. The presence of carbonates could be linked to a CO_2-rich atmosphere, which allows the presence of liquid water due to potential greenhouse effect. The aim of our work was to investigate the formation of mineralogical assemblages found on the Martian surfaces as a function of variable parameters (atmosphere composition, pH of the aqueous solution) in order to better constrain and understand the environmental conditions during the Noachian epoch of Mars.

To this purpose, hydrothermal experiments were performed in order to point out the general trend leading to the formation/limitation of the specific mineralogical assemblages observed on the Martian surfaces. The hydrothermal experiments were performed on basaltic volcanic glass of tholeiitic composition. Batch reactors and open systems were used with variable atmosphere compositions, water/rock ratio and/or initial acidity for duration of 3 weeks. The characterization of the minerals formed during the reaction were analysed by X-ray diffraction measurement and infra-red spectroscopy.

The variations in the resulting alteration products obtained show the strong influence of the environmental conditions (initial pH, atmosphere composition) on the formation of reacted products. The decrease of acidity leads to an increase of the relative proportion of di-octahedral phyllosilicates (such as kaolinite-rich mixed-layer minerals) compare to the tri-octahedral one (such as smectite-chlorite mixed-layer minerals). The formations of various types of carbonates (Calcite or Ca-Mg-Fe solid solution) with di/tri phyllosilicates are strongly dependent of the initial geochemical conditions (such as CO_2 content). The mineralogical assemblages obtained during these experiments are similar to the Martian ones, and thus give general trends to better evaluate the environmental conditions for the epoch and location at which these mineralogical assemblages are observed.

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MICROSTRUCTURAL CHANGES IN BENTONITE AFTER 18 YEARS IN BARRIER CONDITIONS

María Victoria Villar*, Rubén Javier Iglesias, Rocío Campos, Luis Gutiérrez-Nebot, Beatriz Castro

Centro de Investigaciones Energéticas, Medioambientales y Tecnológicas (CIEMAT), Madrid, Spain

The aim of the FEBEX project (Full-scale Engineered Barriers Experiment) was to study the behaviour of components in the near-field of a nuclear waste repository in crystalline rock. As part of this project an "in situ" test, under natural conditions and at full scale, was performed at the underground laboratory in Grimsel (GTS, Switzerland). A gallery of 2.3 m in diameter was excavated through the granite and two heaters, simulating the thermal effect of the wastes, were placed inside, surrounded by a barrier of highly-compacted bentonite blocks. The external surface temperature of the heaters was 100 °C and the bentonite barrier was slowly hydrated by the granitic groundwater. The bentonite used to construct the engineered barrier was the FEBEX, extracted from the Cortijo de Archidona deposit in SE Spain [1].

In 2015, after 18 years operation, the FEBEX Dismantling Project (FEBEX-DP) undertook the dismantling of the experiment, and numerous bentonite samples were taken from different vertical sections along the barrier and sent to CIEMAT's facilities [2]. These samples were tested to characterize their physical state (dry density, water content) and microstructure. The latter was investigated by determining the pore size distribution by mercury intrusion porosimetry and measuring the basal spacing by X-ray diffraction (XRD) [3].

Because of the water inflow from the host rock, the water content of the bentonite increased from the inner part of the barrier towards the granite, whereas the dry density decreased.

Basal spacing

Under hygroscopic water content, which was the condition of the bentonite used to manufacture the blocks of the barrier, the basal spacing of the FEBEX bentonite is about 1.48 nm. The basal spacings measured in the blocks retrieved after 18 years of testing were above the initial one and corresponded mostly to a completely developed 2-layer hydrate, except for those samples that were taken at less than 20 cm from the heater. These samples had water contents below 25%. Above this water content the basal spacing tended to increase with water content, i.e. towards the granite. A few samples had basal spacings close to those corresponding to the 3-layer hydrate. The values obtained for the FEBEX-DP samples for water contents below 27% were similar to those measured in samples of the reference FEBEX bentonite of the same water content saturated with deionised water. It can be concluded that the water retention capacity of the bentonite did not change during the 18-year operation.

Pore size distribution

Two pore families appeared systematically in all the samples, one in the size range of macropores and another one in the size range of mesopores. This is the usual pore size distribution pattern obtained by MIP in compacted FEBEX bentonite, irrespective of the water content or dry density. The percentage of pores non-intruded by mercury (mostly because they were smaller than 7 nm, the porosimeter lower limit) was on average of 53%. Additionally, more than 70% of the pores of all the samples had a diameter smaller than 50 nm after operation. In fact, the proportion of pores smaller than 50 nm increased with respect to that in the reference sample (which was 61%), while the proportion of pores larger than 50 nm decreased (from 39% to an average of 30% in the samples retrieved). This would point to the homogenisation of the pore sizes towards the smaller ones. The difference between the percentage of pores larger and smaller than 50 nm increased from the granite towards the internal part of the barrier, although the maximum difference between the proportions of the two pore sizes was mostly found in the middle part of the barrier, particularly in those barrier sections around the heater.

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HYDRAULIC AND MECHANICAL PROPERTIES OF COMPACTED BENTONITE AFTER 18 YEARS IN BARRIER CONDITIONS

María Victoria Villar*, Rubén Javier Iglesias, Carlos Gutiérrez-Álvarez, Beatriz Carbonell, Pedro Luis Martín

Centro de Investigaciones Energéticas, Medioambientales y Tecnológicas (CIEMAT), Madrid, Spain

The aim of the FEBEX project (Full-scale Engineered Barriers Experiment) was to study the behaviour of components in the near-field of a nuclear waste repository in crystalline rock. As part of this project an “in situ” test, under natural conditions and at full scale, was performed at the underground laboratory in Grimsel (GTS, Switzerland). A gallery of 2.3 m in diameter was excavated through the granite and two heaters, simulating the thermal effect of the wastes, were placed inside, surrounded by a barrier of highly-compacted bentonite blocks. The external surface temperature of the heaters was 100 °C and the bentonite barrier was slowly hydrated by the granitic groundwater. The bentonite used to construct the engineered barrier was the FEBEX, extracted from the Cortijo de Archidona deposit in SE Spain [1].

In 2015, after 18 years operation, the FEBEX Dismantling Project (FEBEX-DP) undertook the dismantling of the experiment, and numerous bentonite samples were taken and sent to CIEMAT’s facilities [2]. These samples were tested to characterize their physical state (dry density, water content) and determine, among others, their hydraulic and mechanical properties, such as permeability and swelling capacity. Over the last 20 years an extensive database on the variation of these properties with different parameters (dry density, water content, temperature, salinity) was obtained [1]. This has allowed to assess if the operation under repository conditions implied irreversible changes on the main properties of bentonite [3].

Hydraulic conductivity

The hydraulic conductivity was measured in samples drilled from blocks in the laboratory after they were saturated with deionised water. Basically, the hydraulic conductivity is mainly related to dry density and the latter in turn should be related to the position of the block in the barrier. Since the dry density of the bentonite increased towards the heater, the hydraulic conductivity tended to decrease towards it. Overall the values measured in the samples retrieved were in the order of 10^{-14} m/s and were lower than those corresponding to the reference bentonite.

Gas permeability

The gas permeability was measured in core samples drilled onsite during dismantling and preserved to keep the degree of saturation they had when the blocks were dismantled. Most of the samples had high degrees of saturation, and consequently gas pressures higher than 0.2 MPa had to be applied to get the gas flowing through the samples.

The results show that the increase in confining pressure caused a slight reduction in gas permeability. Dry density and water content had the main effect on permeability, which decreased with the decrease in accessible void ratio. The permeability of the samples retrieved from the GTS was lower than that obtained in samples of the reference bentonite with the same accessible void ratio tested under the same confining pressure. The reason could be the modification of the pore size distribution towards smaller pore sizes during operation [3].

Swelling under load tests

The swelling under load tests determine the strain capacity of the soil when it saturates under a fixed axial pressure. The samples for these tests were drilled from blocks in the laboratory and saturated with deionised water in the oedometer under a vertical load of 0.5 MPa. As expected, the results showed that the swelling capacity increases with initial dry density and decreases with initial water content. For this reason the final strain of the samples closer to the heater was higher. However, the swelling measured was in general slightly lower than that expected for samples of the reference bentonite of the same initial characteristics (-10% vs. -12%).

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CLAY MINERAL AS NANOCARRIERS FOR DRUG DELIVERY

César Viseras (1,2)

(1) Department of Pharmacy and Pharmaceutical Technology, School of Pharmacy, University of Granada, Campus of Cartuja, 18071 s/n, Granada, Spain, (2) Andalusian Institute of Earth Sciences, CSIC-University of Granada, Avda. de Las Palmeras 4, 18100, Armilla (Granada), Spain
ecarazogil@ugr.es

Over 300 articles have cited the review of 2007 “Use of clays as drug delivery systems: Possibilities and limitations” [1]. A decade later, there are many advances in this field that continue to be a hot topic among clay scientists around the world. The greatest challenge continues to be the development of clay-based materials and systems capable of effectively controlling the release of the drugs once administered, optimizing their biopharmaceutical profile, as well as improving stability [2]. Moreover, therapy often requires the concomitant administration of several drugs, and interactions between them, before and once administered, may compromise the efficacy of the treatment. In all these cases, the use of clay based nanocarriers appears as an interesting strategy in the design of improved pharmaceutical dosage forms capable of overcoming technological and clinical challenges. I would like to acknowledge all the authors and groups behind the developments on this topic and I am confident that the present contribution will provide a useful reference on state-of-the-art research in this exciting area of clay mineral applications.

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GEOPOLYMERS FOR INORGANIC BINDER IN 3D PRINTING APPLICATION IN CONSTRUCTION

Vera Voney (1)*, Gnanli Landrou (1), Andrei Jipa (2), Pietro Odaglia (2), Isolda Agustijuan (1) Benjamin Dillenburger (2), Guillaume Habert (1)

(1) Chair of Sustainable Construction, ETH Zürich, Switzerland, (2) Digital Buildings Technologies, ETH Zürich, Switzerland

Digital fabrication and more specifically, 3D printing allows the production of very complex shapes with no extra cost for complexity and customization. This mass customization revolution opens new possibilities for the construction industry [1]. For instance, structural elements can be designed with the exact amount of materials positioned in the right place. Recently 3D printing has been used to produce a formwork for high performance fibre reinforced concrete [2] which would reduce the environmental impact of the structure by one third. However, this large scale binder-jet technology with organic binders (phenolic and furanicresins) causes serious problems for the indoor environmental quality of buildings through the release of volatile organic compounds when they are used as building structure.

In this study, we replaced the organic binder in the binder jetting technology by geopolymer, which has no volatile components and therefore does not affect the indoor air quality. An additional advantage of this mineral binder compared to conventional cementitious material is the recycling of the unused powder at the end of the printing.

To 3D print geopolymer, different approaches exist where the matrix and the activator are in different states. In the liquid/solid option the alkali source is injected in liquid state and the aluminate powder is mixed in the sand bed. The solid/solid method describes an option where only water is printed on the sand bed mixed with both components in solid state. Finally a liquid/liquid option is feasible where all components are injected in the liquid state.

To do so, the viscosity of the liquid phase was measured by rheology in order to fit the viscosity range required by the print head of the 3D printing system. Furthermore, we carried out oscillatory measurements to determine the setting time and identify the optimal composition. The final strength of geopolymer-sand compounds was measured using a vicat apparatus.

To optimise the process, we studied the relation between viscosity of the liquid and porosity of the support in order to be able to develop a mix where the liquid drop flow through the sand layers will be counter balanced with the setting time of the geopolymer.

First results show that the liquid/solid option is an ideal solution as it allows a fine control of the initial porosity of the sand bed and perfect recycling possibilities after the printing. Furthermore, this new mineral binding option in 3D printing opens a potentially low cost and low environmental way of producing prefabricated concrete structures.

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FAULT DATING OF AUTHIGENIC CLAYS - HISTORY AND STATUS

Peter Vrolijk (1)*, David Pevear (2)

(1) Retired, New Mexico Tech, Socorro, NM 87801, USA, (2) Retired, Jamul, CA 91935, USA

Fault dating has become a useful tool for regional tectonics studies and for probing fault and earthquake processes. Fault dating methods achieved a solid scientific foundation almost 25 years ago when the development and application of Illite Age Analysis (IAA) [1] for interrogating sedimentary burial and thermal histories found a new potential application - defining the age of fold-and-thrust development. IAA is based on a kinetic model of smectite-illite reaction and thus reflects the integration of processes that drive the reaction; burial diagenesis temperature and fluid chemistry (K-concentration) are considered the two most important parameters [2].

IAA was adapted in 1991 at Exxon to address a technical business problem - could the method help identify traps in the Canadian Rockies formed after gas generation had ceased and where conventional geologic methods of defining deformation timing (i.e. stratigraphic constraints) are unavailable. Early on we documented three observations that encouraged us that fault ages might be reasonable [3]:

1. Smectite-illite reaction progress in fault gouge is advanced beyond undeformed shales
2. The distribution of K/Ar ages measured on multiple size fractions differed from undeformed shales
3. Measured K/Ar ages are younger than depositional ages

On the basis of these early positive results, we undertook more extensive tests of precision and accuracy by evaluating ages across a series of faults (imbricate stack), within the context of available stratigraphic and independent geologic constraints, and replicate analysis of 2-3 samples from individual outcrops. The results of these tests provided further support for the significance of the ages.

At the same time, we pursued investigations to reveal what geologic processes might be responsible for these ages. We often found in fault gouge samples fibrous illite morphologies that are more common in sandstones than shales, and we evaluated interpretations based on the existing burial diagenesis kinetic model of the smectite-illite reaction [2,3]. Throughout this exercise we became suspicious that whatever processes were occurring, they were similarly effective at dissolving and re-precipitating 1Md illite. At this point, however, the business imperative for further scientific investigation diminished, and further research ceased.

Since that time others have picked up, refined, and applied this method in tectonics and fault process studies. The two most notable modifications to the procedures we used include the incorporation of 40Ar/39Ar methods [4] and the interpretation of illite-rich samples using quantitative models of illite polytypes. Although progress on understanding microscopic processes is difficult, developments in earthquake seismology (e.g., recognition of a wide spectrum of earthquake behaviour) and recognition of fault-derived clay morphologies, like clay nano-particles and other fabrics, suggests that a significant advancement in understanding is possible.

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GEOPOLYMERISATION OF AN ILLITIC MUD FROM GRAVEL WASHING

J. F. Wagner*, D. W. Yui Cardenas

Geology Department, Trier University, Trier, Germany

Gravel Wash Mud is widely available and considered suitable for geopolymer synthesis due to a high Si and Al concentration. To analyze a Gravel Wash Mud from aggregate mining as a potential geopolymer binder, it was first thermally activated to form a metaclay (at temperatures 550 - 950 °C) and second chemically activated by mixing with NaOH (1.5 M; 4.5 M; 8 M; 10 M and 14 M). The resulting geopolymer cement was then characterized by X-ray diffraction, scanning electron microscopy and compressive strength testing, in order to determine the reactivity of the illitic mud, the mineralogy and microstructure as well as the strength of the geopolymers. Grinding of the material increased the reactive surface areas of the metaclay significantly, and by this ground particles activation with NaOH lead to higher strength geopolymers than for ungrounded material. Furthermore NaOH activation was best at a temperature of 50 °C and 28 days curing time. Geopolymerisation seemed to have formed Phillipsite crystals and amorphous material and resulted in a geopolymer cement with relative high compressive strength (highest result 16 N/mm²). The research has shown that Gravel Wash Mud is suitable for geopolymer formation and using Gravel Wash Mud as a geopolymer binder will benefit the environment because it is recycling of a waste material from aggregate mining. It will further significantly reduce the CO_2 emissions because gravel wash mud is free of CO_2 and the calcination temperature is lower if compared to Portland Cement.

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PHOTOSTABILITY BETA-CAROTENE/ MODIFIED KAOLINITE FROM WEST KALIMANTAN INDONESIA

Nelly Wahyuni (1,4), Georges Zissis (2), Zéphirin Mouloungui (1,3)*

(1)Université de Toulouse, INP-ENSIACET, LCA (Labo de Chimie Agro-indistrielle), 4 Allée Monso, F-31030 Toulouse, France, (2) Université de Toulouse, Université de Toulouse, LAPLACE (Laboratoire Plasma et Conversion d'Energie), UPS, INPT, 118 route de Narbonne, F-31062 Toulouse, France, (3) INRA, UMR 1010 CAI, F-31030, Toulouse, France, (4) Department of Chemistry, Mathematic and Natural Science, Tanjungpura University, Jl. Prof. H. Hadari Nawawi Pontianak 78124, Indonesia
*zephirin.mouloungui@ensiacet.fr

West Kalimantan is one of province in Indonesia that has abundance of mineral like quartz and kaolin [1]. This natural kaolin is composed by kaolinite and associated with quartz, and muscovite. The improvement of properties of kaolinite can be done by two main different treatment such as (a) physical modification with thermal/microwave treatment, and (b) chemical treatment with acid, bases or organic compound. Physical modification involved alteration of chemical composition and crystalline structure by the high temperature, but in chemical modification usually by alteration of structure, surface functional groups and surface area [2].

Beta-carotene is pro-vitamin A, which can be extracted from carrot. It has absorbance in wavelength zone from 415-508 nm, therefore it was used as sensitizer on DSSC (dyes sensitizer solar cell) [3]. Freitas et al [4] used beta-carotene in formulating sunscreen.

As natural organic compound, beta-carotene is sensitive to the light. Some researchers have found away how to improve the stability of the pigment. Stabilization of curcumin was enhanced by complexation with Zn^{2+} [5]. Photostability of natural pigment can enhanced by photoprotector, such as gold nanoparticles which improved photostability of chlorophyll-a [6]. Hiendro et al [7] using activated kaolinite to improve the photostability of bixin.

In this research, we studied the photostability of beta-carotene with kaolinite from West Kalimantan, Indonesia (KN) and modified kaolinite. Kaolinite was calcinated 6 hours at 600 °C (KC), and modified by $ZnCl_{2.}$ Kaolinite was modified by interacted with $ZnCl_2$ solution and then dried (KM). Beta-carotene (Aldrich) 2.5 ppm in acetone was interacted with modified kaolinite (kaolinite/acetone = (0.25g/10 mL) at 1 hour and then irradiation with UV light 365 nm until 9 hours. Before analysis, the effluent was sentrifuged 5 minutes at 5000 rpm. Absorption spectra of beta-carotene was mesured using UV-spectrophotometer (SHIMADZU 1800). The percentage photostability by modified kaolinite then was calculated using the formula as described by Claes. Rate photodegradatian was calculated using pseudo-first order reaction data.

Modified kaolinite was identified by X-Ray Diffraction (XRD), surface area analyzer, infrared-spectroscopy (FTIR), and Scanning Electron Microscope-Electron Diffuse X-ray (SEM-EDX). Difratogram XRD demonstated that calcinating at 600 °C caused the layer kaolinite kolaps. Mean pore volume of modified kaolinite increased and infrared-spectroscopy showed reducing -OH functional group.

From this research, we have observed that kaolinite increased the photostability of beta-carotene. Percentage photostability of beta-carotene by modified kaolinite at 5 hour was 61.87%. The amount of beta-carotene which absorbed in kaolinite was related to the photostability of beta-carotene.

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MOLECULARLY ENGINEERED, LIGHT-ADAPTIVE SELF-ASSEMBLED NACRE-MIMETICS

Andreas Walther

A3BMS Lab - Adaptive, Active and Autonomous Bioinspired Material Systems, Institute for Macromolecular Chemistry, Freiburg Materials Research Center (FMF), and Freiburg Institute for Interactive Materials and Bioinspired Technologies (FIT), Albert-Ludwigs-University Freiburg, Freiburg, Germany
www.walther-group.com

Nature provides prime examples of lightweight, strong, stiff and yet tough materials. Their unique properties are realized via the hierarchical self-organizing growth of hard (inorganic, protein crystals, crystalline polysaccharides) and soft (organic, biopolymeric) building blocks into well-ordered structures with tailored energy dissipation mechanisms. Nacre, wood or silk are paradigms in materials design and considered near perfect marriages of hard and soft components.

Herein, we will demonstrate large-scale self-assembly approaches to mimic the natural structure found in the nacreous layer in mother of pearl and focus on how to tune the mechanical and functional properties, and make the overall structures light adaptive.

We use polymer-coated inorganic nanoclay platelets with intrinsic hard/soft character, which form nacre-mimetic composite films with highly defined and tuneable mesostructure upon water-removal due to excluded volume effects. We will show how nanoplatelet dimensions (aspect ratio from 25 - 3500), thickness of the organic layers, supramolecular bonds in the soft phase and humidity influence local dynamics and macroscopic material and fracture properties. We furthermore demonstrate how the mechanical properties can be modulated in a spatiotemporal manner using light irradiation, and how this relates to non-equilibrium materials.

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STRUCTURE EVOLUTION AND WHITENESS OF RED PALYGORSKITE CLAY INDUCED BY HYDROXYLAMMONIUM CHLORIDE

Wenbo Wang (1,2), Zhifang Zhang (1), Guangyan Tian (1), Yuru Kang (1,2) Aiqin Wang (1,2)*

(1) Key Laboratory of Clay Mineral Applied Research of Gansu Province, Lanzhou 730000, P.R. China, (2) Center of Xuyi Palygorskite Applied Technology, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Xuyi 211700, P.R. China
*aqwang@licp.cas.cn

Low-grade brick-red palygorskite (Pal) clay can be found almost everywhere on the earth with huge reserves, but they are hardly to be applied in industry on large scale because of their deep color and complex components [1,2]. The isomorphism substitution of Fe(III) and Al(III) toward the Mg(II) on octahedral sites in the natural Pal makes it have deep color and complex structural formula of $(Mg_{5-y-z}R_{y\square z}{}^{3+})(Si_{8-x}R_x{}^{3+})O_{20}(OH)_2(OH_2)_4R^{2+}{}_{(x-y+2z)/2}(H_2O)_4$ (where, □ is a vacant site, and *R* represents Mg, Al or Fe) [3,4]. In addition, red Pal clay are mainly formed in marine, bay, lagoon, and lake conditions by a deposition mechanism [5], so the associated minerals (i.e., quartz, feldspar and muscovite) are usually present in it. Hence, to study the structure evolution and color transformation of natural red Pal clay under different conditions is extremely significant to extend its applications in industrial fields. In this work, we successfully convert brick-red Pal to white by a simple hydrothermal process in the presence of hydroxylammonium chloride (HAC). The color of brick-red Pal does not change using water as the reaction medium; while the brick-red Pal converts to white using aqueous solution of HAC as the reaction medium. The HAC with strong reduction capability contributes to convert the brick-red Pal as white under atmospheric condition. The rod-like crystal morphology of Pal shows no obvious change after conversion to white, as confirmed by XRD and SEM analyses. The ^{29}Si MAS NMR analysis confirms that some metal ions in octahedral sheet were leached, but the silica framework of Pal remains well. The Mössbauer spectroscopy shows that hematite (α-Fe_2O_3) phase exists in the Pal clay, which disappears after hydrothermal treatment. The Fe(III) and Fe(II) exist in the octahedral sheet of Pal, with the Fe^{3+} (52.4%) to Fe^{2+} (19.8%) area ratio of about 3:1. Hematite (α-Fe_2O_3) phase disappeared after hydrothermal reaction, and the red Pal clay was transformed as white. The chemical composition analysis reveals that after reaction with HAC, the content of Al_2O_3, Na_2O, CaO and K_2O does not obviously change, but the content of MgO, SiO_2 and Fe_2O_3 changed greatly. The MgO content decreased from 4.02% to 2.07%, the content of Fe_2O_3 decreased from 7.30% to 2.84%. This indicates that Mg(II) and Fe(III) or Fe(II) were leached from the octahedral sheet of Pal under the action of HAC; while Al(III) and Si(IV) still remain in the crystalline framework. It was revealed that the leaching of partial Fe(III) ions and reduction of Fe(III) ions as Fe(II) simultaneously contribute to conversion of color. The white products show the whiteness of 70.01-85.6%, which is potential to be used in many fields such as fine chemicals, paper making, paints, coating and reinforcing filler.

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ON THE AVAILABILITY OF CLAY MINERAL "CRYSTALLINITY" INDEX STANDARDS

LAURENCE WARR

Institute of Geography and Geology, University of Greifswald, Greifswald, Germany

The clay mineral "Crystallinity" Index Standard (CIS[1]) is a method of full-width-at-half-peak-maximum (FWHM)calibration using rock chip standards that allows the same numerical results to be obtained from the clay mineral XRD basal reflections of the same samples, regardless of interlaboratory variations. It is most commonly applied for standardizing the illite "Kübler" and chlorite "Árkai" "crystallinity" indices for the purpose of consistent metamorphic grade determinations. Standard samples for this method of standardization have been available from the author over the period of 1994-2016. All sample batches originate from the well-studied diagenetic to low-grade metamorphic Palaeozoic rock sequence exposed in the coastal section of North Devon and North Cornwall, southwest England. This contribution reports on a resampling study of previous locations, as well as some additional sites designed to increase the number of available standards. New CIS values were determined following the original methodology of Warr & Rice (1994) [1] and based on internal calibration against older CIS samples. The new material were also tested for homogeneity and the statistically reproducibility of measurements quantified based on multiple sampling of each batch. The metamorphic grade was also reassessed following the recent revision of the CIS anchizonal boundaries to true (original) Kübler equivalent values [2]. In addition to presentation of the new CIS standard collection, some recommendations are given on how to improve the calibration of data sets based on experience gathered since the introduction of the method.

A summary of old and new* CIS standards is given below (L = Lower, M =Middle, U = Upper).

Standard	Locality	Source	Age	Metamorphic zone
SW1-1992	Widemouth Bay	BudeMudrock	U. Carboniferous	Diagenetic
SW1-2012*	Widemouth Bay	BudeMudrock	U. Carboniferous	Diagenetic
SW2-1992	Crackington Haven	CrackingtonMudrock	U. Carboniferous	L. anchizone
SW2-2012*	Crackington Haven	CrackingtonMudrock	U. Carboniferous	L. anchizone
SW3-2000	Widemouth Bay	BudeMudrock	U. Carboniferous	L. anchizone
SW3-2012*	Polzeath Beach	Polzeath Slate	U. Devonian	U. anchizone
SW4-1992	Portgaverne	Trevose Slate	M. Devonian	U. anchizone
SW4-2012*	Portgaverne	Trevose Slate	M. Devonian	U. anchizone
SW5-2000	Strangles Beach	CrackingtonMudrock	U. Carboniferous	U. anchizone
SW6-1992	Trebarwith Strand	Tredorn Slate	U. Devonian	Epizone
SW6-2012*	Trebarwith Strand	Tredorn Slate	U. Devonian	Epizone
SW7-2012*	Delabole Slate Quarry	Delabole Slate	U. Devonian	Epizone

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LOW-FREQUENCY CONDUCTIVITY OF CLAY SUSPENSIONS: ELECTROKINETIC POTENTIALS, SURFACE CONDUCTANCE AND COUNTERION MOBILITY

Christian Weber (1)*, Helge Stanjek (2)

(1) Physikalische Chemie TU Freiberg, Freiberg, Germany, (2) Ton- und Grenzflächenmineralogie RWTH Aachen, Aachen, Germany

Judged by the number of publications on the electrochemical properties of clay mineral- aqueous solution interfaces, the interest in electrokinetic potentials and related parameters is high. Although the importance of accounting for the non-spherical particle shape and surface conductance originating in the Stern layer has been emphasized repeatedly [2,3,4], the great majority of studies disregards these aspects entirely. Apart from other peculiarities of clay minerals, these aspects may be responsible for the fact that electrokinetic consistency has not been observed in clay systems.

This work presents results on the low-frequency electric conductivity of kaolinite dominated clay suspensions. The theoretical interpretation of conductivity data is guided by the theory of O'Brien & Ward [1] which accounts for the non-spherical particle shape and surface conductance. All parameters necessary for solving their equations have been determined experimentally, which eliminates uncertainties due to fitting procedures. Essential outcomes of the conductivity experiments are the surface conductance and electrokinetic potential. Alongside with the conductivity experiments the surface charge density of the particles has been measured under similar conditions. A correlation of the surface conductance and the surface charge density allows to estimate tangential counterion mobilities in the Stern layer and a consistency check of the conductivity interpretation.

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BRICK CLAYS OF AUSTRIA - MINERALOGICAL AND GRAIN-SIZE CHARACTERISTICS

INGEBORG WIMMER-FREY (1)*, FRANZ OTTNER (2), BERND SCHWAIGHOFER (2)

(1) Geological Survey of Austria, A-1030 Vienna, Austria, (2) Institute of Applied Geology, University of Natural Resources and Life Sciences, A-1190 Vienna, Austria

According to Austrian mining data, approximately 1.9 million tonnes of clay raw materials were mined in 2015 [1]. Currently, 55 clay pits are in operation and supply 25 brickworks. The material produced is used primarily for rising back-up masonry, roofing tiles, clinker bricks, and in the production of expanded clay. The economically important clay raw materials are extremely varied and widely distributed. In terms of age, they range from Palaeogene and Neogene to late Holocene. The genetic classification shows marine, brackish, limnic or aeolian sediments in all stages of weathering.

Clay deposits from the Quarternary period are found all over Austria. In Tirol, Vorarlberg, Salzburg and parts of Carinthia, post- and late glacial lake deposits are the only source of brick clays. In Upper and Lower Austria and in Styria, Pleistocene eolian deposits, such as loess and loamy loess still have considerable economic importance, even though they were much more widely used in the past.

Sediments from the Paleogene and Neogene are by far the chief and most important sources of raw material for all kinds of bricks. The clay pits are concentrated mainly in the Austrian MolasseZone, an Alpine foreland basin extending between the Bohemian Massif in the north and the Alpine front in the south. Other important resources are found in the Vienna Basin, and in the Styrian and other associated intramontane basins.

In Upper Austria, the Austrian federal state with the largest number of brickworks, the marine pelitic sediments from the Ottnangian period are the most important source of raw material. The silt content is relatively high and the clay content quite low. The bulk mineralogy is characterized by high carbonate content. When finely and homogenously distributed, the carbonates have a favourable influence on the firing behaviour. However, they also have a determining influence on the fired colour of the brick, and it is only possible to obtain the traditional brick-red colour with an admixture of Quaternary loam. The clay mineral assemblage is characterized by the absence of kaolinite. In addition to traces of chlorite, the predominant clay minerals are smectite and muscovite/illite.

In Lower Austrianorth of the Danube, marine pelitic sediments from the Karpatian periodwith little variation in mineralogy and grain-size distribution offer the best conditions for consistent brick qualities. The bulk mineralogy consists of carbonates und high amounts of phyllosilicates. The clay mineral assemblage is dominated by smectite followed by illite/muscovite, kaolinite and chlorite. South of Vienna, in the Vienna Basin, where the centre of the Austrian brick industry started to develop 150 years ago, a brackish to limnic sequence of clayey silty sediments of Pannonian age is still extensively exploited.

In Burgenland, the so-called “Stoober Tone” have been used for centuries as an important raw material for pottery. Today, these kaolinitic, early-sintering silty clays fromthe Late Miocene Period are also widely used for roof tile production.

In Styria, the brick clays in use show greater variation. For example, Pliocene to Lower Pleistocene maar lake sediments and Late Miocene limnic-deltaic sediments are used in the production of lightweight expanded clays.

Bulk rock composition, clay mineralogy and grain-size analyses -- including geological information --onAustrian clay deposits that are currently or have been exploited in the past are stored in a digital database maintained by the Geological Survey of Austria. An overview of petrographic characteristics is represented in order to illustrate the diversity of Austrian brick clays and their common characteristics.

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QUANTITATIVE ANALYSIS AND VALORISATION OF KAOLINITE FROM CALUQUEMBE (ANGOLA) BY X-RAY POWDER DIFFRACTION AND THERMOGRAVIMETRIC TECNIQUES

Jingyao Xu (1)*, Sandra Amores (1), Esperança Tauler (1), Joan Carles Melgarejo (1), Salvador Martínez (1), Antonio Olimpio Gonçalves (2), Marc Campeny (1,3)

(1) Departament de Mineralogia, Petrologia i GeologiaAplicada, Facultat de Geologia, Universitat de Barcelona, 08028 Barcelona, Spain, (2) Departamento de Geologia, UniversidadeAgostinho Neto, Luanda, Angola, (3) Natural History Museum of Barcelona, Barcelona, Spain
*jingyao.xu@ub.edu

Kaolin deposits has been for long exploited in several regions of Angola, and some of the most important are produced by weathering of anorthositic rocks from the Cunene complex. However, a systematic research has not been carried out until the present moment. Some extensive outcrops of kaolinitic weathering profiles developed on Precambrian granitic rocks were discovered during a recent trip in the Caluquembe area, in the Huila province (SSE of Luanda).

The present study determined the mineralogical features and thermal properties of the clay minerals fromthese outcrops. The mineral composition was determined by means of X-ray diffraction, Raman spectroscopy and scanning electron microscopy. The quantitative mineral phase analyses of the samples were obtained by X-ray diffraction profile refinement using Topas V2.2. The thermal behaviour was studied by differential thermal and thermogravimetric analysis.

Whole-rock geochemical analyses on random powders (XRPD) reveal that samples are mainly composed of kaolinite, quartz, feldspars (e.g. albite and microcline) and muscovite. In addition, smectite and hematite have been detected only in some samples. The obtained results indicate that samples present high kaolinite contents (~85 wt%), although a few samples which contain smectite have lower percentages of kaolinite (~28% wt%).

Thermal analyses were carried out to check the quantitative results of mineral phasesby XRPD. The differential thermal analysis (DTA) curve showsonly an endothermic peak at about 540 °C in dry air which confirms the dehydration of kaolinite [1] in samples lacking smectite. Mass loss in the samples, measured by thermogravimetric analysis (TG), is between 4 to 11 wt% until 650 ºC; samples with higher kaolinitecontents show the highest mass loss values. The amount of kaolinite calculated by mass loss is between 90 and 25 wt%.

We can conclude that XRPD and TG results have a good correlation and the combination of both techniques is suitable to determine the kaolinite content in this kind of clay deposits. Based on the high content of kaolinitefrom the deposit of Caluquembe, this area is very suitable for the exploration and potential exploitation of kaolinite, which is a very valuable raw material demanded in the fabrication of ceramics, cosmetics, paper or pharmaceutical products.

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MICA-VERMICULITE INTERGROWTH EXPANSION THROUGH NATURAL PROCESSES IN PYROCLASTIC CARBONATITES FROMCATANDA (ANGOLA)

Jingyao Xu (1)*, Marc Campeny (1), Esperança Tauler (1), Joan Carles Melgarejo (1), Antonio Olimpio Gonçalves (2)

(1) Departament de Mineralogia, Petrologia i Geologia Aplicada, Facultat de Geologia, Universitat de Barcelona, 08028 Barcelona, Spain, (2) Departamento de Geologia, Universidade Agostinho Neto, Luanda, Angola
*jingyao.xu@ub.edu

Catanda carbonatites are found in the Kwanza Sul province, about 350 km SE of Luanda (Angola). Theseare formed by small volcanic cones consisting of a series of pyroclastic rocks with minor interbedded carbonatitic lavas [1]. Phlogopite as a carbonatitic mineral and annite as xenocrystal provided from hosted granites are found in the Catanda pyroclastic carbonatites. Secondary minerals such as vermiculite have also been reported [1].

Under petrographic study, phlogopite and annite present textures as non-expanded, slightly expanded and strongly expanded defining accordion texture. Vermiculite can be distinguished using SEM-EDS in back-scattered electron (BSE) mode. Bothphlogopite and annite are affected by the vermiculitization process.

Previous work [2,3] has proposed that vermiculitization of micas proceeds through the sequence: mica to interstratified mica-vermiculite to vermiculite, and this is determined byXRD as peaks at 10, 12 and14 Å, respectively. In the present study of the Catanda samples, diffraction peaks were identified at 10 and 14 Å only, and no 12 Åpeak was found. We propose that the Catanda intermediate product of phlogopite-vermiculiteshould not be considered as an interstratified phlogopite-vermiculite but a mixture of phlogopite and vermiculite, consisting of intergrowths of both minerals inan intermediate stage of alteration, similar to theintergrowth of phyllosilicates described inother works [4,5]. By EMP analysis, vermiculite generated by the alteration of phlogopite is dominated by Ca in the interlayer position, it has d_{002} values of 14.6-14.8 Å identified by XRD, so the alteration of phlogopite produced Ca-vermiculte. For the alteration of annite, all analysis shows Mg <0.5 and K_2O contents of >5 wt.%. We propose that annite altered to K-vermiculite which has d_{002} spacing of 10.42 Å, so the intermediate product between annite and K-vermiculite has d_{002} about 10 Å. The d_{002} spacing of 10.07 Å corresponds to annite and phlogopite, also could be K-vermiculite, so as intergrowth or interstratified annite and K-vermiculite.

Pure vermiculites have little ability to expand but do increase in polyphase intergrowths, which are definedas intra-particle mosaics between mica and vermiculite, a rapid heating (>300 °C) may generate theexpansion of mica-vermiculite intergrowths [4]. We propose that the formation of the accordions texture as product of expansion is related to the rapid heating caused by the volcanic process that occurred in the Catanda area [1]. The intergrowth vermiculite-phlogopite stimulated the expansion. To the authors' knowledge, this is the first report of the accordion texture related to the vermiculite expansion occurring under natural conditions.

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WEATHERING OF PYROXENE TO SMECTITE IN HARZBURGITES FROM THE LOMA ORTEGA NI-LATERITE DEPOSIT (DOMINICAN REPUBLIC)

Jingyao Xu*, Cristina Villanova-De-Benavent, Esperança Tauler, Joaquín A. Proenza, Cristina Domènech

Departament de Mineralogia, Petrologia i Geologia Aplicada, Facultat de Geologia, Universitat de Barcelona, 08028 Barcelona, Spain
*jingyao.xu@ub.edu

Hydrous Mg silicate-type Ni-laterite deposits, like the Falcondo district (Dominican Republic), are dominated by Ni-enriched serpentines and garnierites. Recently, abundant Ni-smectites were discovered in the Loma Ortega Ni-laterite deposit included in the Falcondo area. In this work we discuss the mechanisms of formation of this Ni-smectite from pyroxene in the harzburgite parent rock.

Enstatite and diopsideare detected at 9.8 m deep in the Ni-laterite profile. Enstatite has an average NiO content of 0.06 wt% (N=10 analyses), and an average structural formula $Mg_{1.70}Fe_{0.16}Ca_{0.04}Cr_{0.02}Al_{0.08}Ni_{0.002}(Si_{1.88}Al_{0.12})O_6$(based on 6 oxygens). Enstatite occurs as prismatic crystals with irregular borders, frequently interstitial to olivine grains, and may show exsolution lamellae of diopside. Other prismatic pyroxene grains consist of a core with enstatite composition and a ~50 µm-thick border of diopside. Enstatite contains 0.03 wt% NiO(N=12 analyses) with the structural formula $Mg_{0.94}Ca_{0.90}Al_{0.07}Cr_{0.03}Fe_{0.06}Ni_{0.001}(Si_{1.87}Al_{0.13})O_6$. Diopside contains 0.05 wt% NiO (N=11 analyses), with the structural formula$Mg_{1.08}Ca_{0.80}Al_{0.06}Cr_{0.01}Fe_{0.05}Na_{0.01}Ni_{0.001}(Si_{1.91}Al_{0.09})O_6$. The average structural formula calculated on the basis of 11 oxygens for smectiteis $(Ca_{0.20}Na_{0.01})(Ni_{1.65}Mg_{1.35})(Si_{3.72}Al_{0.08}Fe_{0{\cdot}13}Cr_{0.03})O_{10}(OH)_2$ (N= 69 analyses). The structural formulae reveal a trioctahedral smectite with the tetrahedral position fully occupied by Si and minor amounts of Al and Fe^{3+}, with Ni and Mg as major octahedral cations, and Ni>Mg. The Ni content in Ni-smectite is highly variable, but one of the highest reported in the literature, with 16.15-40.72 wt% NiO (0.95-2.70 apfu Ni).

During lateritic weathering of ultrabasic rocks, the alteration of primary pyroxene leads to the formation of smectite[1], favoured by the fitting of the lattice structure of pyroxene with the smectite structure. Previous authors [2,3] studied the transformation of hedenbergite to nontronite and proposed that nontronite may grow topotactically from hedenbergite after the formation of a tetrahedral and an octahedral sheet from the shift of ½ [101] between adjacent pyroxene tetrahedral chains and octahedral cations. Actually, the **c** parameter of nontronite is approximately 1.5 times the **a** parameter of hedenbergite (1.5 x $\mathbf{a}_{pyroxene}= \mathbf{c}_{smectite}$, $\mathbf{b}_{pyroxene} = \mathbf{b}_{smectite}$ and $\mathbf{c}_{pyroxene} = \mathbf{a}_{smectite}$) [3], and this would facilitate the transformation of pyroxene to smectite. In the case of Loma Ortega, the cell parameters of diopside are **a**=9.74, **b**= 8.92, **c**=5.23 Å, and those of Ni-smectite are **a**= 5.48, **b**= 9.13 **c**= 14.8 Å.

In Loma Ortega, the alteration of pyroxene to smectite seems an "isovolumetric transformation" characterized by a conservation of the parent mineral texture and a remarkable concentration of Ni.

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AMELIORATION OF ADSORPTION CAPACITY OF ALGINATE'S BEADS BY INCOPORATING MAGADIITE: THE EFFICIENT REMOVAL OF CRYSTAL VIOLET DYE IN AN AQUEOUS SOLUTION

Youcef Yahia (1)*, Amel Djelad (1), Lala Setti Belaroui (1,2), Abdelkader Bengueddach (1), Mohamed Sassi (1)

(1) Materials Chemical Laboratory (LCM), University of Oran 1, BP.1524 Oran El M'Naouer, Oran 31100, Algeria, (2) Dep. of Pharmacy, Fac. of Medicine, University of Oran 1, BP 1510 Oran El M'Naouer, Oran, Algeria

Dyes are widely used in printing, food, cosmetics and in textile industries for their chemical stability, the ease of synthesis and variety of colors. However, these dyes are can potentially cause pollution once they are released in the environment [1]. Crystal violet (CV) is a cationic dye that is widely applied to colour paper, hair, dye cottons, and wool. The dye is regarded as a biohazardous substance [2]. Magadiite is a rare polysilicates, which has unique adsorption and swelling properties [3]. These properties could promote its application as an adsorbent for environmental pollutants [4]. The main aim of this study was to combine the gelling and adsorption properties of alginate (a linear polysaccharide, natural, hydrophilic and biocompatible) with magadiite's characteristics for efficient removal of CV dye from an aqueous solution. We started by the preparation ofalginate's beads. Then, synthesis of composite's beads (Alg:Mag) to finally carry out the adsorption's CV test on these materials. The dye removal adsorption studies were performed by varying different parameters like pH (0-8), initial concentration of CV (10-300 mg/L), ratio of Alg/Mag (5-60%) and adsorbent's dose (0.2-6g). Maximum dye removal was observed by (Alg:Mag) at a pH of 3.5, 3 g of adsorbent with ration 60% of Mag/Alg, 50 mg/L dye concentration and 120 min of contact time. The process of dye removal followed a pseudo second-order kinetics rather than pseudo first order. The results from the experimental data reveal that beads of (Alg:Mag) have proved to be an excellent adsorbent material for the removal of CV dye.

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STRUCTURAL REGULATION OF BIOMACROMOLECULES INSIDE MESOSCOPIC CAVITY

Akira Yamaguchi (1)*, Tsubasa Masuda (1), Yuuta Shibuya (1), Jun Kijima (1), Tetsuji Itoh (2)

(1) Institute of Quantum Beam Science, Ibaraki University, Mito, Japan, (2) Research institute for Chemical Process Technology, AIST, Sendai, Japan

Mesosized cavities within metal oxide and clay materials are promising reaction space for functional biomacromolecules, because biomacromolecules confined in the mesosized cavities can retain their functions under both physiological conditions and harsher reaction conditions. It has been considered that both surface character and size matching between cavity sizes and molecular sizes affect the stability of the three-dimensional structure of a biological macromolecule inside a nanopore. However, the impact of the cavity size on stractural stability of a biomacromolecule has not been realized due to lacks of its quantitative study. Although thermodynamic study on the confined biomacromolecules are important aspects to understand the molecular functionalities, it has not been made due to difficulties of the direct measurement. Herein, we present our recent studies on impact of cavity size for stability of DNA secondary structure [1].

In the present study, we synthesized FSM-type mesoporous silica prepared by kanemite [2], MCM-type mesoporous silica [3], and SBA-type mesoporous silica [4]. For the study of DNA duplex stability, positively-charged trimethyl aminopropyl (TMAP) layer was formed at the inner pore surface of mesoporous silica for the adsorption of DNA molecules by electrostatic interaction [1]. The 5’ FAM-modified DNA (d-TTTT or d-TTT) and 3’ TAMRA-modified DNA (a-AAAA or a-AAA) fragments were introduced into the TMAP-modified silica mesopores, and fluorescence energy transfer (FRET) responses from the confined DNA fragments were observed at temperature between 40 and -60 ºC.

In the study on duplex stabilities of short DNA fragments (d-TTTT/a-AAAA and d-TTT/a-AAA), it was found that the duplex stabilities were significantly enhanced by confinement inside the TMAP modified silica mesopores [1]. The d-TTT/a-AAA duplex was formed inside the pore (BJH pore diameter = 2.4 nm) with high efficiency (fraction of duplex = ca. 0.7), whereas it hardly formed in bulk aqueous solution due to its energetically instability. In addition, by utilizing supercooled pore water, almost complete duplex formation could be achieved at -60 ºC [1]. From thermodynamic study on the duplex formation within mesoporous silica with a series of pore diameters, it was concluded that spatial confinement was responsible for the enhanced duplex stability inside the mesosized cavity.

It is well known that the solvent water, which is confined inside mesosized cavity, can be deeply and reliably supercooled [5]. In the present study, we demonstrated that the combination of the spatial confinement and the supercooling condition could be useful to regulate the DNA secondary structure.

In contrast to the enhanced stability of DNA duplex confined inside the mesosized cavity, tertiary structure of protein was sometimes destabilized by the confinement. We examined the structural stability of globular protein (myoglobin) confined inside the mesosized cavity by optical absorption, differential scanning calorimetry (DSC), and neutron and X-ray scattering spectroscopies. The results suggested that the destabilization of myoglobin was due to the interaction of silica-myoglobin interaction.

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CRYSTAL GROWTH OF THE LAYERED SILICATE GRAFTED WITH ORGANIC GROUPS ON MONODISPERSE SPHERICAL SILICA PARTICLES

Masahiro Yamauchi, Tomohiko Okada*

Department of Chemistry and Materials Engineering, Shinshu University, Nagano 380-8553, Japan
*tomohiko@shinshu-u.ac.jp

Surface modification of smectites group of layered clay minerals (swelling phyllosilicate) has extensively been investigated for applications as adsorbents and photo- and electro-functional materials [1]. Cation-exchange reactions of smectites with organic cations are a promising method to modify because of their ion-exchange and swelling abilities, leading to various interlayer nanostructures for imparting useful functions. Grafting is another method via covalent attachment of organosilyl groups to the phyllosilicate layers. Apart from a post-grafting method, there are several reports on a one-step method for creation of synthetic smectites grafted with organophilic groups in the interlayer space including sol-gel reactions of organosilanes before the crystallization [2]. With some isomorphous substitution of Li(I) for Mg(II) in the octahedral layer, the resultant charged organo-phyllosilicate hybrids have been produced to be unique adsorptive properties if compared with conventional organoclays derived from cation-exchanges. We have developed direct crystallization of a hectorite-like layered silicate on silica surface (sacrificial template method) [3] in an aqueous alkali solution with preserving the shape of the original silica. A shape-controlled organo-phyllosilicate hybrid thus will be produced using the sacrificial template method. Here we report crystal growth of the phyllosilicate fine crystals grafted with methyl groups on the surface of a monodisperse spherical silica.

Methyltriethoxysilane and monodisperse spherical silica particle powder (2.6 µm) were used as the silica sources. These sources were allowed to react hydrothermally (373 and 423 K) in a Teflon-lined autoclave with an aqueous solution of LiF and $MgCl_2$ at a molar ratio of Si:Mg:Li=1.00:0.19:0.13 in the presence of urea (equal mole of Si) for 2~4 d. A typical molar ratio of the organosilane was 1/25 to the spherical silica particles. The precipitate was then collected by centrifugation, followed by being washed with mixture of water and ethanol (50/50=*v*/*v*).

SEM and TEM images of the products revealed homogeneous coverage with layered fine particles on the spherical silica particles. The fine particles were ascribable to hectorite-like layered silicate as revealed by XRD. The diameter of the whole particles slightly increased to 2.8 µm by the hydrothermal reactions with maintaining the original spherical shape and size distribution. An exothermic mass loss (4%) in the TG-DTA curves observed in the temperature range of 250 to 300 K indicated incorporating methyl groups. The basal spacing of the product was 1.32~1.36 nm slightly larger than 1.25 nm of a hectorite-silica hybrid in the absence of the organosilane. In the solid-state ^{29}Si NMR spectra, signals assigned to hectorite $Q_3(\underline{Si}(OMg)(OSi)_3)$, $Q_2((\underline{Si}(OMg)(OSi)_2(OH)$, and $Q_1(\underline{Si}(OMg)(OSi)_3)$ were observed at -94, -84, and -77 ppm, respectively. While T*n* (*n* = 1,2, and 3) signals were also observed in the range of -64 to -49 ppm for the synthesis at 373 K, those intensity was negligible at 423 K. The disappearance strongly suggests that increased temperature would avoid polymerization between the methylsilanes. Methylene blue, a cationic dye, was strongly adsorbed to the products from an aqueous solution, and the maximum amount adsorbed was 0.17 mmol/g to which the amount is close to that reported hectorite-silica hybrids [3d]. We thereby exemplified that methylsilane in the starting mixture participated the loading of methyl groups as Si-C linkage in the direct growth of the organophilosilicate fine crystals on the silica surface. Owing to the controlled morphology, the resulting hybrids will be useful for packing materials of liquid chromatography.

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IN-SITU NON-AMBIENT X-RAY DIFFRACTION STUDIES OF SEPIOLITE/ POLYAMIDE6,6 NANOCOMPOSITES

Africa Yebra-Rodriguez*, Cristina Fernandez-Barranco

Department of Geology and CEACTierra, University of Jaen, 23071 Jaen, Spain

Clay/polymer nanocomposites (CPN) are hybrid materials in which a small amount of clay is uniformly dispersed in a polymer matrix. These materials have been widely used in a variety of industrial applications since the first CPN manufactured by Toyota [1,2]. Polyamide 6,6 (PA66) is one of the most widely used engineering semicrystalline thermoplastics, combining ease of processing with good technical properties and good price. Depending on the crystallization conditions, different polymorphs can be found (mainly α and γ [3]), resulting from a different arrangement of the hydrogen bonds between the chains of the polymer, which can be affected by the introduction of a nanofiller in the polymer matrix [4,5].

Under certain conditions of use, photooxidation and thermo-degradation also cause irreversible structural changes affecting the technical properties of the material [6]. However, the presence of clay minerals as reinforcing agent contributes to the stability of the crystal structure of the polymer (e.g. in montmorillonite/polyamide6 CPN, where the stability is achieved through mechanisms of pseudoepitaxy between the two phases [7]). The aim of this work is to characterize the structural changes occurring in sepiolite/PA66 nanocomposites during certain industrial uses.

For that purpose we used pristine PA66 and CPN manufactured by adding sepiolite (5 wt%) to a PA66 matrix in a twin-screw extruder as described elsewhere [4]. The samples were afterwards processed simulating industrial processes. X-ray diffraction analyses were carried out on a PANalytical Empyrean diffractometer in combination with the Anton Paar XRK900 chamber which enables to characterize *in situ* the structural changes of the samples at non ambient conditions. The *in situ* changes in the amide groups of the PA66 crystals were observed with the help of a Bruker MultiRAM FT-Raman Spectrometer operating at the same temperature steps. Differential Scanning Calorimetry (Mettler Toledo 820e) was used to determine the crystallinity index, glass transition and melting temperature in the pristine PA66 and CPN samples. The results prove that after the Brill transition temperature of PA66 the sepiolite partially prevents the movement of the amide groups in the chains of the polymer, so the phase transition α → γ is not complete. Crystallinity index is also affected.

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SELENIUM UPTAKE FROMWATERS USING NATURAL ANDWASTE MATERIALS

Nevzat O. Yigit (1)*, Seda Tozum Akgul (1), B. Ilker Harman (2), S. Sule Kaplan Bekaroglu (1), Mehmet Kitis (1)

(1) Department of Environmental Engineering, Suleyman Demirel University, Isparta, Turkey, (2) Technical Science Vocational School, Suleyman Demirel University, Isparta, Turkey
*nevzatyigit@sdu.edu.tr

The main objective of this workwas to investigate the removal of selenium species and natural organic matter from waters using raw and surface-modified natural andwaste materials. The used pumiceslag particles were coated with iron oxide and the raw red mud was activated by acidification and heat treatment. Iron oxide coating of pumiceslags and acid activation of original red mud(ORM) decreased their point of zero chargevalues and increased surface acidity.

Selenite/selenate adsorption on iron oxide surfaces and acid activated red mud (AARM) was very fast with approximately following first-order adsorption kinetics. Iron oxide coating of pumiceslag and acid activation of ORM particles significantly enhanced their adsorption capacity for selenite and selenate. Maximum selenite adsorption capacity(6.3 mg Se/g adsorbent) wasobtained forAARM. The extent of selenate uptake by the surface modified particles was generally lower than those of selenite. Due to the competition among selenium species and other background anions in the water matrix for iron oxide adsorption sites, reduced selenite/selenate uptakes were found in natural water compared to their respective single solute tests. Greaterselenite by iron oxide surfaces were found at pH 7.5 compared to pH 8.9, due to increased electrostatic repulsion among iron oxides and selenite species at higher pH.AARM and iron oxide coated pumice are very effective for selenite uptake. Selenium concentrations less than drinking water standards (5-10 µg/L) can be achieved by using these particles. These low-cost, natural, or recyclable waste materialsappear to be promising adsorbents for selenium removal after their surface modification.

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CLAY MATERIALS FROM FOUMBAN (WEST, CAMEROON): CHARACTERIZATION AND VALORIZATION IN CERAMIC PRODUCTS

Rose Yongue (1)*, Jacques Richard Mache (2), André Njoya (3), Abiba Nkalih Mefire (1), Amadou Pountouenchi (4), Isaac Bomeni (5), Pascal Pilate (6), Laurentvan Parys (7), Nathalie Fagel (8)

(1) Laboratory of Applied Geology-Metallogeny, Department of Earth Sciences, University of Yaoundé I, PO Box. 812, Yaoundé, Cameroon, (2) Local Materials Promotion Authority (MIPROMALO), PO Box 2396 Yaoundé, Cameroon, (3) Fine Arts Institute of Foumban, University of Dschang, PO Box 31, Foumban, Cameroon, (4) Department of Inorganic Chemistry, University of Yaoundé I, PO Box. 812, Yaoundé, Cameroon, (5) Faculty of Science, University of Dschang, Cameroon, (6) Belgian Ceramic Research Center, 4 Avenue Gouverneur Cornez 7000 Mons, Belgium, (7) Materials Research Institute, Université de Mons, Belgique, (8) Laboratory of Clays, Geochemistry and sedimentary Environments (AGEs), Department of Geology, University of Liege, Quartier Agora, 14 Allée du 6 Août, B18, SartTilman, 4000 Liège, Belgium
*rfyongue@yahoo.fr

Since a decade, Cameroon (Central Africa) has been developing a national strategy in the promotion of local raw materials for the infrastructure and habitat. The acquisition of scientific knowledge on those materials especially clays and clayed materials represents a main challenge. In this way, common clay deposits from five localities some 50 kilometers around Foumban (West Cameroon) were investigated for their morphological, mineralogical and geochemical properties to determine their suitabilityfor ceramic applications.

The analytical results were obtained by X-ray diffraction, X-ray fluorescence spectrometry, Thermogravimetric Analysis. In the Koutaba, Bangourain, Marom, NJindare and Njimom localities, two types of clayey materials were identified: an homogeneous clayey layer “lateritic residual clay “ in the upper part of a laterite cover on interfluves; and a clayey heterogeneous hydromorphic material “ alluvial clay” in valleys. At Koutaba and Njimom, the residual clays appear at the foot of hills, but the alluvial clays occur in the flat valley. At Bangourain, alluvial clays outcrop on both sides of the Monoun shore and in the Koutoupi valley. At Marom and Njindare, pockets of clays were identified in a valley and at the foot of hillsides. The mineral composition of the Foumban clayed materials is kaolinite (25-84%), illite (0-18%), smectite (0-31%), and chlorite (0-8%), associated with quartz (2-44%), K-feldspars (0-27%.), plagioclase (0-26%), goethite (0-9%) with traces of rutile and hematite (≤5%). The geochemical analysis shows arelative large amount of SiO_2 (45-71%), Al_2O_3 (14-31%), and low Fe_2O_3 (<11%). Their physical features (variable grain size distribution and plasticity index) reveal the moderately plastic, plastic to highly plastic character.

Most of clays studied here could be used to build ceramic products such as bricks (refractory or not) and tiles. Dry ceramic tests on fired cylinders fired at temperatures between 900-1200 °C indicate that some raw Marom and Koutaba samples may be used in the manufacture of solid fired bricks and tiles. Quartz rich clays and poor in fusible elements must be amended to obtain a good quality final product at temperatures below 1100 °C. Moreover, the Koutaba residual clays appear suitable in the development of semi-refractory and refractory bricks to enhance artisanal furnaces in local technology transfer centers.

Keywords: West-Cameroon, raw clays, construction material, mineralogy, geochemistry, ceramic.

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APPLICATION OF LIQUID-PHASE-SYNTHESIZED TITANATE NANOSHEETS

Daisuke Yoshioka (1)*, Yasumitsu Nishimura (2)

(1) Department of Sciences, (2) Department of hygiene, Kawasaki Medical School, Kurashiki, Japan. 701-0192
*d.yoshioka@med.kawasaki-m.ac.jp

Titanate nanosheets (TNS) are easily synthesized from titanium alkoxide and tetraalkylammonium in liquid phase. TNS made by this method have uniformed shape, high water dispersibility, and the property of photocatalyst. But, the application of liquid-phase-synthesized TNS were rarely reported. So, in this presentation, we will introduce the application of TNS by supporting or substitution.

We tried to afford a new function to TNS by the supporting other metals onto TNS. By the photodeposition method using TNS dispersion and lanthanide oxides (Ln_2O_3: Ln = Sm, Eu, Tb and Dy), we obtained the fluorescent TNSs. The mainly supporting reaction mechanisms were same as conventional photodeposition methods. But, the TNS and Ln_2O_3 were present in liquid phase and solid phase, respectively. Lanthanide supported TNS (Ln/TNS) also had uniformed shape, high water dispersibility as same as liquid-phase-synthesized TNS.

The emission spectra of Ln/TNSs were mostly consistent with those of corresponding Ln^{3+}. The other hand, the excitation spectra of Ln/TNSs were different from those of Ln^{3+}. But, all Ln/TNSs were excited by about 300 nm UV-light and these emitted the fluorescence. It was reasonable to consider UV-light excited TNS. Based on these results, we concluded that Ln/TNSs fluorescence were composed the excitation of TNS, the energy transfer from TNS to Ln^{3+}, and the f-f transition of Ln^{3+}.

Additionally, some transition metals were able to be supported onto TNS by using UV-light, TNS dispersion and these metal oxides. The supporting amounts of lanthanide were slightly increased in the presence of transition metals. As co-catalyst, transition metals supported on surface enhanced the photocatalytic property of TNS.

Also, we tried to enhance the photocatalytic property of TNS by the substitution. We replaced parts of Ti in TNS to Nb or Ta by the mixing of these alkoxides when synthesis. The sheet sizes of TNSs including Nb or Ta (M-TNS: M = Nb or Ta) were little smaller than those of original TNS. M-TNSs could behave as the photocatalyst like TNS and lanthanide were supported onto M-TNSs. Lanthanide supported M-TNS (Ln/M-TNS) also emitted fluorescence. Emission intensity of Ln/M-TNS were increased more than that of corresponding Ln/TNS. We also observed the excitation peak shifted short wavelength with increasing the substitution amount. So that, we concluded that the excitation of M-TNSs need more energy, however M-TNSs transfer higher energy to Ln^{3+} than original TNS.

The photodeposition methods using TNS dispersion and metal oxides is useful to afford or to design various functions to TNS. And, by the substitution to Nb or Ta, we can control the photocatalytic property of TNS and the excitation energy.

We have investigated the supporting and substitution of liquid-phase-synthesized TNS via the fluorescence of Ln/TNSs. Our results showed that the application of TNS were very easy. We think that TNS which have diverse properties can be used for other purposes.

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MINERALS WITHIN K-BENTONITES OF YILANLI FORMATION (LATE DEVONIAN-EARLY CARBONIFEROUS) IN NORTHWESTERN BLACK SEA REGION, TURKEY: FROM A DISTINCTIVE PERSPECTIVE ON DIAGENESIS AND CRYSTAL MORPHOLOGY RELATIONSHIP

Özge Yücel, Asuman Günal Türkmenoğlu

Middle East Technical University, Department of Geological Engineering, Ankara, 06800 Turkey
unluce@metu.edu.tr

Bentonites (smectite-rich volcanogenic clay rocks) form during early diagenesis as a result of alteration of volcanic ashes (tephra), which can be settled down after transportationfor long distances following eruptions. Then, with progressive diagenitic conditions during late diagenesis, bentonites may transform K-bentonites due to chemical modifications and illitization process. Eventually, K-bentonites turn into metabentonites via low-grade metamorphism (Fortey et al.,1996).

In northwestern Black sea region, Turkey;K-bentonite successions are exposed within the limestone-dolomitic limestone successions of the Yılanlı formation which are deposited on within the Upper Devonian-Lower Carboniferous shallow carbonate platform of the Zonguldak terrane. These yellowish-brown and gray-green colored K-bentonite horizons also involveheavy minerals such as iron disulphides (pyrite, marcasite ?) and monosulphides(pyrrhotite).

Based on the Scanning Electron Microscopy coupled with Energy Dispersive X-Ray Spectroscopy (SEM-EDX) analysis, iron sulphides within the K-bentonites and their intercalated dolomitic limestones reveal various types of crystal morphologies such as; platy-hexagonal, cubic, and/or prismatic. On the strength of both SEM-EDX and X-Ray Diffraction (XRD) studies of these sulphide minerals, it is observed that some pyrite crystals present pseudo-hexagonal crystal morphologies. It is suggested that this pseudomorphism can be explained bythe mineral transformation of precursor hexagonal pyrrhotite to pyrite during prograding diagenesis (Sweeney & Kaplan, 1973). During diagenesis, pyrrhotite can be metastable in the presence of excess H_2S and may transform into pyrite (Berner,1967).

In light of this preliminary examination, it is suggested that there may be a relationship between changing diagenetic conditions and crystal morphologies of iron sulphide minerals found within the K-bentonites. In conjunction with illite crystallinity index (KI), the morphological transformation of the sulphide crystals could be used as a meaningful tool for interpretaion of prograding diagenetic evolution of the sedimentary basin in which K-bentonite bearing successions were deposited.

Keywords: K-bentonite, pyrrhotite, pyrite, Yılanlı formation, diagenesis, illite.

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SYNTHESIS OF TERBIUM DOPED LAYERED DOUBLE HYDROXIDECONSISTING MAGNESIUM AND ALUMINIUM AND LUMINESCENT PROPERTIES

Suguru Yukimoto*, Takuya Fujimura, Ryo Sasai

Interdisciplinary Graduate School of Science and Engineering, Shimane University, Matsue, Shimane,690-8501, Japan
rsasai@riko.shimane-u.ac.jp

Layered double hydroxide ($[M^{2+}_{1-x}M^{3+}_{x}(OH)_2](A^{n-})_{x/n}$, M^{2+}: divalent metal, M^{3+}: trivalent metal, A^{n-}: n^{th}-valent anion species; abbreviated as LDH) is one of the promising materials applied to waste water purification by absorbing harmful anions via anion-exchange reaction. In our or other groups' previous works, it was revealed that specific anion can be adsorbed by LDHs and anion selectivity can be controlled by chemical compositions which are kind of metal species and ratio of metal species [1]. This selective adsorption behaviour can be applied to sensing devices. However, to apply LDHs to sensing devices, detection of anion spices by simple method have to be invested to LDHs. Luminescent property is one of expected candidate ability for anion sensing because luminescence properties strongly depends on their surroundings. In this research, luminous rare-earth doped LDHs were synthesized for investing luminescent properties to LDH. In these LDHs, anion exchange site, which would be M^{3+}, was substituted by rare-earth ion, and then the effect of incorporated anion species in LDH toward luminescent properties were investigated.

$[Mg_{2/3}Al_{(1/3-z)}Tb_{z}(OH)_2](CO_3^{2-})_{1/6} \bullet yH_2O$ (abbreviated as LDH:Tbz, $z = 0 - 0.045$) were synthesized by the hydrothermal method at 140 °C for 24 hours according to a literature, and urea or hexamethylenetetramine was used [2]. LDHs incorporatingeachanion (Cl^-, F^-, I^-, NO_2^-, NO_3^-, SO_4^{2-}) were prepared via anion exchange reaction [3]. Evaluation of the obtained LDH was carried out by XRD, FT-IR, ICP-AES and emission spectrum measurement.

XRD patterns and IR spectra of obtained powders were measured to confirm the formation of LDH and incorporated counter anion. XRD patterns of all of synthesized LDH agreed with the typical diffraction pattern of $[Mg_{2/3}Al_{1/3}(OH)_2](CO_3)_{1/6}$. Thus, it was found that the present hydrothermal synthesis method gave us the LDH:Tb$z$less than $z = 0.045$. Moreover, the absorption band ascribed to C-O vibration of carboxyl ion was observed at about 1350 cm^{-1}in IR spectra of all LDH:Tbz. From ICP-AES measurement, the molar ratio of $Mg^{2+} : (Al^{3+} + Tb^{3+})$ was estimated, and then, this molar ratio was almost constant as about 1.83:1, even when Tb^{3+} content was varied. Thus, it was found that the LDH:Tbz with carbonate anions could be synthesized by the present method. Moreover, the present LDH:Tbz exhibited the green emission from Tb^{3+}doped in Al site in LDH skeleton structure.

From emission spectra of LDH:Tb0.003 with various incorporated anion species, it was found for the first time that emission intensity from Tb^{3+} doped in Al sites could be influenced by anion species incorporated in LDH interlayer space, and then, the order of emission intensity was CO_3^{2-}>Cl^-> SO_4^{2-}> F^-> NO_3^-> NO_2^-> I^-. Thus, these results indicate that LDH:Tbz is expectable as anion detector.

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CHLORITE FROM HYDROTHERMAL VMS Fe-Cu-Zn SULFIDE DEPOSITS IN THE NORTHERN APENNINE OPHIOLITES (ITALY)

Federica Zaccarini*, Giorgio Garuti

Department of Geosciences and Geophysic, University of Leobn, Leoben, Austria
*federica.zaccarini@unileoben.ac.at

The Fe-Cu-Zn volcanogenic massive sulfide (VMS) deposits associated with the Northern Apennine ophiolites of Italy have undergone only weak sub-oceanic metamorphism and contain chlorite in different minerogenetic environments: type-1) in sulfide mineralized hydrothermal veins of quartz and carbonate cutting across mafic-ultramafic rocks, type-2) in basalt, gabbro and serpentinite as a result of convective circulation of thermally-modified seawater below the sub-oceanic floor, and type-3) as detrital sedimentary mineral accumulating on the sea-floor at the venting site of metalliferous brines. Due to its great range in composition chlorite exists over a wide range of temperature and pressure conditions. Therefore, chlorite may occur in metamorphic, igneous, hydrothermal and sedimentary rocks. On the basis of more than 1000 electron microprobe analyses, chlorite in the Northern Apennine VMS deposits reflects the different environments of crystallization, showing changes in temperature, interaction with the host rock and composition of the parent hydrothermal fluids. Type-1 chlorite occurring in quartz-carbonate veins in basalt is dominated by Mg-Fe substitution, at constant Al^{VI}, and relatively high Mn-Cr ratio, similar to the chlorite of type-2 in basalt and gabbro. Type-1 chlorite associated with quartz-carbonate veins cutting across serpentinite shows a concomitant substitution of Mg for Fe and Al^{VI}, and high Cr-Mn ratio. Type-3 chlorite from the sea-floor, stratiform deposits is relatively enriched in Al^{VI} with variable Fe-Mg ratio resulting from the mafic or ultramafic nature of the substratum. The Fe-Mg-Al^{VI} exchanges in the octahedral site of the VMS Northern Apennine chlorites resemble those of the chlorite from metabasic rocks that crystallized over a wide range of metamorphic conditions. This similarity in chlorite composition seams to be essentially related to the similarity between the mafic-ultramafic protoliths that have generated both the chlorite in the Northern Apennine deposits and metabasic rocks. Other factors, such as seafloor or sub-seafloor environment of precipitation, have influenced the temperature of chlorite crystallization, causing an increase of the amount of Al^{IV}, that substitutes for Si in the tetrahedral site with increasing temperature. Temperatures obtained from type-1 and type-2 chlorites are comprised between 85-360 °C, with more than 90% of data plotting between 200 and 310 °C. In contrast, chlorite from sea-floor stratiform ores crystallized at relatively low temperatures, in the range of 50 and 298 °C, with 85% of the values clustering at 100-200 °C. Although exchanges in the octahedral site of chlorite, involving Fe, Mg, Al^{VI}, and the other minor elements Cr and Mn appear to be influenced by the mafic or ultramafic nature of the rocks hosting the VMS deposits, our mineralogical data suggest that the thermometric significance of the investigated chlorite is well consistent with the geological constraint of the different deposits. This observation confirms that, under the appropriate conditions, the chlorite composition can be used as a reliable geothermometer. The chemical composition of the investigated chlorite, in terms of Si contents and distribution of some trace elements, is probably also controlled by the nature of the mineralized hydrothermal fluids.

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Rb-Sr AND Sm-Nd SYSTEMATICS OF CLAY SIZE FRACTIONS OF VENDIAN SHALE, UST'-PINEGA FORMATION, RUSSIAN PLATFORM

Tatiana Zaitseva*, Igor Gorokhov, Anton Kuznetsov, Galina Konstantinova, Tatiana Turchenko

Institute of Precambian Geology and Geochronology, RAS, St.Petersburg, Russia

Upper Proterozoic argillaceous rocks often contain mixtures of non-cogenetic illite minerals with different crystallochemical and isotope characteristics. The end-members of these mixtures could be formed at different stages of lithogenesis [1].

The <2-µm fraction of shale sample from the Ust'-Pinega Formation was separated into 1-2, 0.6-1, 0.3-0.6, 0.2-0.3, 0.1-0.2 µm and <0.1 µm subfractions (SF). They were studied by the XRD, Rb-Sr and Sm-Nd methods. The most fine-grained SFs (0.2-0.3, 0.1-0.2 and <0.1 µm) include low-temperature $1M_d$ illite and admixtures of 1M illite and chlorite. The most coarse-grained SFs (1-2, 0.6-1 and 0.3-0.6 µm) include 1M illite and admixtures of detrital $2M_1$ illite and chlorite. Illites in the fine-grained SFs (0.2-0.3, 0.1-0.2 and <0.1 µm) have high CIS (Crystallinity Index Standard) values complying with the zone of diagenesis. The SFs were leached with 1 N HCl to remove mobile Sr adsorbed on the surface and located in interlayer positions of clay particles, or incorporated into the soluble accessory minerals such as carbonates and phosphates. Leachates and residues after leaching were studied by the Rb-Sr and Sm-Nd methods as well. The Rb-Sr isochron age was determined for each SF using data on the untreated subfraction, leachate and residue after leaching.

The Rb, Sr, Sm and Nd concentrations and isotope ratios in the SFs smoothly vary with decreasing clay particle size. In the untreated SFs: Sr concentration decreases from 113 to 45 ppm, Rb increases from 107 to 169 ppm, Sm decreases from 30.1 to 2.3 ppm and Nd decreases from 150.1 to 13.3. In the residues after leaching: Sr concentration decreases from 95 to 18 ppm, Rb increases from 106 to 166 ppm, Sm decreases from 11.3 to 1.2 ppm and Nd decreases from 71.3 to 14.5. In the leachates: Sr concentration increases from 17 to 28 ppm, Rb increases from 1 to 3 ppm, Sm decreases from 19.7 to 1.1 ppm and Nd decreases from 82.5 to 4.8 ppm.

^{87}Rb/^{86}Sr ratios in the untreated SFs and residues smoothly increase from 2.749 to 10.123 and from 3.231 to 26.007 accordingly. ^{87}Sr/^{86}Sr ratios in the untreated SFs and residues vary in the same manner: increase from 0.73989 to 0.78034 and from 0.74467 to 0.88473 accordingly. Binary diagrams (^{87}Rb/^{86}Sr-^{87}Sr/^{86}Sr, 1/Sr-^{87}Sr/^{86}Sr) are linear.

These relationships together with the XRD data suggest that silicate component in the fine-grained SFs (0.2-0.3, 0.1-0.2 and <0.1 µm) includes a mixture of two low-temperature illites with different chemical composition. The coarse-grained SFs (1-2, 0.6-1 and 0.3-0.6 µm) include a mixture of low- and high-temperature illites. One of the end-members (0.3-0.6 µm) in the coarse-grained mixture includes predominantly 1M illite and admixtures of detrital $2M_1$ illite. So the Rb-Sr isochron age for this SF (565±8 Ma) is not real age of diagenesis but it gives an opportunity to estimate its maximum limit. The isochron age (539±10 Ma) for the end-members (0.2-0.3 µm) of the fine-grained mixture, dominated by 1Md illite, apparently formed at a later stage of lithogenesis and shows the minimum age limit of burial diagenesis. The Rb-Sr ages (ca. 460 Ma) for finest SF (<0.1 µm) can be correlated with the stage of postdiagenetic transformation of shale.

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CRYSTALLOCHEMICAL CHARACTERISTICS AND K-Ar ISOTOPE AGES OF CRETACEOUS AND PALEOGENE GLOBULAR PHYLLOSILICATES (SARATOV REGION, RUSSIA). PALEOCLIMATIC AND PALEOGEOGRAPHIC APPLICATIONS

Victoria Krupskaya (1,2), Tatiana Zaitseva (3)*, Olga Dorzhieva (4), Elena Yakovishina (2), Sergey Borisovskiy (1)

(1) Institute of Geology of Ore Deposits, Petrography, Mineralogy and Geochemistry RAS, Moscow, Russian Federation, (2) Lomonosov Moscow State University, Moscow, Russian Federation, (3) Institute of Precambrian Geology and Geochronology RAS, St.Petersburg, Russian Federation, (4) Geological Institute RAS, Moscow, Russian Federation

Practice of globular phyllosilicates using as a material for paleoclimatic and paleogeographic reconstruction as well as for isotopic dating of sedimentary successions has shown that the obtained dates quite often correspond to time of early diagenesis of sediments and are close to their deposition age. However post-diagenetic processes can produce structure transformation accompanied by loss of radiogenic elements and result in “rejuvenated” ages. The complex mineralogical, crystallochemical (XRD, messbauer and IR-spectrocopy, microprobe analysis) and isotope-geochronological study of phyllosilicates enables to estimate, whether the crystallochemical and isotope characteristic are primary or resulted from post-diagenetic transformation of the mineral structure. This complex method was used to assess the peculiarities of the globular phyllosilicates from the Cretaceous and Paleogene sands (Saratov region, Russia).

Both Cretaceous and Paleogene globular phyllosilicates belong to glauconite series of interlayer-deficient micas [1] and 1Md(60^0) polytype modification [2]. The differences between the Cretaceous and Paleogene glauconites occur mainly in crystallite size which varies from 9-10 nm for the Cretaceous grains and up to 13-14 nm for the Paleogene minerals. The content of swelling layers for all samples less than 10%. The results of complex study indicate that the minerals formed at early diagenesis and their K-Ar ages (83±2 and 64.0±1.5 Ma respectively) close to the ages of sedimentation and hence have stratigrafical significance. Distribution of heavy minerals in Cretaceous and Paleogene sands practically unchanged, it can be concluded that the main source of terrigenous material hardly changed and was a regular in the Upper Cretaceous and Paleogene. Magnesium content in globular phyllosilicate can be used to calculate the average paleobasin temperature. According to [3] the temperature in the Cretaceous basin can be estimated about 20 °C, and in the Paleogene basin about 22 °C.

The work supported by the Russian Foundation for Basic Research (Projects 14-05-00297 and 15-05-09095).

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USE OF BIOMASS FROM OLIVE GROVE AS LIGHTENER ADDITIVE IN THE PRODUCTION OF ECOLOGICAL FIRED CLAY BRICKS

Montserrat Zamorano Toro (1), Dolores Eliche-Quesada (2), Luis Pérez-Villarejo (3), María Martín-Morales (4)

(1) Department of Civil Engineering, Higher Technical School of Civil Engineering, University of Granada, Campus de Fuentenueva s/n, 18071 Granada, Spain, (2) Department of Chemical, Environmental, and Materials Engineering. Higher Polytechnic School of Jaén. University of Jaen, Campus Las Lagunillas s/n, 23071 Jaén, Spain, (3) Department of Chemical, Environmental, and Materials Engineering. Higher Polytechnic School of Linares.University of Jaen, Campus Científico-Tecnológico Cinturón Sur s/n, 23700 Linares (Jaén), Spain, (4) Department of Building Construction, Higher Technical School of Building, University of Granada, Campus de Fuentenueva s/n, 18071 Granada, Spain

For some time now, construction industry is focused in the development of new materials that minimise the environmental impact and improve the insulation of the building. One of the best alternatives is the use of waste as additive for construction materials. The thermal conductivity of the fired clay bricks depends on their porosity and bulk density. Because of this fact, some studies have been carried out to reduce the bulk density of bricks using lightener additives. Organic pore forming additives also possess a high calorific value, that could constitute an important heat contribution during the firing process and, in consequence, a reduction of the energy consumption.

Olive leaf, olive pruning and olive wood are agricultural wastes generated largely in all olive regions around the world. On the one hand, during the previous cleaning process of the olive from the field to obtain oil, a considerable amount of olive leaf is separated, which usually represents 8% of the ground olive. Currently the use of olive leaf is limited in livestock feed as well as fuel in power plants. On the other hand, it could be considered that 1 ha of olive trees generates an average of 3 tons of olive pruning and olive wood; this waste often is used to produce energy in thermoelectric generation process; however, because of the difficulty and high cost of removing it, frequently it is burned or deposited in the fields where it is produced.

Consequently, in the present study residues from olive grove have been used for the manufacture of clay ceramic bricks as a new environmental-friendly solution. The influence of the waste type, waste ratio and particle size waste on physical, mechanical and thermal properties of waste-clay bricks has been studied and compared with clay bricks without waste following standards procedures. For this, the wastes were ground into three particle sizes: 0-1 mm; 1-2 mm and 0-2 mm; clay bodies were moulded in pastes with the incorporation of 7.5, 15 and 25 vol. % of waste; and finally green bodies were fired at 850 ºC. The results indicated that the potential use of these biomasses is promising due to the incorporation of organic pore forming wastes produced lightener bricks that could be used commercially as low density clay masonry units with lower mechanical properties and higher thermal insulating capacity. In addition, the environmental and economic benefits of these wastes utilisation as additive in the production of fired clay bricks makes the overall process more attractive.

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TECHNOLOGICAL CONSTRAINTS IN WASTE RECYCLING INTO CERAMIC TILES AND CLAYBRICKS

Chiara Zanelli (1), Roberto Soldati (1), Elisa Rambaldi (2), Michele Dondi (1)*

(1) CNR-ISTEC, 48018 Faenza, Italy, (2) Centro Ceramico, 40138 Bologna, Italy
*michele.dondi@istec.cnr.it

The manufacturing of clay bricks and ceramic tiles is a traditional way for waste disposal, going back at least to the 1970's, with an increasing industrial interest and growing number of scientific papers. In fact, this route offers the advantage of huge output volumes, high temperature treatment, and widespread industrial plants. In addition, in brick-making there is a rather wide tolerance of product and process features, while the tilemakingprocess is versatile and able to accommodate many different raw materials in the body. On the other hand, waste recycling has to face disadvantages stemming from technological constraints: e.g., particle size distribution, moisture, plasticity, drying sensitivity for bricks; slip rheological properties, compaction and sintering behaviour, colour for tiles. In any case, firing takes place with a poor control on chemical reactions of waste with the ceramic body, with possible volatilization or solubilization of harmful substances.

Laboratory testing and full-scale trials have covered a wide range of civil and industrial residues from: water treatment and urban solid waste, energy production, mining and quarrying, and the following industries: chemicals and petroleum, metallurgical and metalmechanics, ceramics and glass, textile and tannery, paper and wood, construction and building, agriculture and food. Besides the large scientific literature and numerous manufacturing experiences, conclusions about recycling of a given waste are often controversial: overall, improved reliability, industrial transferability and connection to tile-making and brick-making technology are needed.

The objective of this presentation is to propose a technological approach to assess waste recycling in tile andbrick production, involving four fundamental aspects that must be considered every time a residue is introduced in a ceramic body, which concern how a given amount of waste may affect the whole body.

1. Technological behaviour during the ceramic process: effect on body preparation, shaping, drying and firing stages; maximum addition in the manufacturing practice without intolerable changes of processing conditions.
2. Technical performance and aesthetic appearance of finished products: physical, mechanical and functional properties with reference to standard thresholds and market benchmark.
3. Impact on human health and the environment: possible cause of solid residues (scrap) and emissions as liquid (eluates, soluble salts and efflorescence) or gas (volatilization during firing).
4. Economic sustainability: prospective and consequence of waste addition, including transportation cost, additional processing steps, energy balance of manufacturing cycle, added value to final product.

Key concepts will be defined and discussed, in particular:

- Role of the ceramic body: the waste behavior in the manufacturing process is changing upon the composition and particle size distribution;
- Supply chain gap: a difference between the waste and the body components, in terms of chemical and physical requirements, can constitute a hindrance to their utilization;
- Inertization degree: the actual extent of immobilization of waste components into the ceramic body;
- Recommended recyclable amount: maximum percentage of waste that can be added to the batch by meeting all technological, technical, environmental and economic expectations;
- Technological profile:summarizing the waste behaviour in the various stages of working cycle and its effect on the ceramicproperties, with potential drawbacks and advantageshighlighted.

This contribution is an output of the MATER_SOS project [1].

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DIAGENETIC TRANSFORMATIONS OF SMECTITE, CHLORITE AND ILLITE IN PRODUCTIVE CRETACEOUS RESERVOIRS OF THE SOUTH GABON BASIN (WEST AFRICA)

Giovanni Zanoni (1)*, Branimir Šegvić (1), Andrea Moscariello (2)

(1) Department of Geosciences, Texas Tech University, Lubbock, TX 79409, USA, (2) Department of Earth Sciences, University of Geneva, Rue de Maraîchers 13, 1205 Geneva, Switzerland
*giovanni.zanoni@ttu.edu

The Gabon coastal region located along the equatorial West African continental margin, hosts several sedimentary basins with well-developed and prolific petroleum systems whose two key elements (source and reservoir) developed prior, during and after the opening of the South Atlantic Ocean in Cretaceous time. In this study, we focus on the Early Cretaceous Dentale and Gamba Formations in the onshore part of the South-Gabon sub-basin formed during the syn-rift and transition to post-rift time respectively. The two formations are both consisting of siliciclastic rocks thought to be accumulated in fluvial and lacustrine environments. The exceptional access to core material retrieved at depths of ~1500 m from two wells from these two reservoirs allowed us to provide unprecedented information on their mineralogy, geochemistry and thus origin and post-depositional diagenetic processes that controlled the distribution of clay parageneses. The latter is considered to be of high importance for the understanding of the basin's burial history and geotectonic development. Sampled material was analysed by X-ray diffraction, automated electron microscopy, and inductively coupled plasma mass spectrometry in order to reconstruct early and burial diagenetic variations directing the formation of clay assemblages in the basin. The clay content in both cores consists of authigenic mixed-layer minerals like illite-smectite (I-Sm), chlorite-smectite (C-Sm) and berthierine-chlorite (B-C) and some minor detrital illite/mica and chlorite. Illite-smectite and C-Sm phase chemistry are interpreted as the product of progressive evolution from the dioctahedral(montmorillonite to beidellite) and trioctahedral (saponite) smectitic precursors formed out of acid volcanic feedstock during early diagenesis (1). Different magmatic fractionation degrees, from rhyodacite to trachyandesite, reflected in the uniform REE curves of the volcanic glass conform to an active geotectonic development of the Cretaceous margins of Africa. If this is confirmed, this will be the first account of active volcanism recorded during Barremian-Aptian times in the eastern coast of South Atlantic. Mesogenesis led to the decrease of smectite and formation of mixed-layered phases; I-Sm composition showed maximal burial depths of sediments to be ~1000 m and ~500 m deeper than today for Gamba and Dentale sediments, respectively. Besides temperature, a major role in the formation of mixed-layer minerals had the porosity of sediments and geochemistry of smectitic precursors. Thus, Fe-Mg smectite showed higher thermal stability and lower rates of transformations in non-expanding clays during burial comparedto Al-rich smectite(montmorillonite to beidellite). Different burial histories of sediments from the two cores can be attributed to rift-related normal faulting and subsequent differential denudation

Finally, the study on clay minerals allowed us to provide accurate description and quantification of pore filling minerals, a new controlling factor for log calibration, all of which having a direct impact on porosity calculation.

Overall the findings provide new insights and ideas at regional and reservoir scale that may assist the future exploration and development of hydrocarbons in these two 'mature' reservoirs formations.

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MANUFACTURE OF NON-FIRED CERAMIC WITH HIGH STRENGTH BY CEMENT-MIXING AND MECHANICAL DEHYDRATION

Kouki Zen* (1), Kiyonobu Kasama (2), Yasuyuki Nakagawa (1)

(1) Department of Joint Research on Environment and Disaster at Port and Sea, Faculty of Engineering, Kyushu University, Fukuoka, 819-0395, Japan, (2) Department of Civil Engineering, Faculty of Engineering, Kyushu University, Fukuoka, 819-0395, Japan
*zen@civil.kyushu-u.ac.jp

A manufacturing technology for non-fired ceramics with high strength and durability has been developed [1] and [2]. It is called the Cement-mixing and Mechanical Dehydration (CMD), herein. Local natural clays, namely dredged clayey sediments, are utilized for the CMD. Re-use and re-cycling of dredged materials as building materials such as concrete blocks bring not only the reduction of disposal cost but also eco-friendly effect to society.

In the CMD, slurry state of dredged clayey sediment is firstly mixed with the stabilizer in which slug cement, type B is usually used and then poured into a cylindrical mold (diameter; 534 mm, height; 1000 mm) in order to dehydrate the cement-mixed slurry (in this experiment, Kaolin clay was used) by applying high dehydration pressures. By applying the high dehydration/consolidation pressure of 5 MPa with this apparatus, non-fired ceramic with the unconfined compressive strength of more than 20 MPa is created under a certain condition. This means that it is possible to make a concrete-like block from slurry of very high water content. In the CMD, dehydration is one of the key of strength increment. When compared with the strength manufactured without dehydration, the strength with dehydration is about 4 to 10 times larger under the identical cement content. Since the strength of clay is basically proportional to the density of clay, it is preferable to apply as large consolidation pressure as possible. For clayey soil, different from sandy soil, electro-chemical effect on strength increase is expected by applying high pressure as well. The unconfined compressive strength notably increases in accordance with the decrease of the water-cement ratio and close correlation is observed between both parameters. The unconfined compressive strength of treated clay is found to be governed by the water-cement ratio, irrespective of clay type and cement content. Note that the water-cement ratio is defined herein as the ratio of water against cement in weight after the unconfined compression test. The relationship between the unconfined compressive strength, q_u, after 28 days of curing and the water-cement ratio, *w/c*, is demonstrated by the following equation [3];

$q_u = \alpha(w/c)^{\beta}$,   where, $\alpha = 7.76$, $\beta = -1.44$

It is noted, however, the difficulty of mechanical dehydration exists in the CMD. Low permeable layer is formed at the surrounding boundary of drainage and slurry state remains inside after dehydration. From the view point of practical application of CMD, dehydration time, say velocity, is very significant, since the uniformity of strength in treated clay block strongly depends on the dehydration time. When dehydration is too rapid, uniformity of strength cannot be ensured and when dehydration is too slow, the production efficiency will remarkably decrease. To meet the designated strength and uniformity of treated clayey soil, the dehydration time as well as dehydration pressure and water-cement ratio is so important that time should be determined appropriately. It was found that the dehydration time can be analyzed with consolidation theory.

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THE CRYSTAL GROWING PROCESS OF SAPONITE: A CRYSTAL CHEMISTRY APPROACH

Chaoqun Zhang (1,2), Sabine Petit (3)*, Hongping He (1), Qi Tao (1), Fabien Baron (3)

(1) Key Laboratory of Mineralogy and Metallogeny, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China, (2) University of Chinese Academy of Sciences, Beijing 100049, China, (3) Université de Poitiers, CNRS UMR 7285 IC2MP, HydrASA, 6 rue Michel Brunet, F-86073 Poitiers Cedex 9, France
*sabine.petit@univ-poitiers.fr

Smectites are 2:1 type swelling clay minerals and widely distributed in the Earth's crust. The unique structure and properties endow them with various applications in many fields. However, the crystal growth process of these clay minerals is poorly known. In this study, we synthesize smectites mixing 2 precursors with defined chemical compositions under various conditions and we study the crystal-chemistry of the synthesized smectites to better understand the growth pattern of smectite. A series of Ni and Mg-saponite precursors were hydrothermally synthesized under different temperatures (50, 120, 220 °C). The two Ni and Mg-saponite precursors obtained in same temperatures were mixed with identical molar weights, and then reacted at 220 °C under autogenous pressure for 3different periods (3 days, 2 weeks and 1 month). All the precursors, as well as the further synthesized samples were identified as saponites by X-ray diffraction analysis (XRD), and Fourier-transform infrared (FTIR) spectroscopy. The chemical composition of the further synthesized saponites and the distribution of octahedral cations reflect the dissolution/ recrystallization process occurring during the hydrothermal treatment. The *v*OH bands due to structural OH allow to probe the octahedral environment. For the precursors synthesized at lower temperatures (50, 120 °C), hydrothermally treated at 220 °C, $v\mathrm{Mg_2NiOH}$ and $v\mathrm{Ni_2MgOH}$ bands are observed giving evidence of dissolution of Mg and Ni precursors and their recrystallization into Mg-Ni mixed saponites. For the Ni and Mg precursors hydrothermally synthesized at higher temperature (220 °C), only $v\mathrm{Mg_3OH}$ and $v\mathrm{Ni_3OH}$ bands are observed, even for the 2 months longer experiment, and no dissolution of the precursors could be evidenced.

Keywords: saponite, FTIR, crystal growth, crystal chemistry.

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BIOINSPIRED ANTI-WETTING COATINGS AND MAYA BLUE-LIKE PIGMENTS BASED ON CLAY MINERALS

Junping Zhang*, Bucheng Li, Lingxiao Li, Aiqin Wang

Key Laboratory of Clay Mineral Applied Research of Gansu Province, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Tianshui Middle Road 18, Lanzhou, 730000, P.R. China

Inspired by self-cleaning and water-repellent properties of the lotus leaf and the legs of a water strider in the natural world, artificial superhydrophobic and superamphiphobic surfaces, characterized by high contact angle (CA > 150°) and low CA hysteresis of liquid droplets, have attracted extensive attention [1]. However, the low mechanical stability of superhydrophobic and superamphiphobic surfaces is the bottleneck we are facing for their practical applications. In addition, organic liquids often have high CAs but adhere stably on the surfaces and cannot roll off, which means lack of the important self-cleaning property. Moreover, most of the methods for the preparation of superhydrophobic and superamphiphobic surfaces are complicated, expensive and limited to specific substrates.

Maya Blue is a famous hybrid pigment composed of palygorskite (PAL) and indigo from the leaves of añil plant, which was widely used in mural paintings and ceramic pieces in Yucatan by Mayan [2]. The extraordinary stability of Maya Blue against acidic, alkaline and organic corrosions and biodegradation has attracted much attention of researchers in the fields of material, chemistry and archeology in the past decades. Inspired by Maya Blue, various organic dyes (or pigments) and clays have been exploited to prepare Maya Blue-like pigments. Although the results are helpful to clarify the host-guest interactions, all these Maya Blue-like pigments show inferior stability to ancient Maya Blue. Wettability issues are among the most frequently encountered problems for scientific research and our daily life. Wettability of a solid surface (or powder) by a liquid (*e.g.*, water) depends on both surface microstructure and surface tension of the solid surface (or powder). Wetting of a solid surface (or powder) by a liquid is essential for the interaction and/or reaction between them. Thus, the stability of traditional Maya Blue-like pigments may be improved by making them hydrophobic.

Here, we report our recent progress about bioinspired anti-wetting coatings and Maya blue-like pigments based on clay minerals [3]. The structure and properties of the coatings and the pigments can be tailored by nanostructure and content of the clay minerals. This is the first time that clay minerals are used for the invention of superhydrophobic and superamphiphobic coatings. Also, for the first time that the bioinspired Maya blue-like pigments with the unique anti-wetting properties are prepared. The coatings and the pigments feature excellent superhydrophobicity, superamphiphobicity and extraordinarily high durability owing to the synergistic effects of clay minerals and the anti-wetting properties. The coatings and the pigments are prepared via simple methods at low cost, which facilitate their large scale production and thus pave the way for their practical applications in various fields.

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SYNTHESIS AND CHARACTERISATION OF LAYER DOUBLE HYDROXIDES (LDHS) FROM RED MUD AND ITS APPLICATION ON DYE REMOVAL FROM WASTEWATER

Yiyun Zhang*, Fei Jin, Abir Al-Tabbaa

Department of Engineering, University of Cambridge, Cambridge CB2 1PZ, UK
yz445@cam.ac.uk, fj232@cam.ac.uk, aa22@cam.ac.uk

Layered double hydroxides (LDHs) are ionic lamellar compounds with anionic exchange capacity and memory effect. In this research, industrial waste Red Mud (RM) has been used to prepare RM-LDHs by a calcination-rehydration method together with magnesium oxide (MgO). The effects of pre-treatment such as grinding and calcination were investigated to enhance the reactivity of the solid raw materials. Characterisation results showed that crystalline $Mg^{2+}/(Al^{3+}, Fe^{3+})$-LDHs intercalated with CO_3^{2-} were successfully synthesised and it made up approximately 20% of the product, with brucite ($Mg(OH)_2$) and hematite (Fe_2O_3) as the main impurities. The as-synthesised RM-LDHs were used as adsorbents to remove Remazol Brilliant Blue R (RBB) from aqueous solutions. It was found that the adsorption kinetics fitted the pseudo-second-order kinetic model, and the adsorption isotherm was well described by Langmuir model with the correlation coefficient (R^2)>0.96. The adsorption capacity of the synthesised product was 116.69 mg/g for RBB. This study confirmed that LDHs can be produced from the industrial waste red mud and demonstrated its potential application in wastewater treatment.

Keywords: Layered double hydroxides, synthesis, red mud, waste utilization, dye removal, adsorption.

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FUNCTIONALIZED MAGNETIC CLAY NANOMATERIALS FOR OIL-WATER SEPARATION

HONGTING ZHAO*, TING LYU, DONG ZHAO, ERPANG ZHANG

Institute of Environmental Materials and Applications, College of Materials and Environmental Engineering, Hangzhou Dianzi University, 310018, Hangzhou, China
*hzhao@hdu.edu.cn

Oily wastewater is generally produced by oil spill accidents and industries that process petroleum, metals, food, and textiles [1,2]. It was reported that a substantial portion of oil can be present in emulsified form, which is usually difficult to separate from the aqueous phase. The presence of emulsified oils in wastewater causes a significant environmental concern. Traditional treatment approaches for emulsified oil wastewaters, such as air flotation, electrochemistry method, adsorption separation and biochemistry methods, generally are not efficient enough to achieve satisfactory cleanup [3]. As a consequence, it is necessary to develop new cost-effective materials and technologies that are able to efficiently remove emulsified oil from aqueous environment.

In recent years, magnetic oil-water multiphase separation technique has attracted considerable attention, in which surface modified magnetic nanoparticles (MNPs) are used as the demulsifier. Magnetic iron oxide (MIO) nanoparticles, such as maghemite and magnetite, are often used as the magnetic substrate, because of their low cost, low cytotoxicity and good biocompatibility. However, MIO nanoparticles generally should be further modified with hydrophobic or amphiphilic substances in order to improve its hydrophobicity or interfacial activity [4-7]. As a result, the modified MNPs can rapidly accumulate inside the oil droplet or at the oil droplet surface, thereby imparting the emulsified oil droplets with magnetic responsiveness for easy removal under external magnetic field.

In this study, a new class of pH-sensitive and thermosensitive magnetic nanoparticle/clay mineral nanocompositess were developed and their efficiencies were evaluated for separation of emulsified oil from aqueous environments. The results indicated that both magnetic nanoparticle/clay mineral could potentially be a new class of promising and environmentally friendly materials for effectively treating emulsified oil in wastewater.

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ACIDIFIED SEPIOLITE CATALYST FOR GREEN CATALYTIC DEHYDRATION OF GLYCEROL TO PRODUCE ACROLEIN

Chun Hui Zhou*, Gui Li Li, Dong Shen Tong, Hao Zhang, Wei Hua Yu

Research Group for Advanced Materials & Sustainable Catalysis (AMSC), Center forAdvanced Clay Mineral-based Materials, State Key Laboratory Breeding Base of Green Chemistry Synthesis Technology, College of Chemical Engineering, Zhejiang University of Technology, Hangzhou 310032, China
*clay@zjut.edu.cn

Sepiolite is a naturally occurring clay mineral and microscopically exists in a fibrous shape. The discontinuous octahedral sheets in a sepiolite crystal created open tunnels (*ca.*10.6 Å in width) with the edges of broken bonds at either side, additional to channels (pores) in the sepiolite crystal. The fibrous sepiolite crystals usually form loosely packed aggregates, which can be unbundled by chemical or physical treatments to give rise to high exposed active surfaces. Such treatments can enhance both surface acidity of sepiolite and its availability so as to be used as a solid acid catalyst or support [1-3]. The catalytic dehydration of glycerol is a typical acid-catalyzed reaction [4,5]. In the search for novel solid acid catalysts for the gas-phase catalytic dehydration of glycerol to acrolein, sepiolite clay minerals were activated with hydrochloric acid to produce acid-activated sepiolite catalysts. The effects of the activation process on the texture and acidity of acid-activated sepiolite, and their roles in gas-phase catalytic dehydration of glycerol to acrolein were investigated [5]. A series of acid-activated sepiolite catalysts were made from purified natural sepiolite treated with hydrochloric acid of different concentrations. The acid-activated sepiolite catalyst samples were characterized using X-ray diffraction, X-ray fluorescence analysis, scanning electronic microscopy, thermogravimetric analysis, N_2 adsorption-desorption isotherms, NH_3-temperature-programmed desorption, Fourier transform-infrared spectroscopy and pyridine adsorption followed by in situ infrared spectroscopy. The catalytic performances in gas-phase catalytic dehydration of glycerol to acrolein were evaluated using a vertical fixed-bed reactor.

Hydrochloric acid-activated sepiolite clay minerals have proved to be active solid acid catalyst for the gas-phase dehydration of glycerol to acrolein. A 92.9% conversion of glycerol, a 59.4% selectivity of acrolein, and a 55.2% yield of acrolein were obtained over the sepiolite catalyst activated with a 2 mol/L HCl aqueous solution when the catalytic dehydration of glycerol was conducted in a fixed-bed reactor at 320 °C with a feed of 15 wt.% aqueous glycerol solution at 0.10 ml/min and air at a flow rate of 20 ml/min. Both the texture and the acidity of sepiolite can be altered by the process of hydrochloric acid activation. Such activation had several effects, including elimination of a portion of the zeolitic water in the tunnels, part of removal of magnesium and aluminum in the octahedral sheets of sepiolite, and the unbundling or unfolding of aggregated sepiolite fibers and even some breakage of the Si-O-Si in the tetrahedral sheets of sepiolite. The extent related to the concentration of hydrochloric acid used for activation. In addition to the type and the amount, the strength of the acid sites on the sepiolite catalysts can also able be tuned by acid activation. The medium to strong Brønsted acid sites from Si—O—H^+ and H^+ adsorbed on the surface were responsible for yielding acrolein. Lewis acid sites could primarily catalyze the formation of acetol. The results also indicate taht for acid-activated sepiolite catalysts, a critical issue is to overcome acid-catalyzed polymerization of acrolein and other intermediate molecules and their further carbonization.

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ADVANCED CLAY MINERAL-BASED MATERIALS: CONSIDERATIONS FOR CLEANER PRODUCTION AND FINER FUNCTIONALITIES

Chun Hui Zhou*, Hao Zhang, Dong Shen Tong, Wei Hua Yu

Research Group for Advanced Materials & Sustainable Catalysis (AMSC), Center for Advanced Clay Mineral-based Materials, State Key Laboratory Breeding Base of Green Chemistry Synthesis Technology, College of Chemical Engineering, Zhejiang University of Technology, Hangzhou 310032, China
*clay@zjut.edu.cn, chc.zhou@aliyun.com

Clay minerals consist of M-silicate-based nanolayers (M: Al, Mg, etc.) and interlayer cations. Such chemical and structural characteristics make clay minerals peculiar in ion exchangeability, swellability and delamination. Moreover, both the layer and the interlayer of clay minerals can be chemically tuned by controlled synthesis or post-modification. Many approaches to synthetic clay minerals and to modification of clay minerals into functional nanomaterials have so far been developed [1-2]. However, most of studies stay on a laboratory scale and the methods often suffer from considerable difficulty on an industrial scale considering the credentials of the clean production and the products of high-quality. We have been developing cleaner approaches to reconstructing, modifying and synthesizing clay minerals to produce advanced clay mineral-based materials with improved functionalities as catalysts, adsorbents, and hydrogel, aiming at commercialization on a large scale.

(1) The synthesis of synthetic saponite and hectorite must be finely controlled because composition, structure and texture all have a pivotal effect on the performances of the resultant synthetic clay minerals. The subtle changes of the layers and the interlayer ions significantly influence the surfaces and the edges which provide reactive and adsorptive sites. Those changes also affected the exfoliation and re-assembly of the clay minerals.

(2) It has been known for long that the interlayer space (usually <1 nm in height) can be intercalated with bulky organic species. However, the conventional organic modification process consumes a large amount of water and brings about much wastewater containing organic compounds. We show that organo-montmorillonite (OMt) with high swellability in a hydrophobic medium such as xylene can be successfully prepared by clean and simple modification of Ca^{2+}-montmorillonite (Ca^{2+}-Mt) with cetyltrimethylammoniumbromide (CTAB) [3]. The results suggested that CTA^+ cations and CTAB molecules adsorbed in the interlayer spaces and CTAB molecules adsorbed on the external surfaces of OMt synergistically modified the Ca^{2+}-Mt. The gel formation of OMt in xylene was related to the distribution of CTAB molecules and CTA^+ cations on the external and internal surfaces of OMt, the arrangements of CTA^+ cations in the interlayer spaces of OMt and the sizes of OMt particles.

(3) Clay minerals can be integrated with biomass to produce clay/biomass-based composites which have wide applications ranging from biomaterials to agrochemicals and advanced materials for energy and catalysis, [4]. We show that clay mineral-biochar composites can be produced via a facile cleaner pyrolysis process starting from two abundant natural Mt and bamboo [5]. Mt acted as a solid acidic catalyst and catalyzed the pyrolysis of bamboo powder to biochar and lower the pyrolysis temperatures. Both biochar and Mt contributed to the texture and structure, which provided varied surface and various adsorptive sites. The composites prepared from low-cost Mt and bamboo can adsorb NH_4^+ and PO_4^{3-} from wasterwater and the resultant NH_4^+- and PO_4^{3-}-laden composites can be reused as an effective slow-release fertilizer of N and P.

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ADSORPTION AND SURFACE SPECIATION OF Sb (III,V) SPECIES ON FERRIHYDRITE

Shuang Zhou (1)*, Tsutomu Sato (2), Keisuke Fukushi (3)

(1) Graduate school of Engineering, Hokkaido University, Sapporo, Hokkaido, 060-8628, Japan, (2) Faculty of Engineering, Hokkaido University, Sapporo, Hokkaido, 060-8628, Japan, (3) Institute of Nature and Environmental Technology, Kanazawa University, Kakuma, Kanazawa, Ishikawa 920-1192, Japan
*mzhou0327@gmail.com

Antimony (Sb) mainly exists two inorganic oxidation states of antimonite (Sb(III)) and antimonate (Sb(V)). TheSb (III, V) adsorption reactions have been thought to play a critical role in the mobility of Sb in the environment. Understanding the variations in the surface speciation of the Sb species is fundamental to prediction of their partitioning between minerals and aqueous solutions. Under such conditions, spectroscopic and theoretical calculations have demonstrated the potential importance of a variety of surface species, but very little is known about its sorption behavior and adsorption mechanism. In the present study, the adsorption behavior of Sb(III) and Sb(V) on to ferrihydrite was examined as functions of pH, ionic strength and solid concentration. The initial Sb(III) concentration ranged from 10 to 100 umol/L and Sb(V) concentration ranged from 10 to 1000 umol/L. Batch adsorption experiments were conducted by adding solid concentration of 0.4g/L with different ionic strength(0.001,0.01 and 0.1M) of $KNO_3$and the pH varying from 2 to 12. Sb(V) adsorption was favoured at acidic pH and decreased dramatically with increasing pH and ionic strength, while Sb(III) adsorption was constant over a broad pH range and the ionic strength had a little effect on the adsorption. Adsorption data were modelled using an extended triple-layer model (ETLM) to infer Sb(III) and Sb(V) adsorption reactions and equilibrium constants. The two principal reactions of Sb(III) adsorption forming inner-sphere and outer-sphere antimonite surface specieswere found to be consistent with the experimental data. Solution pH and ionic strength showed little effects on the adsorption of antimonite. The adsorption of Sb(V) was represented by the formation of a monodendate-mononuclear outer-sphere and a bidentate-binuclear inner-sphere species. The Sb(V) adsorption on ferrihydrite decreases continuously with increasing pH and ionic strength. The predicted model speciation of Sb(V) on ferrihydrite showed that the inner-sphere species increase concomitantly with increasing pH and ionic strength and solid concentration. The outer-sphere species distribute over a wider range of pH conditions and are more important at lower ionic strengths. Additionally, batch adsorption data from previous studies for Sb(V) on ferrihydrite were reasonably reproduced using ETLM with the predicted equilibrium constants. A set of predictive equations for Sb(V) adsorption equilibrium constants on ferrihydrite enabled the prediction of the surface speciation of Sb(V) over a wide range of pH, ionic strength, electrolyte type and surface coverage.

Keywords: antimony, adsorption, ferrihydrite.

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COMPARATIVE STUDY ON THE STRUCTURES AND PROPERTIES OF ORGANO-MONTMORILLONITE AND ORGANO-PALYGORSKITE IN OIL-BASED-DRILLING FLUIDS

Guanzheng Zhuang, Zepeng Zhang*

Beijing Key Laboratory of Materials Utilization of Nonmetallic Minerals and Solid Wastes, National Laboratory of Mineral Materials, School of Materials Science and Technology, China University of Geosciences, Xueyuan Road, Haidian District, Beijing 100083, PR China
*unite508@163.com

Drilling operation is part of global process implemented to localize and extract oil and gas lying underground from the reservoir. Drilling fluids are one of the most important components in any drilling operation since they provide several functions, i.e., removing the cuttings generated by drill bit from the borehole, lubricating and cooling the drill tools, and controlling the down hole formation pressure, etc [1]. Drilling fluids used in practice may be classified into two categories, i.e., water-based drilling fluids and oil-based drilling fluids. Oil-based drilling fluids exhibit excellent lubricity, high rate of penetration, shale inhibition, wellbore stability and thermal stability to overcome some undesirable characteristics of water-based drilling fluids [2]. Hence, oil-based drilling fluids are widely used in deep, offshore and high angle drilling operations.

Drilling fluids are typically shear thinning, thixotropic and strongly thermal dependent. Generally, organo-montmorillonite (OMt) are used in oil-based drilling fluids for rheological control. Recently, our previous work[3] demonstrated that organo-palygorskite (OPal) is also a suitable rheological additive of oil-based drilling fluids. The rheological behavior of oil-based drilling fluids is deeply influenced by the nature and concentration of organoclays [4].

Montmorillonite (Mt) and Palygorskite (Pal) can be considered as 2:1 phyllosilicates, but their structures, morphology and properties are very different. For example, (i) Mt is layered while Pal is fibrous, (ii) the interlayer space of Mt is variable while that of Pal is constant, (iii) the cation exchange capacity (CEC) of Mt ranges from 60-150 mmol/100 g while the CEC of Pal is often less than 40 mmol/100 g and (iv) channels and tunnels exist in Pal but not in Mt. These differences contribute to different structural change, rheological properties and mechanisms of organoclays in oil-based drilling fluids.

This work aimed to reveal the differences between OMt and OPal in oil-based drilling fluids. Organoclays were prepared in aqueous solution and characterized by XRD, SEM and TEM. Organic surfactants can intercalate into the interlayer space of Mt while they can only coat on the Pal surface. Dispersity of organoclays in oil depends on the lipophilicity of surfactants and size of organoclays. Dispersity of OPal in oil is better than that of OMt because of the nanoscale fibers and crystal bundles of OPal. The basal spacing of OMt varies with the aging temperature and surfactants' size. Exfoliation of OMt contributes to improvement of rheological properties. Big size of surfactants lead to large basal spacing of OMt and consequently result in easier exfoliation. The crystal structure of OPal in oil do not change with the temperature rising. But high temperature promotes disaggregation of OPal and rheological properties. OMt can form "house of cards" structure while OPal forms "haystack" structure. The contact face among units in network structure influences the strength. OMt can provides excellent rheological properties of oil-based drilling fluids. However, high temperature often makes the rheological properties to be deteriorative. OPal exhibits excellent thermal stability that keeps rheological properties even aged at high temperatures. Surfactants' polar heads inserting into Pal channels and tunnels is significant for the thermal stability of OPal.

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INDEX OF AUTHORS

NOTICE. THE NAMES OF SOME OF THE AUTHORS WERE NOT ERRONEOUSLY OMITTED BUT THEY WERE NOT AVAILABLE SINCE THEY HAD NOT BEEN INSERTED DURING THE ABSTRACT SUBMISSION PROCEDURE.