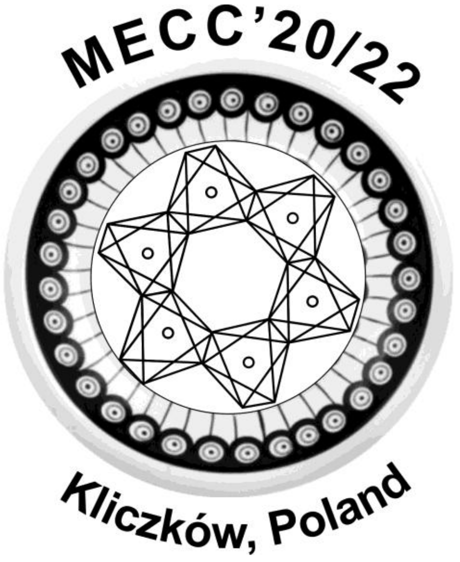
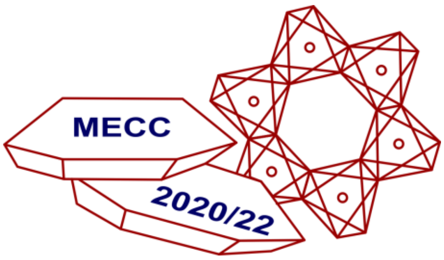
10th Jubilee Mid-European Clay Conference



BOOK OF ABSTRACTS



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Contents

PLENARY LECTURES

Playing with dye molecules in hybrids with clay minerals to achieve photofunctionality.

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Solar cells performing on a molecular level can be a key to an efficient utilization of solar energy. The efficiency of photosynthesis is an inspiration and a challenge for many scientists. The problems with the design and synthesis of efficient artificial materials mimicking natural photosynthetic systems pose a major challenge.

One group of promising materials for an efficient control of solar energy transfer is hybrid systems based on layered silicates (e.g. smectites) and organic dyes. Smectite particles are passive components in terms of photochemistry and photoactivity. On the other hand, layered nanoparticles can control and regulate molecular distribution and distances between adsorbed dye molecules and, secondarily, affect photophysical processes. In this way, resonance energy transfer between molecules of different dye molecules can be controlled relatively easily, to achieve the efficiencies similar to those taking place in green plants. The strategy for the design and synthesis of such systems is to find suitable conditions for regulating the distances between the adsorbed dye molecules to achieve efficient energy transfer and to avoid undesirable phenomena, such as molecular aggregation and losing photoactivity. A last part of the lecture will introduce examples of other interesting phenomena and promising applications associated with dye/clay mineral systems (increased photoactivity and luminescence, photosensitization, and photodisinfection) together with representative types of hybrid, ternary, and composite materials.

Acknowledgment

This work was supported by the Slovak Research and Development Agency under contract No. APVV-18-0075, APVV-19-0487 and the VEGA grant agency (1/0227/20, 2/0166/21).

The quest of proton and deuteron:
hydrogen position and reactions in clay minerals

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High proportions of structural OH groups and the water molecules strongly adsorbed to mineral surfaces, represent unique features of clay minerals. The content and position of the structural OH groups are controlled by the octahedral cation composition, whereas, the adsorbed water content and conformation depends on the interlayer environment and thus the expandability, layer charge, and interlayer cation composition.

The position, content, and reactivity of H-compounds are revealed by spectroscopic methods, gravimetry and thermal experiments, and determination of the H isotope ratio. In this paper the de- and re-hydration, the de- and re-hydroxylation, and the dehydrogenation reactions of clay minerals are discussed. The experimental D/H isotope exchange in both the adsorbed water and the structural hydroxyl groups is presented as a tool to understand the mechanism and kinetics of those reactions in laboratory and natural conditions.

The pattern of de- and re-hydration is specific to the smectitic component of a clay sample. D/H exchange in the water adsorbed on smectites and interstratified smectite minerals has been applied to reveal the speciation and spectroscopic signature of adsorbed water, which is the basis for the O-D method of layer- and surface-charge determination. In the paper, the relationship and distinction between strongly-bound adsorbed water and the OH groups is explored. The structural OH stability and hydroxyl H isotope fractionation/exchange with ambient water are discussed from the perspective of the applicability of clay minerals in paleoenviromental studies.

Acknowledgements: National Science Centre, Poland (grant No. 2021/41/B/ST10/01951) and the German-Austrian-Swiss Clay Group for the Gerhard-Lagaly-Award.

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Clay Conference

Weathering processes and formation of red polygenetic soils and paleosols on hard carbonate rocks: a multiproxy approach (Northern Adriatic, Croatia)

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Red polygenetic soils and paleosols (RPS&P), which overlie subaerial unconformities on carbonate rocks and are susceptible to erosional and redepositional processes, provide useful insights into present and past soil formation processes and landscape dynamics in the Mediterranean region, as they occur along many continental shores and islands of the Mediterranean basin, especially on limestones. Seven RPS&P overlying limestone were studied on the Istrian Peninsula and Susak Island to determine and interpret the superposition of pedological and sedimentological processes that occurred on the youngest subaerial unconformity in the karst landscape. Provenance analysis showed that the allochthonous material from RPS&P was mainly from the Adriatic shelf, with two different signatures, Alpine/Apennine for all RPS&P except Savudrija, where flysch of Eocene age was a dominant source. The RPS&P dominantely formed in reworked loess and colluviated soil-sediments. Values for CIA, the Al/Si ratio, Fe, and Fed increased with depth from the top to the bottom of the RPS&P, which is generally consistent with the increase in clay content and thus with the process of lessivage. The Fed/Fet ratio (considered as weathering index) significantly distinguishes the analysed RPS &P from each other. This ratio varies between 0.20-0.28 in the Bok 1 paleosol and 0.79-0.85 in the Koreniki polygenetic soil. Accordingly, the RPS&P correspond to the RSG of Cambisols, Luvisols, Lixisols and Ferralsols, respectively. The clay mineralogy in the RPS&P corresponds to their weathering index. For example, the main clay mineral phases in the clay fraction of Bok 1 (Hypereutric Chromic Cambisol (Episiltic, Endoloamic)) are smectite and illite, while chlorite, mixed-layer chlorite-vermiculite, and kaolinite are subordinate. The predominant clay mineral phase in the clay fraction of Koreniki (Lixic Rhodic (Hyper)Ferritic? Ferralsol (Clayic, Hypereutric, Raptic)) is pedogenic kaolinite. The formation of RPS&P in the northern Adriatic was a recurrent process, i.e. RPS&P may have formed repeatedly in a specific and favourable soil environment on hard carbonate rocks since the Eocene. Possible favourable periods include the Miocene Climatic Optimum, the mid-Piacenzian Warm Period (Pliocene), and the interglacials during the Quaternary.

Acknowledgemets

This work has been fully supported by Croatian Science Foundation under the project IP-2019-04-8054 – WianLab (Western Istrian Anticline as an ideal natural laboratory for the study of the regional unconformities in carbonate rocks).

Kaolinite madness - 1:1 layered structure which reveals its potential for synthesis of next generation materials

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Kaolinite is the most common member of kaolin group minerals. It is also the most abundant clay mineral with worldwide consumption exceeding 35 million tons per year. This 1:1 layered aluminum silicate devoid of significant structural charge was regarded as a non-swelling clay mineral. Therefore initially its modification was challenging and its interlayer chemistry was less developed than for smectites.

That has changed after first successful intercalation of potassium acetate into the kaolinite structure. After that, several new materials have been synthesized using 1:1 layered structures as building blocks. The most interesting materials were synthesized via grafting involving reaction of the inner-surface OH groups with various organic compounds e.g.: alcohols, organosilanes, aminoalcohols and ionic liquids. The grafted materials show increased chemical and thermal stability in contrast to intercalation compounds. Such reactions were possible due to kaolinite’s asymmetric interlayer environment in contrast to symmetric 2:1 layered structures. The functionalization led to the synthesis of materials with a wide variety of properties and potential applications. Some examples include: selective adsorption, catalysis, polymer-clay nanocomposites, sensing applications, photodegradation of pollutants, luminescence, drug delivery applications as well as synthesis of heterocoagulated mineral hybrids. The tuning of the 1:1 layers also allows to control kaolinite’s morphology to obtain halloysite-like nanotubes of mesoporous texture.

The lecture will provide a brief summary of findings regarding the hybrid organo-inorganic materials based on kaolin group minerals which were reported in the last decades. Moreover, some future perspectives will be highlighted.

The research was partially supported by the National Science Centre Poland, under a project awarded by Decision No. 2017/27/B/ST10/00898.

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The effect of clay minerals on non-aqueous bitumen extraction from Alberta oil sands

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The Alberta oil sands deposit has recently the fourth largest oil reserves in the world, after Venezuela, Saudi Arabia and Iran. The Alberta oil sands consist of sand, clays, water and bitumen. Commercially, the bitumen is extracted from the Alberta oil sands applying water-based extraction process. The alternative non-aqueous solvent extraction processes have been investigated since the mid-1960s, mainly due to the high bitumen recovery, elimination of sludge tailings and significant decrease in water consumption. Clay minerals were recognized as crucial mineral constituent of Alberta oil sands significantly affecting the bitumen extraction. The bitumen recovery is reduced with a higher amount of clay admixture in Alberta oil sands. Kaolinite and illite are the main clay minerals comprising the Alberta oil sands but a small amount of chlorite, illite-smectite, kaolinite-smectite and smectite is also often present. Different types of clay minerals have different impact on bitumen extraction due to their distinct properties. The results of extraction experiments conducted using clay minerals-bitumen mixtures showed that the specific surface area (SSA) was a primary parameter controlling the amount of extracted bitumen from kaolinite, illite, chlorite and illite-smectite. Clay minerals with larger initial SSA retained more organics, thus exhibited lower bitumen extraction. In the case of montmorillonite, the amount of extracted bitumen was heavily affected by swelling ability of smectite. The exposure of montmorillonite to higher relative humidity (RH) conditions dramatically decreased the bitumen recovery. This was related to the opening of the interlayer space (i.e. swelling) of montmorillonite upon exposure to higher RH and subsequent larger retention of bitumen.

George Brown Lecture

Generalized relationships between the ionic radii of octahedral cations and the *b* crystallographic parameter of clay and related minerals

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Over several decades, a wealth of literature has been devoted to correlations between the chemistries of phyllosilicates and the values of their crystallographic unit-cell parameters. The *c* parameter is particularly used because it generally corresponds to the layer-to-layer distance, characteristic of the different families of phyllosilicates. The *b* parameter is also of interest because it allows measuring the lateral dimensions of the octahedral sheet. This unit-cell distance can be extracted from experimental XRD patterns from the (06ℓ;33ℓ) diffraction region and by attributing the main diffraction band observed to a (060) reflection leading to the relationship $b = 6.d(060)$.

The aim of this contribution is to explore the relationships between the mean ionic radius *R* of octahedral cations: $R = \Sigma^i (r_i .x_i)$ (r_i being the ionic radius of octahedral cation i, and x_i being its molar fraction in the structural formula ($\Sigma^i x_i = 1$)) and the *b* parameter value (or equivalent) of the main phyllosilicates and hydroxides families.

The data are collected from literature and concern both natural and synthetic samples. Notably, the results are discussed in light of the dimensional misfit that often occurs between the tetrahedral and octahedral sheets. The *b* parameter values are clearly linked to *R* for families of minerals having the same (or similar) tetrahedral composition, and well suitable regressions were obtained for all the studied structures.

Teaching clay sciences

Teaching clay sciences at Polish Universities

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The use of clays and clay minerals in modern human life has increased the interest in this group of minerals and rocks. Currently, crystallography and mineralogy of clay minerals are included in the curricula of the following fields of study: geology, ceramics and pottery, chemistry, catalysis, medicine, soil science and environmental protection. Thanks to the use and development of new analytical methods: structural, geochemical and geological, clay minerals have been particularly intensively studied since the mid-twentieth century. In Poland, the leading research and teaching centers are the AGH University of Science and Technology, the University of Warsaw, and the Jagiellonian University. To a limited extent, teaching is conducted at the University of Silesia, Wrocław University, Adam Mickiewicz University in Poznań, and the Universities of Life Sciences and leading Polytechnic Universities. The Institute of Geological Sciences of the Polish Academy of Sciences, which promotes talented young scientists, plays a special role in specialist education at the high doctoral and postdoctoral level. The Polish Geological Institute plays a similar role.

The foundations for a modern research and teaching base in the leading academic centers in Poland were: L. Stoch, M. Budkiewicz, A. Morawiecki, A. Wiewióra, K. Szpila, S. Dyjor, T. Chodak, in recent years J. Środoń and their students. Currently, clay minerals are taught in the form of lectures, lab practices, seminars and field trips. In geological studies, the curriculum covers the structure of layered silicates, their classification, genesis, research methods as well as physicochemical and technological properties. The scope of the program of individual subjects is included in the syllabuses approved by the faculty program councils and made available by the departmental program councils in accordance with the Ministry of Science and Higher Education standarization of studying, 2018. The syllabus system makes it possible to configure such a program of higher studies so that the material is not repeated but that it is an extension of knowledge, among others on clays and clay minerals. In addition, the following magazines play an important role in the individual education of students: Clays and Clay Minerals, Applied Clay Science, Clay Minerals Journal, Chemical Geology, American Mineralogist, Elements and other.

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Clay science in the higher education: a Hungarian overview

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The position of clay science in STEM higher education (HE) is defined, in general, by the following factors: a) expertise of the university staff, strongly related to the embedding of the field into the research+development+innovation (RDI) demands and ecosystem of a country; b) HE structure in general and curricula in particular; c) student numbers and research infrastructure.

In Hungary, the weakest point currently is probably the powerless self-promotion of the largely interdisciplinary, collaboration-needy and complex clay science. Therefore, clay science (with clays as versatile natural nanomaterials) is poorly embedded into the RDI ecosystem of the country, despite the relative richness of clays among the earth materials available.

Concerning staff expertise, in the past 20 years, a complete change of generation took place gradually, and collective expertise is regarded as good. Basic research (collecting information about earth materials) fully survived, however, applied science − agriculture, ceramics, waste management − is partly retained, partly weakened (*e.g.,* colloid science-related fields at some places). A further problem in knowledge transfer can be in a small country if the often highly specialised expertise of research technology organisation (RTO) personnel is not fully integrated into the HE. Collaboration between universities and RTOs is still regarded as good.

The HE structure changed largely, to accommodate the needs of the Bologna system. Clay science, needing a complex approach, shifted to later years, and is only sporadically transferred in the B.Sc. level (no clay subjects), whereas at M.Sc. and Ph.D. levels, subjects with major clay components are offered. Clay content is usually offered in optional courses and the clay-related course offer is largely dependent on the personal motivation of HE staff.

Student numbers in curricula with clay focus (science, engineering, and agriculture) is decreasing, however, this is partly compensated by the presence of international students in these fields, thanks to the gradually broadening offer of curricula in English. These problems could be overcome by a more harmonised and effective use of micro-credentials, taught by cooperation between several universities. MECC can provide a good background network for this kind of shared teaching.

Clay-related Hungarian research infrastructure can be regarded as good overall, but local differences exist – these are mostly bridged by the collaboration between universities and RTOs.

The authors may serve as a starting point for connection to the clay scientist community of the major universities in Hungary.

Selected lectures related to clay minerals taught in the Czech Republic

Czech National Clay Group

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Research of argillaceous matter and geological observation of clay raw materials have a long history in Czechia (Konta, 1961). Roots of the Czech National Clay Group are generally seen in an increased concern and research activity focused on clay minerals at the Department of Petrology, Charles University in Prague, in the years 1950 - 1957 under the leadership of Prof. Konta.

Overview of contemporary lectures related to clays are spread among various institutions in Czechia and taught by several members of clay society. Lecture “Clay matter in geological process” at Charles University, Faculty of Science is taught by David Hradil. Lectures “Introduction to Mineralogy” and “Chemistry of the environment” are taught by Barbora Doušová at University of Chemistry and Technology, Prague. Next lecture there “Structure and properties of zeolites” is taught by David Koloušek. Both lecturers participate at “Formation and use of ore deposits” describing deposits creation in different geological formations and conditions. “Hybrid materials” by František Kovanda include using of modified clay minerals. Two subjects “Laboratory of natural inorganic materials” and “Specialised laboratory – materials in forensis chemistry” are trained at the University of Chemistry and Technology, Prague. At Nanotechnology Centre VŠB TU Ostrava are several lectures given by Gražyna Simha Martynková: “Methods of preparation and modification of layered materials”, “Nanomaterials based on layered silicates”, “Nanotechnology III - nanocomposites”, and “Advanced methods of preparation of inorganic nanomaterials and composites” all include applications of various clay minerals. At Charles University, Faculty of Mathematics and Physics, lectures related to clay minerals structure are “Molecular simulations for solving of material structure”, and “Computational experiments in molecular theory I” given by Miroslav Pospíšil. In all these places, the clay research and teaching is organized, bachelor, diploma works and doctor theses in various branches of clay science are solved and defended.

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Konta, J. (1961): Research work on clay minerals and argillaceous rocks in Czechoslovakia. Clays and Clay Minerals, 10, 426-442.

An attempt to summarize the process of teaching clay sciences in Slovakia

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The process of teaching clay sciences in Slovakia takes place in the bachelor's and master's degrees practically only at the Faculty of Science, Comenius University Bratislava (FNS CU). Clay science theses in the doctoral study program, the third, highest level of higher education, is provided not only by the FNS CU, but also by the Institute of Inorganic Chemistry of the Slovak Academy of Sciences.

Last and this year, FNS CU is changing and adjusting its study programs at all three levels of higher education in the frame of accreditation. Accreditation itself was a means of responding to the declining number of students, making studies more attractive and more intensively educated students to market needs. As part of these changes, two specialized subjects related to clays have disappeared in bachelor and master study programs. The subject "Mineralogy and crystal chemistry of natural nanomaterials" have been divided into several more general subjects e.g. "Applied mineralogy and petrology". Subject "Clay minerals as indicators of geological processes" was moved from Master study program to PhD study program.

Despite the decline of students in bachelor's and master's studies, the number of PhD theses related to clay science remains the same as 10-15 years ago. One of the reasons is the expansion of the fields from which students start their doctoral studies. The second reason is the growing number of foreign students admitted to doctoral studies.

Until the future, we still have many challenges to increase the attractiveness of clay sciences for students and especially for primary and secondary school students.

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Workshop

Molecular modeling of clay minerals' interactions with molecules

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Computational chemistry is an integral part of modern physiochemistry and clay mineralogy fields. It allows to efficiently study the physiochemical phenomena from a different perspective than it was previously possible - with experiments. The computational methods utilized for this task vary enormously in cost and complexity: from high-level quantum mechanical calculations, via atomistic molecular dynamics or Monte Carlo simulations, to coarse grained methods.

This short workshop aims to introduce researchers to the field of molecular mechanics simulations, supported with examples of the application of this methodology in the field of interactions of clay minerals with various molecules (e.g., methane and water; Szczerba et al., 2016; Ziemiański et al., 2021).

The main topics of the workshop are the introduction to molecular mechanics modeling, interatomic potentials, optimization methods, molecular dynamics, and the basics of Monte Carlo sampling techniques. The most commonly used force fields employed for simulations of clay minerals will be discussed: CLAYFF and INTERFACE. The basics of the methodologies will be presented, aiming at discussion of the fundamentals of algorithms.

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Szczerba M., Kuligiewicz A., Derkowski A., Gionis V., Chryssikos G. D., Kalinichev A. D. (2016) Structure and Dynamics of Water-Smectite Interfaces: Hydrogen Bonding and the Origin of the Sharp O-Dw/O-Hw Infrared Band From Molecular Simulations. Clays Clay Miner. 64, 452–471

Ziemiański P. P., Derkowski A., Szczerba M. and Guggenheim S. (2021) Smectite Crystallite Swelling Under High Pressure of Methane. J. Phys. Chem. C 125, 7598–7610

Program

Lecture 1: Marek Szczerba – Introduction to molecular simulations, interatomic forces

Lecture 2: Marek Szczerba – Energy minimization, molecular dynamics

Lecture 3: Paweł Ziemiański – Monte Carlo molecular simulations

Abstracts

Sorption of CO_2 on pillared montmorillonites

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The work aimed at determination of CO_2 sorption capacity of Ti-, Zr-, and [Ti,Zr]-pillared montmorillonites obtained from Ca-bentonite (Kopernica, Slovakia). Two methodological approaches were adopted: a) measurement of CO_2 sorption at 0^{o}C on samples previously outgassed at 200^{o}C for 3 h, using ASAP 2020 adsorption analyzer, and b) measurement of CO_2 sorption on as received samples placed in the thermal analyzer (Netzsch STA 449 F3 Jupiter), exposed for 6 h to the flow of CO_2 at room temperature, followed by temperature ramp to 1000^{o}C and QMS analysis of the emitted gaseous products.

The order of sorption capacity (mmol/g) in the first type of experiment was: [Ti,Zr]-PILC (0.67) > Ti-PILC (0.57) > Zr-PILC (0.53) > Ca-bentonite (0.16), which roughly paralleled the order of micropore volume (cm^3/g) : [Ti,Zr]-PILC (0.12) ≈ Ti-PILC (0.12) > Zr-PILC (0.06) > Ca-bentonite (0.02), in accordance with the recognized role of microporosity in CO_2 trapping. In the second type of experiment, the order the desorbed CO_2 amount (mmol/g) was: Ti-PILC (0.67) > [Ti,Zr]-PILC (0.51) > Zr-PILC (0.22). The dependence followed the order of hydration by weakly bound water (mmol/g) determined from TG analysis: Ti-PILC (5.11) > [Ti,Zr]-PILC (4.51) > Zr-PILC (4.19), pointing to the favorable effect of water on CO_2 capture ability.

Acknowledgements: This research received financial support from National Science Foundation within project Opus 13 nr 2017/25/B/ST10/00768.

The effect of organics removal using cyclohexane and bleach on mineralogy, chemistry and settling behavior of mature fine tailings (MFT) from Alberta, Canada

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Oil sands surface mining in Alberta has generated over a billion cubic meters of mature fine tailings (MFT) (Government of Alberta, 2021), consisting of water, fines, and organics. If left untreated, it requires hundreds of years to fully dewater and settle out. Residual organics and in particular clays have significant (negative) impact on the settling behavior of MFT. In present study, two different agents (cyclohexane and bleach) were used for removal of residual organics from MFT to determine the effect of these treatments on the (clay) mineralogy, chemistry and settling behavior of MFT. After the organics removal, different size fractions were isolated from the bulk MFT and they were examined by XRD, FTIR, SEM, thermal analysis, elemental analysis (CHNS) and particle size measurements. The results show that removal of organics using bleach is more effective than cyclohexane. After bleaching, the amount of 0.2–2 μm fraction decrease in favor of <0.2 μm fraction. The partial desintegration of 0.2–2 μm clay aggregates indicated that organics were removed by bleach even from the clay sized particles.

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Ion transport and cation exchange in semi-technical scale Sandwich sealing system experiments for HLRW disposal

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The Sandwich sealing system is an engineered barrier system for high-level nuclear waste disposal, consisting of alternating bentonite sealing segments (DS) and equipotential segments (ES). ES are required to augment functionality of bentonite segments. Semi-technical scale experiments (d = 80 cm, h = 180 cm) were performed to probe the effectiveness of the Sandwich sealing system under exposure to artificial pore fluids. Experiments were terminated when fluid penetrated through to the final DS. Experimental columns were dismantled level by level, providing a snapshot view of the bentonite system during the saturation process via physical and chemical characterization of samples.

Highest salt concentrations were in sampling levels closest to the fluid inflow and decreased with increasing distance. A near-constant decrease in CEC was observed in DS samples regardless of salt content. Sample position in the column was an indicator of Ca-Mg-bentonite to Na-bentonite transformation as samples with longer exposure to fluid had greater exchange of Ca^{2+} and Mg^{2+} for Na^{+}. Peak decomposition temperatures of carbonate phases during thermal analysis decreased according to position of the sample in the column, indicating that exposure to saturating fluid causes changes in soluble phases. Alterations to sulfate phases were also noted during thermal analysis.

Concentrations of soluble ions within a DS or ES showed little variation. Artificial hydraulic defects had minimal impact on overall ion concentrations within the defected segment, except within the immediate vicinity of the defect. Final fluid flows were <10 $cm^3\ h^{-1}$, indicating that the swelling of the bentonite DS at the fluid inflow performed as expected and reduced hydraulic conductivity. Persistence of Ca^{2+} and Mg^{2+} in the interlayer of smectite in bentonite samples after >400 days exposure to artificial pore fluid indicates that $Na^{+}/Ca^{2+}/Mg^{2+}$ exchange was ongoing. Bentonite soluble phases likely contribute to available Ca^{2+} and Mg^{2+} in the bentonite pore-fluid and thus impact long-term exchangeable ion composition.

CuO decorated vermiculite particles in polymer nanocomposites

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Polymer nanocomposite materials with metal oxide nanoparticles and clay particles are currently the most required material types that allow to combine different properties of these components.

The copper oxide nanoparticles are used in a wide range of applications. In the polymer matrix are well dispersed, act as a reservoir for the controlled release of copper ions and thus inhibit their toxicity. Their disadvantage is the ability to oxidize, which can be suppressed by anchoring/growing on the surface of clay minerals while maintaining their specific properties.

The copper oxide nanoparticles decorated a vermiculite particle (CuO/V) with specific surface area and ζ-potential value has been used as nanofillers for different polymer matrices. The CuO/V in the polyvinyl acetate matrix already at 0.1 wt% concentration produced a smooth surface with antibacterial activity against *S. aureus* and *E. faecalis* with long-acting after 24 h. and increased the thermal stability of the nanocomposite (Čech Barabaszová et al., 2020). In the polyvinylidene fluoride matrix a 3 wt% of the CuO/V caused a decreased of the spherulitic grains and a partial transformation of the α to the β PVDF phase, increased the wettability angle against water by 10 % and reduced the thermal stability of nanocomposite materials (Plesník, 2022).

The CuO/V particles intensively affected not only structural and phase changes but also contributes to the mechanical stability, increases mechanical strength and contributes to reducing abrasion. They extend the possible applications of this materials to meet several requirements in the field of biomedicine, membrane technologies, in batteries, catalytic or thermal conductive devices.

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The clay-based nanocomposite with luminescent properties

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In order to develop hybrid pigments with luminescent properties, variable amounts of laser dye rhodamine 6G (R6G) were incorporated into the smectites saponite (Sap) and montmorillonite (Mt). Moreover, two-component systems underwent further modification by tetraoctylphosphonium and tetraoctylammonium surfactants with varying degrees of saturation.

The X-ray diffraction analysis captured a gradual increase in d_{001} with the degree of surfactant saturation, whereas the presence of the dye had only a minor impact on the expansion. The infrared spectroscopy provided information on the presence of organic cations and has been especially useful in terms of dye detection in three-component systems. UV-vis spectra of solid samples shed light on the understanding of the structure of intercalated dye supramolecular species. The increasing concentration of the dye resulted in the bathochromic shift of the main absorption band and the appearance of a lower intensity band at shorter wavelengths which predicts the formation of dye molecular aggregates. Modification with surfactants caused even a greater shift and splitting of both absorption bands. Emission spectra were measured in order to analyze the effect of all variables on the luminescent properties of prepared materials. Samples based on Sap displayed much higher fluorescence intensities in comparison with those based on Mt, and exhibited photoactivity even without the modification by organic cations. The spectra of all pigments with co-intercalated surfactants showed a substantial increase in fluorescence, whereas the highest photoactivity was observed in samples based on Sap with moderate concentrations of both R6G and surfactants. Moreover, emission bands at unusually high wavelengths were observed, reaching the near-infrared region. Emission spectra exhibited complex profiles, yet chemometric analysis was able to differentiate among all spectral forms.

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Chlorite minerals diversity in the mineralized hydrothermal systems related to Variscan granite magmatism evolution from the Iberian Massif

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Chlorite minerals are related with the evolution of mineralized hydrothermal systems corresponding to syn-C3 orogenic biotite granite (316 Ma), syn- to late two mica granites and pegmatite (311 Ma), and post-C3 biotite granites (<305Ma) which intruded the Paleozoic metasedimentary rocks from the Iberian Massif.

Tungsten, Cu (Mo) mineralized hydrothermal systems. Fe-chlorite $(Al_{1.50}Fe^{3+}_{0.12}Fe^{2+}_{3.98}Mn_{0.13}Mg_{0.1})_{5.74}(Si_{2.72}Al_{1.28})_4O_{10}(OH)_8$ and Fe,Mn-chlorite $(Al_{1.35}Fe^{3+}_{0.01}Fe^{2+}_{3.77}Mn_{0.54}Mg_{0.31})_{5.98}(Si_{2.66}Al_{1.34})_4O_{10}(OH)_8$ accompany wolframite ($Fe,MnWO_4$) and scheelite ($CaWO_4$). In the first case, Mn^{2+} is partitioned primarily to Mn-bearing wolframite and Fe^{2+} enriched the Fe-chlorite composition. In the second case, $[WO_4]^{2-}$ combined preferentially with Ca^{2+} to form scheelite, favoring the incorporation of Mn^{2+} into the Fe,Mn-chlorite structure. Both mineral assemblages were found in the steady-state equilibrium with the hydrothermal fluid. The Mn/Fe ratio for chlorite minerals emphasized the importance of the Mn/Fe ratio of the mineralizing fluid as the main factor controlling chlorite and wolframite composition. The Mn/Fe and Fe/Mn ratios (6.3 to 34.12) for coexisting chlorites vary with the redox state exchange between fluid and mineral. The Mn/(Fe+Mn) ratio ranges from 0.12 to 0.16 in Fe,Mn-chlorite and Fe/(Fe + Mn) ratios 0.86 and 0.97. Fe,Mg-chlorite accompanies the molybdenite + bismuthinite assemblage, whereas Mg,Fe-chlorite accompanies chalcopyrite. Crystal chemistry of Fe-chlorite corresponds to daphnite and Fe,Mn-chlorite to a mixed composition between daphnite and amesite. Fe,Mg-chlorite corresponds to ripidolite and Mg,Fe-chlorite to pycnochlorite.

Gold mineralized hydrothermal systems. Mg,Fe-chlorite accompany gold orogenic mineralizations. Crystal chemistry $[(Al_{1.23}Fe^{3+}_{0.01}Fe^{2+}_{1.76}Mn_{0.1}Mg_{2.39})_{5.4}(Si_{2.71}Al_{0.79})_4O_{10}(OH)_8]$ corresponds to clinochlore.

Lithium mineralized hydrothermal systems. Cookeite + quartz and cookeite + kaolinite ± mica assemblages replaced spodumene were identified in the Li-bearing aplite-pegmatite. Two distinct compositional varieties were found: one corresponding to ideal cookeite, whereas the second belongs to the cookeite-donbassite join. Crystal chemistry of cookeite corresponds to: $(Al_{3.80}Li_{1.17}Mg_{0.004}Fe_{0.09})_{5.06}(Si_{3.23}Al_{0.75})_4O_{10}(OH)_8$.

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Tectono-metamorphic evolution of the Codru Nappe System, Apuseni Mountains (Romania): relationships between clay-metamorphic indicators and K-Ar illite dating

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The Apuseni Mountains form an internal mountain belt within the Carpathian system, belonging to a major terrane Tisza (Csontos & Vörös, 2004), along with the Mecsek and Villany Mts. (Hungary) and the Slavonian Inselberg (Croatia). The Codru Nappe System (CNS), which is the object of this study, contains Permian rhyolite and basalt rocks, which were deformed during the Alpine metamorphism (Nicolae et al., 2016). The CNS is constituted from bottom to top by the following units: Finis-Gârda, Dieva, Moma, and Arieseni. Illite and chlorite from the CNS rocks were studied by optical microscopy, X-ray diffraction (XRD) and electron probe microanalysis (EPMA). Also, the separated illite clay fractions were K-Ar dated.

Illite is the dominant mineral in the coarse clay fractions extracted from the deformed rhyolites, shales, and bentonites. Kübler-index measured for illite from deformed rhyolite ranges from 0.2 to 0.25 Δº2θ, and 0.23 to 0.26 Δº2θ for the illite from shales. The "*b*" cell parameter measured for illite minerals is about 8.98 Å. These data indicate a very low-grade metamorphic conditions. Illite chemistry corresponds to end-member illite with phengitic composition: $K_{0.83}(Al_{1\cdot63}Fe_{0\cdot16}Mg_{0\cdot26})_{2.05}(Si_{3\cdot38}Al_{0\cdot62})_4O_{10}(OH)_2$. Also, illite + chlorite (<30%) assemblage was identified in the rhyolitic rocks containing small amounts of chloritized biotite. Crystal chemistry of Mg-chlorite (pycnochlorite) corresponds to:
$(Al_{1.19}Fe^{3+}_{0.13}Fe^{2+}_{0\cdot94}Mn_{0\cdot03}Mg_{3\cdot38})_{5.68}(Si_{3\cdot0.6}Al_{0.94})_4O_{10}(OH)_8$.

Chlorite + epidote ± calcite ± magnetite assemblage was identified in the deformed basalts. The <2µm clay fractions extracted from deformed basalt and doleritic rocks are constituted by chlorite, with the Árkai-index pointing also to the low-grade metamorphic conditions. Chlorite in deformed basalt rocks shows variable composition corresponding to Fe,Mg-chlorite: $(Al_{1\cdot16}Fe^{3+}_{0.02}Fe^{2+}_{2\cdot03}Mn_{0\cdot01}Mg_{2\cdot74})_{5.96}(Si_{2\cdot87}Al_{1\cdot13})_4O_{10}(OH)_8$ (pycnochlorite) and Mg-chlorite: $(Al_{1.25}Fe^{3+}_{0.06}Fe^{2+}_{0\cdot94}Mn_{0\cdot02}Mg_{3\cdot57})_{5.85}$ $(Si_{2\cdot79}Al_{1.21})_4$ O_{10} $(OH)_8$ (ripidolite) in slightly deformed basalt rocks. Chlorite geothermometer (Bourdelle et al., 2013) indicates paleotemperatures from 300 to 350 ºC.

K-Ar dating of illite yielded ages between 112.4 and 122.2 ±3.2 Ma for the deformed rhyolite rocks and 135.9 ±3.6 Ma for a shale from the Moma nappe, 114.2 ±2.9 Ma for a

Dye aggregation-induced changes of photosensitizing properties of hybrid systems based on porphyrin dyes and smectite

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The ability of various dyes to photosensitize highly reactive singlet oxygen is a very useful tool with the potential for applications in the field such as synthetic photochemistry, environmental applications, and applications in medicine such as antibacterial materials or photodynamic therapy reagents. For most applications, it is necessary to capture photosensitizers on the surface of solid carriers. Unfortunately, this brings a challenge in the form of quenching of singlet oxygen production due to molecular aggregation of the dye molecules. This work analyzes the relationship between dye molecular aggregation of two different traditional photosensitizers from the group of porphyrins in the hybrid systems with synthetic saponite Sumecton SA, and the efficiency of singlet oxygen production. Dye molecular aggregation of porphyrins was controlled by varying silicate/dye ratio ($n_{\mathrm{dye}}/m_{\mathrm{silicate}}$ - mmol/g) and/or by premodification of saponite by cetyltrimethylammonium cation.

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10th Jubilee Mid-European Clay Conference

The source of pedogenic minerals in young Icelandic soils

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Icelandic soils develop in a dynamic environment and are strongly affected by frequent tephra deposition and influx of aeolian material from proximal and distal sources. We present the results from an extensive study on soil mineralogy and pedogenesis in various Icelandic soil types and different soil environments in the lowlands south of Vatnajökull, SE Iceland. Two distinct tephra layers, a rhyolitic tephra from the Öræfajökull eruption in 1362 CE (Ö1362) and a basaltic Veiðivötn tephra from 1477 CE are well preserved in all soils and form an important parent material.

The determining driver for pedogenesis in the histosols was the organic matter, but aeolian transport of tephra over long distances and re-deposition as well as local site conditions were the important factors in the development and mineral alteration of all investigated soils. Despite the overall predominance of non- and poorly-crystalline short-range order secondary materials and Fe (hydr)oxides in the clay-size fraction, we found indication of layer silicates (smectite, hydroxy interlayered minerals and secondary chlorite) at all sites; most likely inherited by aeolian deposition from glacial out-wash plains within the country, or sources even from outside Iceland. High exchangeable Ca^{2+} and Mg^{2+} concentrations in the soils reflected enhanced aeolian input of volcanic material, while elevated exchangeable Na^{+} concentrations were most likely caused by the oceanic composition of precipitation. Both, soil and tephra layers appeared disturbed by erosion–deposition processes over time. Changed weathering patterns and properties in the soils above the Ö1362 tephra indicated soil degradation following the deposition of the rhyolitic tephra, irrespective of the soil type.

H/D exchange in clays by real-time infrared spectroscopy

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The vibrational spectroscopy of the O-H bond is of paramount importance in the characterization of clay minerals and clay-based materials, because it provides intrinsic proxies that are specific to the octahedral sheet, the termination of the tetrahedral sheet, the layer charge, the contents of the interlayer etc. As H_2O is an essential part of the clay structure and a determinant of its properties, data acquisition ought to be non-invasive and able to accommodate variable hydration.

H/D exchange, monitored in real-time under controlled hydration conditions, is an elegant tool for determining the accessibility of the various OH species in addition to enhancing their resolution. This talk presents briefly the instrumentation needed for this type of work in the mid- and near-infrared and reviews relevant case studies from own research. Examples include the separation of the structural OH and H_2O in palygorskite/sepiolite (Bukas et al. 2013) and smectite (Kuligiewicz et al., 2015a), the latter leading to a method for determining layer charge (Kuligiewicz et al., 2015b; Tsiantos et al. 2018). New results about the interlayer accessibility of kaolinite, intercalated kaolinite and halloysite will be also presented.

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Quantification of disordered trioctahedral mica of the phlogopite – annite series using Rietveld refinement and its structure description

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Trioctahedral micas of the phlogopite – annite series (“biotites”), are highly abundant minerals in several types of rocks and soils. “Biotites” are more susceptible to weathering compared to dioctahedral micas, e. g., muscovite and hence, can serve as nutrient suppliers for plants releasing K^+ and $Fe^{2+/3+}$. Being able to precisely quantify these minerals is another step in getting to know and understand our soils better. Powder X-ray diffraction in combination with Rietveld refinement is a reliable method to get closer to this step. However, in order to adequately describe the diffractograms of "biotites", an ideal structural model is often no longer sufficient, because the disorder of these minerals must be taken into account.

In the present study, a structural model applicable to the Rietveld method was developed, which is able to describe the 1M polytype of “biotite” (phlogopite – annite series) including its structural disorder which is limited to n * 120° rotations. Six samples from different localities covering the phlogopite – annite series, and another two siderophyllite samples were used to test the model. For this purpose, preferred oriented specimens as well as random powders were used.

Not only the goodness of the fit was considered, but also the refinement results (refined parameters) were checked for plausibility and compared to calculated values from structural formulas, which based on X-ray fluorescence data. Furthermore, three out of the eight samples were intensively mixed with 25.0 % w/w corundum reference material and these mixtures measured and quantified as unknown samples to test the correctness of the deduced quantification results. The quantified corundum contents of 26.8 % w/w, 25.7 % w/w, and 26.8 % w/w were within the expected range of uncertainty of 25 ± 3 % w/w. The overestimation of corundum contents could indicate the presence of X-ray amorphous phase (e.g. Fe-oxy-hydroxides).

During this study, the $2M_1$ polytype was additionally identified, especially in Fe-rich samples which raises the need to create a $2M_1$ polytype disorder model for the phlogopite – annite series next.

Adsorption of phosphate, arsenate and chromate on surface-modified aluminosilicate waste

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Increasing amount of building waste has found new applications as a secondary material. The aluminosilicate-like properties of these wastes, as well as their environmental friendliness open up the possibility of using some of them in environmental technologies.

Powdered waste sludge from the production of technical stone (TSW – Techni Stone®Company, Czech Republic) consisting mostly of quartz, with a minor portion of feldspar and illite was surface modified with Fe^{2+} and Mn^{2+} inorganic salts and then testified as a potential adsorbent of environmentally risk oxyanions (phosphate PO_4^{3-}, arsenate AsO_4^{3-} and chromate CrO_4^{2-}) from contaminated waters.

The batch adsorption experiments were performed with 0.3 $mmol.L^{-1}$ model solutions of PO_4^{3-}, AsO_4^{3-} and CrO_4^{2-} simulating a moderately to heavily contaminated aquatic environment, and the TSW fraction of <0.1 mm, at 20 °C. The obtained data were fitted by the Langmuir model.

The adsorption of oxyanions on the original TSW was ineffective, with the maximum yield of 8% for CrO_4^{2-}. The Fe and Mn surface modification increased the adsorption efficiency to >99% for the PO_4^{3-}, to 99% for the AsO_4^{3-}, and to 82–86% for the CrO_4^{2-} adsorptions. While the use of TSW_{Fe} indicated the highest adsorption yield for all tested oxyanions, the Langmuir parameters (K_L) and the Gibbs energy consumption (ΔG) revealed the adsorption on TSW_{Mn} as more robust. The selectivity of the oxyanion adsorption to TSW_{Fe} and TSW_{Mn} decreased in the order: $PO_4^{3-} > AsO_4^{3-} > CrO_4^{2-}$.

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Simultaneous removal of As(V) and safranin O dye by Mg/Al LDH-zeolite heterocoagulated materials in static and dynamic conditions

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In recent years, layered double hydroxides (LDHs) have been intensively investigated as components of hybrid materials. For instance, the combination of LDH and zeolite induces dual adsorption properties, thus providing a simultaneous removal of both anionic and cationic pollutants from aqueous solutions. Such approach enables the reduction of adsorbent production costs. Additionally, it allows to overcome the limitations of individual components in terms of their adsorption properties while retaining their benefits.

This study investigated the synthesis of LDH-zeolite heterostructures via two approaches: (i) facile, one pot hydrothermal method (resulting in HM samples) and (ii) co-precipitation of LDH on the hydrothermally derived zeolite (CM samples). Due to high availability and low-cost, kaolin group minerals were used for the zeolite synthesis. The structure, texture, surface morphology and chemical composition of obtained materials were characterized by XRD, FTIR, SEM-EDS, thermal analysis, N_2 adsorption/desorption and XRF. The adsorption efficiency of HM and CM hybrid materials was compared both in single and dual systems containing As(V) anions and/or cationic dye – safranin O (SO). The high S_{BET} values of HM samples positively affected their external cation exchange capacity (ECEC). Therefore the superior SO removal properties were observed. All of the obtained samples were efficient in As(V) removal, which was related to their anion exchange properties (AEC) observed in a range of 56.5-120.4 meq/100 g.

One of the most effective HM materials was transformed into hydrogel beads using a natural, biodegradable polymer – sodium alginate. The obtained granules were tested in a custom-made flow-through column. In addition to the efficient As(V) and SO adsorption, the dynamic experiments emphasized the significance of the physical behavior of the alginate beads in the fixed bed.

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Shaft sealing with the Sandwich sealing system

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Shaft seals are designed to limit the fluid inflow in the early stage after closure of a radioactive waste repository and to delay a possible release of radionuclides from the repository at later stage. Current German concepts of shaft seals contain the hydraulic Sandwich sealing system as a component of the lower seal in the host rock.

The Sandwich sealing system consists of alternating sealing segments (DS) of bentonite and equipotential segments (ES) of higher hydraulic conductivity. Within the ES fluid is evenly distributed over the cross section of the seal and a more homogeneous hydration and swelling of the DS are obtained.

A large-scale experiment was launched at the Mont Terri rock laboratory in 2019 (funded by the German Federal Ministry for Economic Affairs and Energy under contracts 02E11587 and 02E11799) with partners from Germany, Switzerland, Spain, UK, and Canada. The experiment consists of two experimental shafts of 1.18 m diameter and 10 – 12.6 m depth in the sandy facies of the Opalinus Clay drilled in 2020. The Sandwich seal in each shaft consists of 5 ES and 4 DS. DS are constructed of German Ca-bentonites, *i.e.* either Calcigel or Secursol MHP.

Measurements in the rock (Opalinus clay) were started prior to shaft sinking and characterization of the excavation damaged zone was performed before seal emplacement. The seals and the surrounding rock are intensely monitored.

The in-situ work is backed by laboratory testing and numerical modelling work. Solution of minerals, ion transport and cation exchange during saturation and permeation are studied in semi-technical scale experiments and MiniSandwich experiments. An overview of the experiment will be presented.

A mineralogical and stable H-O-C-isotope study of clay-rich alteration zones in the Fennoscandian Shield, Norrbotten, Sweden

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We present new results of a detailed mineralogical and stable isotope geochemical study of deep and significant, probably Precambrian clay alteration zones in Paleoproterozoic metavolcanic rocks in the Kiruna and Malmberget magnetite underground deposits and the Vahtanvaara iron skarn prospect in northern Sweden (Gilg et al., 2017). They are presently studied as natural analogues for bentonite buffers in nuclear waste depositories (Schneeberger et al., 2022)

XRD and SEM analysis of bulk rocks and various grain size separates down to less than 0.02 μm indicate that at Kiruna, montmorillonites with variable but low iron contents and minor very fine-grained calcite are observed as alteration phases, while at Malmberget greenish Fe-bearing R3 illite-smectites dominate with minor chlorite, but carbonates are notably absent. At Vahtanvaara, montmorillonites are associated to stilbite, minor chlorite and corrensite.

The variable alteration assemblages are mirrored by the distinct ^{2}H/^{1}H, ^{18}O/^{16}O and ^{17}O/^{16}O ratios of the clay separates indicating contrasting formation temperatures of about 30°C for Kiruna smectites, 50 to 90°C for Vahtanvaara smectites, and more than 120°C for Malmberget illite-smectites. The alteration fluids were dominated by meteoric waters that were isotopically heavier than present-day precipitation. The stable C-O-isotope compositions of clay-associated calcites at Kiruna are distinct from the carbonates associated to ore mineralization, but are not in isotopic equilibrium with the clays suggesting formation at a later stage.

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10th Jubilee Mid-European
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The heterogeneity of the sealing rock matrix on a micrometer scale with emphasis on clay distribution: an example of cap rocks from the Outer Carpathians (Węglówka Marls, Upper Cretaceous, Poland)

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A seal is a critical component of the petroleum system. One of the most important properties for evaluating seal integrity is homogeneity. Homogeneous rocks make good top seals, whilst lithologic heterogeneity generates variation in physical and fluid-flow properties. As the global interest in sealing rocks has increased due to, e.g., the sequestration of CO^2 in hydrocarbon-depleted formations, imaging the homogeneity on a range of spatial scale became important. This paper deals with imaging the homogeneity of the effective seal from the Węglówka Oil Field (Węglówka Marls), which is currently at the end of its production. The sealing rocks are calcareous mudstones composed mostly of about 50% of I-S and about 30% coccoliths. This paper elaborates on the unexplored problem related to quantification of heterogeneity of mudstone-type cap rocks. Simple mineralogy justifies the use of the relationship between clay and calcite grain contents as an indicator of heterogeneity of the rock matrix. The imaging was performed using a FEI Quanta 200 FEG-SEM. Mechanically polished surfaces were observed using BSE and EDX modes of imaging. The distribution of clay and calcite grains less than 5µm in size was documented in 15 randomly selected areas by imaging at the magnification of 40.000x and then quantified using JMicroVision software. This study reveals small-scale variation in mineralogy of the cap rock matrix. Despite the observations presented here being preliminary, the results obtained allow us to point out the differences in rate and timing of compaction of clay- and calcite-rich areas of the rocks. Porosity was longer preserved in the calcite-rich areas than in more compressible, clay-rich areas. The distribution of areas where the mixture of clay and calcite grains occur, which are able to form a closer packed structure, is an important variable that controls the effectiveness of the cap rocks.

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An XRD and TEM study of illite polytypes in shales and sandstones: Examples from the Illinois and the North German Basins

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Illite in shales and sandstone can be of authigenic or detrital origin. In shales, the origin of the illite polytypes is primarily identified by combined XRD and K-Ar age dating analysis. Typically the $1M_d$ and $1M$ illites are authigenic while the $2M_1$ is detrital. In sandstones, the same methods can be used when detrital grains are present. Typically the amount of $1M$, cis-vacant or trans-vacant, is significantly higher than in shales. A controversy exists on how to identify mixtures of $1M$ and $1M_d$ illites. $1M_d$ illites can have polytype specific reflections, however, not as sharp as for $1M$ illites. The transition of $1M_d$ to $1M$ can also be continuous and broad reflectins may be mininterpreted as grain size effecrt. The occurence of $1M$ illite polytype reflections alone does not indicate the sole presence of $1M$ illite. Therefore the occurrence of physical mixtures of $1M$ and $1M_d$ illites are likely underestimated. We present a method to identify mixtures using the peak shapes (such as the FWHM parameter) of polytype specific reflections in comparison with 00l reflections. With the availability of new Rietveld structure files, especially Ufer et al. (2012), it is now possible to quantify the illite polytypes using BGMN/Profex. In addition to XRD methods, electron microscopy provides additional evidence of an authigenic origin by observing euhedral crystal shapes by SEM and/or TEM. Such studies typically reveal a mixture of illite consisting of pore-filling euhedral laths and plates to hairy illites.

In this investigation, we examine illite polytype data from the Illinois Basin: Maquoketa, New Albany, Eau Clair shales and the Mt Simon Sandstone ss well as from the North German Basin: Rotliegendes Sandstone and Posidonia Shale. We aim to improve our understanding of the complexity of illitization in these two basins by improved recognition of mixtures of illite polytypes based on their crystallography, chemical composition and isotopic age.

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Mineralogical and geochemical characteristics of Early Sarmatian bentonite and marls from the Hrvatsko Zagorje Basin, Croatia

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A bentonite layer deposited between horizontally laminated marls was documented in the Sutla-II column recovered from northwestern part of the Hrvatsko Zagorje Basin (i.e. southwestern marginal belt of the Pannonian Basin System). Mineralogical analyses were performed by XRD and thermal analyses, while geochemical methods on the bulk sample included ICP-OES and ICP-MS. Additional chemical analyses were carried out on the coeval bentonite from northeastern Bosnia and Herzegovina (Ugljevik) to establish a potential regional correlation. Calcite and clay minerals (smectite, illite, kaolinite and in some samples chlorite) are the most abundant minerals in marls. The bentonite is dominated by montmorillonite (60-70%). Besides them, it contains opal-CT, calcite, and small content of quartz. CEC of marls varied between 16.5 and 24.5 meq/100 g and in bentonite it revolved around 83 meq/100g. Provenance analysis indicates that bentonite was formed by intensive weathering of felsic to intermediate type volcanic ash. Smectite in marls, apart from its terrigenous origin, was likely sourced from the alteration of volcanic ash as well. The described occurrences of bentonite are associated with a distant volcanic eruption. Coeval deposition times and similar trace element abundances of bentonite analyzed herein and that from Ugljevik (Badurina et al., 2021) suggest that both likely originated from the Apuseni Mts or Eastern Carpathians via Early Sarmatian volcanism.

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Diversity of surface properties of synthetic feroxyhyte

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Feroxyhyte is an uncommon ferrimagnetic iron oxyhydroxide with an ideal formula δ-FeOOH. Due to its low crystallinity and specific properties feroxyhyte is a potentially interesting material to be used in e.g. water treatment, catalysis, nanoelectronics and medicine. Therefore synthetic analogues of the oxyhydroxide have been recently extensively studied. Surprisingly little is known, however, how the method of synthesis affects the feroxyhyte properties, including sorption efficiency. Filling this gap in the current knowledge was the main aim of this work. Four synthetic feroxyhytes obtained by oxidation of $FeCl_2$ by 30% H_2O_2 at pH 8 (Fx-pH8) and at pH 10 (Fx-pH10), by oxidation of $(NH_4)_2Fe(SO_4)_2$ with 30% H_2O_2 at pH 14 (Fx-SM), and by oxidation of $FeSO_4$ with $KMnO_4$ (Fx-Mn) were used for the study. The products were characterized by X-ray diffractometry (XRD), scanning electron microscopy (SEM-EDS) and simultaneous thermal analysis (STA). Specific surface area (SSA), porosity and pH_{pzc} were also determined. Sorption properties towards Pb(II) and Cr(VI) were investigated in batch experiments.

Although all the materials obtained were low crystalline, there was a significant variation in feroxyhyte properties depending on synthesis conditions. Fx-Mn showed the highest crystallinity, the lowest SSA and the lowest volume of micropores. Conversely, Fx-SM revealed the lowest crystallinity, the highest SSA and the highest volume of micropores. Both feroxyhytes obtained from $FeCl_2$ oxidation (Fx-pH8, Fx-pH10) showed intermediate properties. The pH_{pzc} ranged from ca. 3.7 to 5, and was apparently neither directly related to other surface features nor to pH conditions during synthesis. Feroxyhyte sorption properties were also diversified, with lead and chromate sorption capacities ranged from 27 to 87 mg/kg, and from 32 to 44 mg/g, respectively. Interestingly, the relation between SSA and sorption capacity is noticeable in the case of Pb(II) sorption, but not in the case of Cr(VI) sorption. Desorption experiments showed that lead was bound much stronger to the feroxyhyte surface than chromate. Our results clearly show that the properties of feroxyhyte obtained by different synthetic routes differ significantly despite chemical and structural similarities of the products.

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The effect of antimicrobial clay nanofillers on the functional properties of biodegradable polymer films

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Microbial infections caused by pathogenic microorganisms are becoming a growing problem in health care, hygienic applications, or food storage and packaging. The current topics of material research focused on medical use deal with development of antimicrobial polymer nanocomposites. It is already known that the properties of polymers can be improved by the addition of *nanofillers*. Some of the most progressively, and for the past few years extensively studied nanofillers are *clay minerals*. The clay minerals are commonly used materials in pharmaceutical field both as inorganic excipients or active agents, because they may undergo ion exchange reaction with functional antimicrobial molecules via intercalation process.

Especially organoclay based polymer nanocomposites exhibit remarkable improvement in materials properties compared with virgin polymer or conventional micro and/or macro composites (Holešová et al., 2021). Besides they offer minimizing problems with residual toxicity of conventional antimicrobial agents and guarantee increasing and prolonging antimicrobial efficiency.

This study is focused on development of thin antimicrobial polymeric films based on biodegradable polycaprolactone with clay mineral natural vermiculite as a carrier for antimicrobial compounds, where the active organic antimicrobial components are ciclopirox olamine, chlorhexidine diacetate or octenidine dihydrohloride also combinated with ZnO particles. We studied effect of theses nanofillers on structural, thermal and antimicrobial properties of final polymeric films.

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Stability of the Maldegem Formation under extremely acidic conditions

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The Maldegem Formation (Bartonian, Eocene) occurs in the subsoil of the East Flanders, Belgium and consists of alternating layers of clay and loamy sands. Specifically, the ~10 m thick clay layer known as Zomergem Member is investigated as potential barrier for containment of highly acidic plume from the historical crude oil treatment.

In this context, laboratory batch and flow-through experiments are performed on powdered and intact core samples at 25°C using 2M H_2SO_4 solution as reactant in order to assess the long-term resistivity of the clay against acid attack. To meet the objectives, the solutions and solids were examined by pH, ICP-AES, XRF, QXRD, SEM-EDX and SSA techniques as a function of the reaction time. Geochemical simulations support the experimental findings.

The stoichiometry of clay dissolution was assessed by comparing the elemental ratios in the leachates with those in the intact clay. The dissolution rate decreases in the order Al>Fe>Mg>K, whereas Si release into solution is rather limited. Based on QXRD analysis, kaolinite and chlorite dissolved and sum of 2:1 clay minerals decreased from 28 wt% in the initial sample to as low as 12 wt% after 90 days of the interaction. In addition, Mg-sulphates (hexahydrite, pentahydrate and starkeyite) were found in variable amounts in the solid products. It is presumed that main source of Al, Fe and Mg release are octahedral sheets of clay minerals, while K originates from the ion-exchange and dissolution of illite/mica interlayers.

SSA analysis by N_2 adsorption revealed a decrease in the SSA from 57 m^2/g in the undisturbed sample to 15 and 17 m^2/g and mode pore size values increased from 3 to 12 and 16 nm after 30 and 90 days respectively. The adsorption analysis indicates partial loss of the micro-porosity and formation of the mesoporous structure.

The column tests with the core samples are at the present moment on-going in order to couple the mineralogical and structural changes of the clay to transport properties.

Composites of iron-based layered double hydroxides and biochar: Metal(loid) removal and structural change investigations

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Recently, a large number of studies dealing with layered double hydroxide/biochar composites (LDH/BC) have been published, but the development of advanced modeling approaches, detailed structural investigations and/or their testing in real waters and soils are still rare. In this study, attention was focused on Mg-Fe LDH/BC composites and their ability to remove metal(loid)s from aqueous solutions. The sorption data were further modeled using standard empirical models (pseudo-first/pseudo-second order models and Langmuir/Freundlich model) and a quasi-mechanistic non-electrostatic surface complexation model (NEM). The study also evaluated the influence of the biochar matrix on the total metal(loid) uptake, where it was found that LDHs play a major role. The contribution of pristine BC was evident only in systems containing the most effective type of BC. This behavior was also described using the component additivity (CA) modeling approach. The materials have been subjected to a variety of solid phase analyzes to detect the metal(loid) capture and removal mechanisms (XRD, SEM/EDX, FTIR-ATR and XPS). Although inner-sphere complexation was the main mechanism at low metal(loid) concentrations, the effects of other processes at higher concentrations, e.g., precipitation, cannot be neglected. Moreover, significant structural changes leading to LDH destruction were observed at high As loadings. Therefore, such comprehensive studies are necessary to fully understand and optimize the behavior of materials before their subsequent use in environmental technologies.

Various techniques for the study and characterization of non-conductive materials using dual beam SEM/FIB microscopes

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Double beam microscopes equipped in a scanning electron column and focused ion beam column are attractive and powerful tool for the study and characterization of non-conductive materials like for example clay minerals, diamonds, struvite, zeolite and many more [1]. Due to measurements held in ultra high vacuum a sample should be well prepared and especially target with low conductivity should be carbon or gold coated which is needed to discharge charge and enable electron column imaging and other techniques to be performed.

Moreover SEM/FIB setup with EDS detector (Energy Dispersive Spectroscopy) is capable of performing elemental mapping of material placed in the microscope chamber. Which despite topography (SEM) gives us morphological and phase structure of the sample [2]. Both of the above techniques can be used in combination to create 3d reconstructions of at least minerals, so that we get models that contribute a lot of knowledge [3]

TEM (transmission electron microscopy) requires specialized and high quality preparation to enable imaging of material at the atomic scale, with the use of the SEM/FIB microscope this is possible because we can use the lift-out technique and make a lamella, for example, from peat [4]

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Impact of provenance, weathering, and sedimentary processes on mineral and chemical composition of the Ediacaran and Cambrian mudstones from the East European Craton

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Detailed quantitative mineralogical and geochemical data were obtained from 71 wells and outcrops from the Ediacaran East European Craton (EEC) to assess the impact of the climate, provenance, sedimentation, and authigenesis on the geochemistry and mineralogy of the mudstones deposited in various environments. Sedimentological and facies analysis allowed us to identify several continental and more distal (basinal) environments and their temporal-spatial distribution in Ediacaran and early Cambrian times. The sedimentological data were then used for reconstructing palaeogeography of the western part of the ECC in the Ediacaran-early Cambrian times, which supports the view of the existence of the large estuary opening eastwards, with sediments delivered from north and west. Our study offers clear evidence that during relatively stable lateritic-type weathering on the Ediacaran Baltica land, an intense mineral authigenesis, possibly mediated by microorganisms, also indicative of tropical climate, took place in subaquatic environments, both continental and transitional (marine/lacustrine). The tropical and disoxic conditions in the Ediacaran basin were indicated by the widespread presence of the berthierine, whereas in the Cambrian strata glauconite starts to dominate the authigenic minerals pool, indicating more oxidised waters and more likely marine conditions.

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Combining mineralogy and chemistry to evaluate palaeosalinity proxies: example from the Ediacaran mudstones of the East European Craton

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For many years, the contents of trace elements such as boron, gallium, strontium, and barium in mudstones were utilised to assess palaeosalinity conditions in various basins of different ages around the world. Those palaeosalinity indices were based on the observation that marine water contains much more B and Sr than freshwater. B and Sr were supposed to be adsorbed on clay mineral surfaces, thus preserving the original marine signal. This approach was put to test in the present study (Jewuła et al., 2021). Understanding palaeosalinity proxies is important for the Ediacaran environmental studies, trying to explain the Cambrian life explosion.

The geochemical data obtained from over 500 Ediacaran fine-grained sedimentary and volcanic rock samples from the East European Craton (EEC) were compared with the mineralogical data. Although boron-based proxies indicated that most of the samples could have been deposited in the freshwater environment, modelling results and the following calculation of boron budget show that detrital micas, weathering minerals (kaolinite plus hematite), or diagenetic clays are dominant carriers of boron in different regions of the EEC. These results were verified by applying the same approach to some Phanerozoic mudstone sequences. Similar results were obrained for the Ba/Sr proxy, thus the use of both proxies in the paleosalinity studies is not recommended.

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Heterocoagulated materials based on smectite and layered double hydroxides of different chemistry with dual adsorption properties

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The use of positively charged layered double hydroxides (LDH) and negatively charged montmorillonite (MMT) enables simultaneous removal of anions and cations in aqueous solutions. Nanocomposites in which LDH are precipitated on the surface of montmorillonite are considered to be more effective in comparison to the physical mixtures of the discussed materials. This is due to a high degree of dispersion of the materials and their mutual interactions which improve, among others, their rheological properties. One of the most popular method of obtaining MMT/LDH nanocomposites is an in-situ synthesis using high temperature treatment during at least one synthesis stage.

In the performed experiments, an in-situ synthesis method at room temperature was developed. Four materials were synthesized by LDH co-precipitation - Mg-Fe (CMF), Mg-Al (CMA), Ni-Al (CNA) and Ni-Fe (CNF) - in the presence of a smectite sample from Wyoming (SWy). The assumed mass ratio of MMT:LDH was 1:1. For comparison, four analogous physical mixtures of MMT/LDH were used in the experiments. The obtained materials were characterized by means of: XRD, FTIR, SEM/EDS analysis, thermal and textural analysis based on N_2 adsorption/desorption. In order to determine the effectiveness of removing pollutants form aqueous solutions, the materials were tested in the reactions with chromium(III) cations and the anionic dye Acid Blue 129.

The research showed a high removal capacity of both pollutants by the CMA and CMF composites, in single-, two- and multi-component systems. The obtained materials show promising properties in terms of their use as adsorbents for treatment of industrial wastewater containing various anionic and cationic pollutants.

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For you are mica and to mica you shall return – Potassium fixation within dioctahedral vermiculite

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The aim of the study was to investigate potassium uptake by dioctahedral vermiculite (divermiculite) from seawater. Two portions of the Na-saturated soil sample rich in divermiculite (1E) were kept for a year in a closed system of 1 dm^3 of artificial oceanic water (OW) and natural sea water from Gdańsk Bay (GB), respectively. Immediately after the experiment was finished, those portions were dried and Na-saturated. Two other portions packed into dialyzing tubbing were kept in 5 dm^3 of GB, changed every 3-4 days. After 6 months, one portion was dialyzed in deionized water (DI), dried, and Na-saturated. The second portion was dried immediately after the experiment had finished followed by Na-saturation. The fifth portion was kept in 1 dm^3 of OW for 120 days. After 3, 9, 90, and 120 days, a small portions were taken out, dried, dialyzed, and dried again. The final products were characterized using X-ray diffractometry, ICP-OES, and an O-D method. The products of the experiments showed an increase in the mica-like 10 Å interlayers relative to the starting 1E sample. The sample kept in OW for three days showed a significantly lower LC (0.68 per formula unit (pfu)) than sample 1E (0.79 pfu). Similar values showed products that were dried immediately after the experiment (0.65-0.68 pfu), whereas products that underwent dialysis first showed slightly higher LC (~0.73 pfu). The K$_2$O content was higher in all the products of the experiments (up to 3.66%) compared to the sample 1E (2.65%) and showed a strong negative correlation with the LC of external surfaces of swelling clays. The fixation of K within vermiculite interlayer space occurred regardless of duration of the experiments and the chemistry of the water used; however, the dilution of marine water with DI during dialysis caused desorption of K from some interlayers positions (likely those having lower LC). **Acknowledgments:** This study was financed by the National Science Center, Poland [grant number: UMO-2016/23/N/ST10/01388].

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Lattice parameters of well-ordered kaolinites determined by an optimized Rietveld refinement procedure

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The crystal structure and the lattice parameters for well-ordered Keokuk kaolinite have been published several times. Bish & von Dreele (1989) applied a Rietveld approach on laboratory powder diffraction data, and Neder et al. (1999) used the single-crystal technique and synchrotron radiation. Their coordinates and lattice parameters were used by several authors, e.g. Drits et al. (2018), in order to propose an orthogonal layer symmetry, useful for the description of disorder in layer stacking by well-defined translation vectors. However, more precise lattice parameters of kaolinites may be helpful to discuss the details of kaolinite structures.

Two well-ordered kaolinites (geode from Hamilton/Illinois, rhyolithic lithophyse from Börtewitz/Saxony) have been prepared and measured in conventional Bragg-Brentano geometry using Cu radiation and diffracted beam graphite monochromator. An internal standard Si NIST SRM 640c Si was used to adjust the instrumental zero point and sample height errors as well as the profile shape changes due to the beam penetration effects of the low absorbing sample material. Thus, the quality of the Rietveld profile fitting could be significantly improved and estimated standard deviations of lattice parameters have been minimized. The parameter values of the two samples were found to be significantly different, but the a/b ratio was found to be identical.

The outcomes demonstrate that precise lattice parameters may be obtained by the Rietveld method when the profiles are optimized by using an internal standard.

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The influence of temperature on acid activation of bentonite from Kopernica (Slovakia)

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The literature reports describe acid treatment of different kinds of clays. A common treatment applied of acid treated bentonites, montmorillonite-bearing rocks is to produce sorbents (bleaching earths), catalysts or catalyst supports, carbonless copying papers, etc. (Komadel, 2003).

In this study, the influence of temperature on the new acid activation method was presented. It consisted of two steps - drying of the material and subsequent dry impregnation with sulphuric acid (H_2SO_4). Three temperatures (100, 200, and 300 °C) and four different cation exchange capacities (CEC) of montmorillonite, namely: 0.5; 1.0; 1.5 and 2.0 were evaluated. Structural evolution of materials were observed immediately after activation and after 1, 2, 3, and 4 weeks. For this purpose X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR) analyses were used. Under less acidic conditions the monohydrated H-montmorillonite changed upon storage to bi-hydrated form. This phenomenon might be due to migration of leached Mg, Al, and Fe cations to the interlayer, in the process of clay minerals. The best effects were obtained for treatment under 200 °C with the usage of H_2SO_4 (CEC = 2.0) (Bahranowski et al. 2022). At such conditions, cation exchange occurred immediately after activation, whereas no visible changes were observed on the diffractogram after aging. On this basis, it was found that a chemical equilibrium was established. At 100 °C the form of H-Montmorillonite was found to be unstable and to undergo auto-transformation. The temperature of 300 °C was too high, which was confirmed by the results suggesting a partial degradation of the structure of montmorillonite.

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Changes in clay mineralogy of ploughed and unploughed topsoils

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In 2018-2021, the mineralogy of topsoil (0-5 cm) of the long-term small plot field experiments with crop rotation and different soil agrotechnical practices (direct sowing~unploughing, ploughing) was studied at Žabčice locality. The experiment was established in 2004 on a gley Fluvisol. Treatments included the combinations of winter wheat grown after alfalfa and spring barley after sugar beet with ploughing or unploughing practices. The site Žabčice is located 25 km south of Brno (altitude 179 m a. s. l.) with an average annual temperature of 9,2 °C and an average annual rainfall of 480 mm. All plots of the experiment was fertilised by potassium chloride and by superphosphate.

The mineralogical composition of soil samples sieved under 2mm, and of clay fraction separated by sedimentation was determined by X-ray diffraction using Bruker D8 Advance diffractometer (CuKα, primary and secondary Soller slits 2.5°, detector Lynxeye XE) with automatic divergence slit (ADS, 10 mm). X-ray diffraction patterns of oriented preparations were fitted with the Sybilla Version 2.2.2 software (Chevron ETC proprietary, Aplin et al., 2006). Individual mixed-layered minerals were identified and fitted according to Viennet et al. (2015), and Bakker et al. (2018). The models were counted on the relative proportions of different layer types (smectite-S, illite-I, kaolinite-K and chlorite-C layers, C including layers with a non-complete Al-hydroxide interlayer).

The mineralogy of the whole-rock soil samples (under 2 mm) reflected the Fluvisol type, which is sorted by flow, where the content of phyllosilicates (muscovite, kaolinite, less chlorite+vermiculite) increased with decreasing amount of feldspars, especially plagioclases. Crop rotation (winter wheat or spring barley) did not affect mineralogy. The mineralogy of clay fraction reflected agrotechnical practices (ploughing, unploughing). In the clay fraction of topsoil, the proportion of illite layers decreased and the proportion of smectite layers increase with ploughing, probably due to the rotation, and homogenization of soil by ploughing. The proportion of kaolinite and chlorite layers remained unchanged.

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Downhole lithological profile reconstruction based on chemical composition of core samples and drill cuttings measured with portable X-ray fluorescence spectrometer

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Reconstruction of a lithological profile based on geophysical logs of chemical composition provided by geochemical gamma-gamma well logging probes has been increasingly used for geophysical interpretation during the prospecting of hydrocarbons resources. A chemical profile, analogous to the measurements mentioned above, can be determined based on measurements made with a portable X-ray fluorescence spectrometer (pXRF). Using the models combining results of chemical composition analysis with results of mineral composition analysis (XRD) it is possible to obtain the mineralogical profile of the borehole. Very reliable results could be also obtained for rocks containing clay minerals. The basic assumption of the proposed methodology is the application of timesaving and inexpensive portable XRF spectrometer measurements in the everyday practice of lithological reconstruction (Kowalska et al., 2020). That approach is based on the observation that the results of chemical composition measurements taken with a pXRF well correlate with the results of the research made in a renowned stationary lab. Owing to this, it is possible to calibrate these results on the basis of a detailed chemical composition analysis conducted for a set of representative samples. Because this is a non-destructive method, the same sample can be subsequently used for a mineral composition analysis with the XRD method, simultaneously controlling obtained results with regard to the chemical composition and receiving mathematical models combining both the mineral and chemical composition.

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Carboniferous (Mississipian) K-bentonites in the Sudetes (SW Poland): mineralogical and geochemical data

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Clayey interbeds have been searched for in 13 exposures of the Carboniferous molasse-type deposits in the Central Sudetes. Mineralogical analyses revealed that A group bentonites are composed of mixed-layer I/S, illite and kaolinite, B group of illite, smectite and kaolinite (+/- chlorite), and the mudstones of group C – of quartz, illite and chlorite. The yellow-colored bentonites are typical K-bentonites, composed of mixed-layered I/S, illite and kaolinite. A bentonites show the highest LOI (c. 13 wt.%) and Al_2O_3 (c. 27%), and relatively low SiO_2, Fe_2O_3 and Na_2O. They are also richer in incompatible elements - Zr, Nb, Hf, Y, HREE, U and Th. Bentonite B has also high Al_2O_3 (~27%) but different concentrations of some other elements. The mudstones of Group C plot closely, having rather high Si, Fe, Na, Ti, Ba, Cr, Ni and low LOI, Al, Hf, Y, U, Th and Ta. In the multi-element diagram normalized to the primordial mantle all the samples are rather similar, with a decreasing trend from the most to the least incompatible trace elements, and with several distinct anomalies. In the diagram normalized to the upper continental crust, the plots are broadly horizontal, at c. 1 – 2x the normalization values for the upper crust. There are many distinct anomalies, including two positive – for Th and U in bentonites A. The patterns for the pairs of bentonites B and their background mudstones are broadly parallel, with significantly higher values for the bentonites. Chemical features of A bentonites, e.g. high concentrations of incompatible elements: Zr, Nb, Hf, Y, HREE, U and Th (but low Ti and LREE) suggest their possible affinity to intermediate rocks (andesites?) of magmatic-arc setting. B bentonites are not homogeneous, thus it might be related to a different type of volcanic eruption. Bentonite B2 shows geochemical similarity to the surrounding mudstones. This suggests a different origin of this clay, e.g. via mixing of volcaniclastic material with “background” sediment during deposition or re-deposition (Kryza et al.2011).

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Oxygen isotope composition of the Ediacaran weathering crusts from the East European Craton

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The western part of the East European Craton (EEC) presents an unique opportunity to study the Ediacaran strata with a minimum diagenetic overprint. These strata contain~~s~~ a number of weathering crusts (paleosols), which were demonstrated to had been formed as a result of the Ediacaran tropical weathering. The aim of the present study was to confirm this finding by investigation of the oxygen isotope composition of the paleosols, in order to apply a clay-iron (hydr)oxide paleothermometer.

Bulk material and separated clay fractions of paleosol samples coming from the most highly weathered portions of the Ediacaran profiles were characterized by X-ray diffraction, chemical analysis, and thermogravimetric analysis. Oxygen isotope compositions were measured for materials which had undergone different selective dissolution treatments in order to determine $\delta^{18}O$ values of phyllosilicates and iron (hydr)oxides present in the samples.

Comparison of the results coming from bulk samples and clay fractions points to the conclusion that phyllosilicate and iron(hydr)oxide components are in isotopic disequilibrium in the investigated samples (Kuligiewicz et al., 2021). The disequilibrium was likely caused by the Paleozoic illitization. The paleotemperature estimation based on the average oxygen isotopic composition of kaolinite and iron (hydr)oxides from the investigated samples is in qualitative agreement with weathering under hot climate, however, this approach results in a very large uncertainty associated with the estimated paleotemperature value.

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Oxygen and hydrogen isotope composition of soil clay minerals from the Tatra Mountains, Poland

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Oxygen and hydrogen isotopic composition of pedogenic clay minerals is commonly assumed to reflect isotopic composition of water present in the environment during their formation. This relationship is used for inferring mean average temperature in isotope-based paleoclimatic studies of paleosols. The goal of the present study was to test this assumption for postglacial soils of the Tatra Mountains, Poland.

Four soil profiles developed on granitic material with $\delta^{18}O = +9.3‰$ were investigated. The clay fraction (<0.2 μm) was separated and characterized by X-ray diffraction and chemical analysis. Oxygen and hydrogen isotope compositions were measured on a CO_2 laser fluorination line and thermal conversion elemental analyzer, respectively, both connected to isotope ratio mass spectrometer.

The main phyllosilicate components of clay fractions were dioctahedral mica and mixed layer illite-smectite, with addition of high-charge expandable minerals and kaolinite. Oxygen isotopic compositions of samples, which were in the +6.4 to +13.0‰ range indicated that the clay fractions were not fully equilibrated with the isotopic composition of rainfall and stream water in the area, however, $\delta^{18}O$ values tend to evolve towards the expected +18-22‰ range with the increase of the pedogenic component. Relationship between hydrogen isotopic composition and both oxygen isotopic composition and pedogenic component content is less clear.

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Cation exchange capacity- An alternative method to investigate the geological barrier of landfills?

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Clays and clay minerals are ideal raw materials for geological barriers and landfill liners because of their low-hydraulic permeabilities, their swelling properties and adsorption capacities. The geological barrier is a supplementary barrier beneath the body of the landfill, intended to protect the environment from uncontrolled leachate from the waste material. An Austrian standard defines the procedure for site exploration and the necessary laboratory tests and parameters for the analysis of the geological barrier. The most important laboratory tests besides grain size analysis are the Atterberg limits and the determination of the clay mineralogy using X-ray diffraction. However, the analysis of the cation exchange capacity (CEC) is not included in the list of laboratory tests. CEC is a numerical value that describes the physical properties of clays, such as the diffusion of charged and uncharged molecules and the cation retention. Hence, the objective of this study is to clarify whether the determination of the CEC (after Meier & Kahr, 1999) represents a possible alternative to currently used laboratory tests.

For this purpose, three samples (loess, sand and clay) from two landfill sites owned by the company Zöchling GmbH as well as six mixtures of these samples were examined for their mineralogical, chemical and geotechnical properties. The samples consist of varying amounts of quartz, feldspar, calcite, dolomite and the clay minerals smectite, illite, kaolinite, vermiculite and chlorite. The results show that the bulk clay mineralogy correlates well with the Atterberg liquid limit ($R^2=0.73$) and the CEC ($R^2=0.88$) and furthermore, the results of the two methods – Atterberg liquid limit and CEC- even correlate better ($R^2=0.95$).

This implies that the CEC is an alternative to the Atterberg liquid limit and/or the mineralogical composition of the material. Advantages of the CEC are rapidness, good reproducibility and cost-efficiency of the analyses compared to the other two methods. Based on the results of this work, a partial substitution of the currently used laboratory tests is considered feasible and CEC could at least be used for quick screening.

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Determination of Texture Characteristics of Clay Minerals

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Porous substances occur in many areas of chemical technology, most often as catalysts, membranes, adsorbents. Clay minerals can also be considered porous materials and therefore the knowledge of textural properties is one of the important characteristics of these materials. Clay materials are divided into several groups, which differ in their structure and also have different textural properties. Therefore, the knowledge of the basic textural characteristics of these substances, such as the shape, width, pores volume and classification, porosity, specific surface area (S_{BET}), true and apparent density, as well as the appropriate methods for their determination are necessary for the processing and use of clay materials. The methods for examining porous materials vary according to the size of the pores. The adsorption methods are preferably used for micro and mesoporous materials, while the Hg-porosimetry for macroporous materials. The methods of studying the structure of solids are mostly based on adsorption phenomenon. The goal of all adsorption theories is to predict the amount of adsorbate needed to covering the surface with the monolayer of gas molecules and to determine the area required to the adsorption of one molecule of adsorbate. From the number of theories the "BET" isotherm is currently used to the S_{BET} calculation. As the example of clays characterization, the determination of structural characteristics of rehydroxylated kaolinites, which are of interest as selective sorbents of various contaminants, can be performed. The rehydroxylation of metakaolinite to kaolinite strongly depends on the temperature and time of the hydrothermal process. Optimal conversion in terms of surface properties was observed at temperature 175°C and the reaction time of 7 days, when the S_{BET} of the original kaolinite increased more than threefold. In this study, results concerning complex clay textural analysis were obtained. In conclusion, although there is a wide variety of methods applicable to the clay texture characterization, each method has the limitations, which must be taken into account when evaluating the results.

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The modification of bentonite using water-soluble polymers varying in charge and molecular weight

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Water-soluble polymers are used in numerous geotechnical and geoenvironmental applications to replace bentonite or improve its performance, e.g. in supporting fluids, in clay-based barriers, as lubrification agent and to control strength properties in mechanized tunnelling. The mechanisms behind the enhancement of bentonite by polymer modification can be identified as adsorption, intercalation, and bridging, as well as the alteration of the pore fluid properties. The geotechnical properties of a modified bentonite arise from the combination of these different mechanisms, which, however, can vary greatly depending on the mixing conditions and the bentonite and polymer used. While the influence of the bentonite composition on the hydro-mechanical behaviour of a pure bentonite has been widely studied, there is a lack of knowledge about the corresponding effects of the polymer properties on a modified bentonite.

This study addresses the impact of the charge properties and molecular weight of a polymer used for modification on the properties of a bentonite. For this purpose, bentonite (MX80) was modified with linear polyacrylamides of different charge properties and molecular weights in a wet mixing procedure. The mixtures were investigated with regard to their hydro-mechanical properties and micro fabric. In addition, special characteristics of polymers in solution, such as the shear rate-dependent viscosity and the non-linear relationship between osmotic pressure and concentrations, are investigated and discussed with regard to their effects on the modification of bentonite.

The results reveal that molecular weight has a more pronounced influence in the case of the cationic polymers than in the case of the more coiled non-ionic polymer chains due to their rather stretched shape. In the case of the non-ionic polymers, a significant influence of the mixing method was found, which was attributed to the rather weak interactions between polymer and clay and the ability of the polymer chain to adopt different conformations depending on the mixing energy.

Precambrian paleosols of EEC: parent rock control and clay mineral formation

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Paleosols are formed at the Earth's surface in direct contact with climatic and environmental conditions that prevail at the time of their formation, and therefore they offer a unique opportunity for studying past climates. In this contribution we investigate paleosols collected from different areas of the East European Craton (EEC) which offer a chance to examine continental weathering and alteration sequences from early stages of weathering to completely weathered paleosols on a variety of Meso- and Neoproterozoic parent materials.

The paleosol profiles are on average 10 m thick, reddish coloured and many of them are characterized by a well-developed and well-defined alteration sequence with a lateritic uppermost horizon. The paleosols have been affected by the Paleozoic diagenesis, however some profiles offer a unique record of paleoweathering with minimum diagenetic overprint.

A well-developed weathering profile is characterized by a gradual decrease of primary rock-forming minerals and simultaneous increase of secondary clay minerals towards the top. The paleosol profiles developed on mafic parent materials show a weathering trend where dioctahedral smectite is the first weathering product at the bottom, it dominates in the middle-upper horizons and it later becomes unstable and alters into kaolinite. The paleosols developed on acidic parent materials show a different weathering trend: kaolinite forms already at the first stages of weathering as a result of plagioclase dissolution and primary (pure) smectitic zone is absent. Fe-oxides show a clear increasing trend towards the top of all well-developed profiles which indicates oxidative weathering and is usually related to formation of deep kaolinitic paleosols interpreted to represent warm and humid climate.

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Characterization of montmorillonite modified with polyoxazoline

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The ability of Na-montmorillonite (Na-Mt) to interact with two different polymers: linear cationic poly(ethylenimine) (PEI) and non-ionic poly(2-methyl-2-oxazoline) (PMeOx) was studied. The effect of the initial concentration of polymers, used for samples preparation, on their arrangement was investigated. The carbon and sodium analysis confirmed basically full exchange of Na^+ with PEI cations compensating the layer charge of Mt, while almost all Na^+ remained in PMeOx-Mt after polymer intercalation. The XRD patterns of the Na-Mt, PEI-Mt and PMeOx-Mt were analyzed to evaluate the impact of the initial concentration of the polymer on the expansion of the Mt interlayer space. At low PEI loading the d_{001} value was comparable with that of Na-Mt (1.25 nm). At the concentration corresponding to ~100% CEC of Na-Mt the increase in basal spacing (1.38 nm) revealed the monolayer arrangement of the PEI chains. The samples prepared with even higher PEI concentrations, however, showed no further increase of the d_{001} value. Different course of the XRD patterns was observed for PMeOx-Mt. A stepwise expansion of the interlayer space with increasing amount of PMeOx showed gradual transformation of the monolayer arrangement of polymer to bilayers and at the highest concentrations used pseudotrilayer stacking. In contrast to XRD, the IR spectra of PEI-Mt showed the increasing intensities of the bands related to CH and NH vibrations of PEI also for samples, for which no change in the d_{001} value was detected. It is evident, that not all polycations were intercalated in the Mt interlayers, some PEI molecules are supposed be trapped on the Mt outer surface. The IR spectra of PMeOx-Mt, as expected, demonstrated the increasing intensities of the CH_3, CH_2 and C=O bands with growing concentration of the polymer. On the contrary, within the whole range of the concentrations the positions of the bands remained almost the same as those found for net PMeOx. Most probably, some of the hydrated Na^+ cations are located close to the Mt layer, thereby partly restricting the direct interactions of the polymer with Mt layers.

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Iron oxyhydroxides formed at the expense of glauconite in temperate climate soils

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Presented studies of glauconite-bearing soils aimed at identification of glauconite weathering products and processes. Special attention was paid to iron oxyhydroxides as important indicators of weathering conditions. Five soil profiles from southeastern Poland where glauconite was the main (if not the only) phyllosilicate and the source of Fe were investigated.

Basic physical and chemical soil properties were analyzed for the bulk soil samples. Separated clay fractions and glauconite pellets were analyzed using XRD, FTIRS and ICP-OES. Parent glauconite pellets and clay fractions from selected soil horizons were also studied using ^{57}Fe Mössbauer spectroscopy (MS). The MS analyses of clays were performed at room temperature, 80 K, and 4.2 K.

Three of the studied soils were acidic and the remaining two were alkaline. Chemical composition of parent glauconites from each profile was similar, except that in one case Fe(II) was much more abundant than in the others. XRD showed that smectite-rich glauconite-smectite mixed-layered minerals and kaolinite were the main glauconite weathering products in both the alkaline and acidic soils. Only small contents of goethite and lepidocrocite were indicated in some of the XRD patterns. MS spectra, however, showed that fine crystalline and especially nanocrystalline iron oxyhydroxides were substantial products of glauconite weathering in all the studied clays.

Formation of the Fe oxyhydroxides was controlled by hydrological conditions and related redox activity, and by soil pH. Alkaline conditions favored goethite crystallization, whereas redox activity led to formation of lepidocrocite and likely ferrihydrite.

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In situ measurements of the hydration behavior of compacted Milos (SD80) Bentonite by wet-cell X-Ray diffraction

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Bentonite represents one of the most promising materials for backfilling nuclear repositories within the framework of the multi-barrier-concept due to its low permeability and self-sealing capacity. However, as bentonites represent diverse types of materials that vary in mineral content and their physical-chemical properties, the optimal choice remains unclear. In this study, a commercial Ca-bentonite (SD80) from the island of Milos (Greece) was hydrated using two artificial types of groundwaters in flow-through reactor (wet) cells designed for in situ XRD measurements. This device was used to investigate the swelling behavior in a confined reaction volume using bentonite specimens of equal packing density. Using in situ XRD measurements and CALCMIX calculations (Pançon & Drits, 2000), the formation of waterlayer (WL) structures in the interlayer was quantified. During the hydration of the SD80 with an Opalinus clay solution (20.23 g/L TDS), mainly 3- to 4-WLs formed. Only 10% of the interlayer water remained in the 1-WL state, while 2-WL was absent in the final steady state after which no further swelling occurred. In contrast, hydration in the more saline diluted cap rock brine (155.19 g/L TDS) showed a higher abundance of 1-WLs (ca. 15%), which is attributed to a slight difference to occurrence of more K in the interlayer. During the steady state of this sample, notable suppression of the WL-thicknesses occurred with 2- and 3-WLs remaining as the predominant structures. Comparison with previous wet-cell experiments of bentonites , the ratio of packing density to total layer charge of the smectites is presented as a useful proxy to predict the hydration behavior of various bentonites without conducting time consuming experiments.

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Excitonic coupling in the interlayer space of layered silicates

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High packing density, restricted torsional motion, and negative interaction term are the main prerequisites needed to achieve strong intermolecular interaction between organic molecules leading to excitonic coupling phenomena (Würthner et al., 2011). Van der Waals interactions between the non-polar moieties and relative orientation of molecules shifts the transition energy of dimers and higher aggregates with respect to its monomeric constituents to higher or lower energies. The so-called J-aggregate arrangement is formed in a case when the excitonic coupling results in a shift to lower energies enabling the electron-hole and exciton transport across this structure. Due to these properties, the J-aggregates are essential in applications like thin-film organic semiconductors or light-harvesting systems.

The interlayer space of layered silicates creates an environment suitable for such 2D J-aggregate arrangements. Due to the negative layer charge and exchangeable Na cations, the organic cations can be thus easily intercalated. A huge advantage of the encapsulation into the interlayer space is seen mainly in the exposure of the organic cations to the electrostatic pressure minimizing their molecular torsional motion. Moreover, layered silicates come in a huge variety regarding their layer charge enabling directly to control packing density of intercalated organic species.

In this study, thin hybrid films consisting of synthetic saponite, synthetic stevensite, and montmorillonite with cationic organic dye were prepared. The formation of monomeric and J-aggregate species in the interlayer space can be controlled by changing the height of the interlayer space by additional swelling with dimethyl sulfoxide. The control over the formation of monomeric and J-aggregate species in the interlayer space depends not only on the loading level but also on the layer charge of the used silicate.

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Montmorillonite as support for titania nanoparticles prepared by inverse microemulsion method – physico-chemical and photocatalytic properties

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The aim of the work was to obtain TiO_2/clay composites according to a novel design, based on combining the synthetic chemistry involved in the preparation of organoclays with the inverse micellar route of producing oxide nanoparticles in an organic medium. Inverse micelles are spheroidal water in oil droplets, formed when aqueous solutions of surfactants are added to organic solvents. Upon collision, micelles may exchange their water content, enabling coprecipitation of reactants dissolved in aqueous droplets.

Ti aqueous sol from $TiCl_4$ precursor was used for preparation of inverse Ti-microemulsion. 1-hexanol served as an oil phase and cetyltrimethylammonium (CTA) bromide as a surfactant. Montmorillonite (Mt) component was prepared in two ways: a) as organo-Mt (CTA-Mt) dispersion in 1-hexanol, and b) as Na-montmorillonite (Na-Mt) in water droplets dispersed in the form of inverse micelles in 1-hexanol. Ti-microemulsion and Mt suspensions were mixed in different proportions, left to interact and neutralized by addition of NH_3(aq). The recovered precipitates were lyophilized and calcined at 450^{o}C for 4 h. Samples containing 5, 10, 15 and 30 mmol Ti/g Mt were obtained. In selected cases the precipitates were treated hydrothermally at 180^{o}C for 3h. The materials were characterized with XRD, N_2 adsorption/desorption at -196^{o}C, SEM/TED/EDS, TG/DSC. Their photocatalytic properties were tested in the reaction of Rhodamine B decomposition.

Results pointed to the importance of the form of Mt component. In particular, composites prepared from CTA-Mt, were characterized by less uniform dispersion of TiO_2 nanoparticles than those obtained from microemulsion of Na-Mt. The latter materials showed better performance in the photocatalytic tests. Also, hydrothermal treatment was shown to improve the photocatalytic properties of the composites.

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10th Jubilee Mid-European Clay Conference

How atrazine and diuron are adsorbed into spiral halloysite structure

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The spiral tubular morphology of the halloysite mineral presents a large specific surface area, porosity, and high adsorption capacity on both surfaces. Thus, the halloysite is a suitable adsorbent agent for pollutants like herbicides, e.g., the atrazine and diuron molecules that negatively affect the environment and animals. Therefore, the main aim was to study the immobilization of the atrazine and diuron molecules by the halloysite tubular structure and the possible interactions on the different surfaces of this clay.

Force field methods were applied for the geometry optimisation and molecular dynamics using the COMPASS force field (Sun, 1998) on the atrazine-halloysite and diuron-halloysite models. Different herbicide loading ratios on the inner and outer parts of the halloysite structure were selected to find the preferable adsorption surface. The simulations showed that the inner surface of the halloysite presented stronger interactions with both herbicides, especially with diuron (e.g., binding energies per atrazine and diuron molecules were 134 ± 8 and 151 ± 4 kJ.mol^{-1}, respectively) than on the outer surface. Besides, the herbicide's arrangement on both halloysite surfaces depended on the concentration and mutual interactions. Finally, increasing herbicide concentration on the inner surface was limited by free space and the adsorption capacity became gradually saturated for both atrazine and diuron.

Acknowledgements

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10th Jubilee Mid-European Clay Conference

Reduction of ammonia emission from cattle manure after bentonite addition

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Ammonia (NH_3) in the atmosphere contributes to secondary aerosol formation and elevated particulate matter concentrations. The atmospheric NH_3 deposition is of environmental concern due to eutrophication and acidification of sensitive ecosystems but can also affect human health.

The emission of ammonia from agriculture and biogas plants represent the main sources of NH_3 in the atmosphere. In Germany, 95% of the annually released 760.000 t NH_3 are emitted by the agricultural sector of which more than half is attributed to the application of farm manures for fertilization.

Currently, several additives to manures are proposed in order to reduce ammonia emission such as ground rock powder, biochar or leonardite but until now, none of them have been proven (or dis-proven) to be effective.

In our study, we hypothesize that bentonite addition is able to reduce NH_3 emissions from manure due to the ability of the smectite fix NH_4^+ in its interlayers. We therefore compare the effect of mineral additives to cattle manure in incubation experiments of cattle manure. Ammonia was trapped in sulfuric acid traps and according to the Berthelot reaction determined as ammonium.

We confirm our hypothesis, that smectites, compared to other non-expandable layer silicate minerals, are effective in reducing the NH_3 emissions from cattle manure. All three tested bentonites showed nearly identical NH_3 reduction in the incubation trials. At application rates of 59 kg per t manure the emissions were reduced by about 25%. The NH_3 reduction potential appears to be directly related to – and limited by – the cation exchange capacity.

Intercalation of drugs poorly soluble in water into Mg-Al layered double hydroxide host

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Layered double hydroxides (LDH) attract increasing attention in medical applications as drug carriers and drug delivery systems. The drugs very poorly soluble in water, antidyslipidemic atorvastatin and antihypertensive valsartan were intercalated into Mg-Al LDH using a restacking procedure (Zhang et al., 2016); the drugs dissolved in ethanol were added to aqueous dispersion of LDH nanosheets, prepared by coprecipitation of Mg and Al nitrates in aqueous ammonia solution. The products with surprisingly high drug loading (75.8 wt.% of atorvastatin and 43.7 wt.% of valsartan) were obtained. The increase in d_{003} basal spacing from 0.876 to 3.808 and 2.068 nm in the LDH intercalated with atorvastatin and valsartan, respectively, confirmed the drugs intercalation.

The computational modeling applying the force field methods was used to calculate the most probable arrangement of the interlayer components at the atomic scale through energy minimization. The models showed good agreement with experimental results (powder XRD, FTIR, and solid-state NMR) and confirmed weak electrostatic interactions between LDH layers and terminal carboxyl groups in the drug molecules, together with bonding between the valsartan tetrazole rings and the LDH layers.

The intercalation of drugs into LDH host slightly affected their back-release in aqueous media. The measured release profiles corresponded to the pseudo-second-order kinetics, indicating the intraparticle diffusion as the rate-limiting step.

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Clay as a traditional raw material for earth buildings in Austria

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In some parts of Austria, Hungary, Slovakia, and the Czech Republic clay was one of the most frequently used building materials, at least until the 20th century. Many farmhouses and farm buildings were built using different earth construction techniques.

From the geological point of view, in the Eastern part of Austria (the Vienna Basin and the Molasse Zone) huge areas of Tertiary clay and Quaternary loess deposits are the raw materials known for local earth building traditions. The mineralogical composition of the clays has a strong influence on local building techniques.

Properties of raw material used for building purpose are certainly a crucial aspect in understanding a technology applied at historical building structures. Type and quantity of clay minerals affect the physical behavior of clay as a building material, for example, by its capability to balance and store humidity, to swell and shrink, or to bind other minerals and fibrous organic components.

Mapping of historical earth buildings gives a useful overview of existing earth buildings. This so-called “Lehmbaukataster” is an important basis for comparative earth building observations (Schauppenlehner et al. 2021).

The most widespread type of wall construction found in Austria used adobe bricks. In older buildings, earth lumps and cob walls can also be found in many parts of Austria. Rammed-earth walls are lacking in the Weinviertel, because of the excellent fine-grained raw material, poor in coarser fractions.

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The effect of the occupancy of the octahedral sites on the mechanochemical stability of smectites

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The effect of the configuration and composition of the octahedral sheet on the mechanochemical stability of different smectites, both trioctahedral (natural and synthetic hectorites, Hc, and saponite, Sp) and dioctahedral (montmorillonites, Mt) subjected to a short period of high energy grinding (HIG) was evaluated. The higher extent of amorphization for dioctahedral than for trioctahedral smectites was confirmed from the results obtained from XRD analysis, infrared and MAS NMR spectroscopy. After extensive grinding, ^{29}Si MAS NMR spectra indicated transformation of the Si-tetrahedra from a layered structure (Q^3 sites) to Si-tetrahedra in a threedimensional network (Q^4 sites). However, the Q^3 signal still dominated the spectra of trioctahedral samples, rather than the Q^4 signal that indicates formation of an amorphous phase. ^{27}Al MAS NMR spectra confirmed the transformation of the octahedral Al_{oct} and tetrahedral Al_{tet} present in the layered structure of Mt into an amorphous phase containing both Al_{tet} and Al_{oct} coordination. FTIR spectra of the unground samples showed the presence of absorption bands associated with OH groups attached to octahedra with Mg atoms in the central positions, while none of the bands attributed to structural OH groups in Mt could be seen in the spectra after grinding. The ^{1}H NMR spectra exhibited strong signals of structural OH after 6 min of grinding for Hc and Sp. Similar trends were seen in the DTG and H_2O mass profiles for the dehydroxylation step: the peaks attributed to structural OH groups were not observed in Mt after treatment, while they were still detected for both hectorites and saponite.

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Illite morphologies in aeolian Rotliegend sandstones: insights into the stability and clogging of particles during high-pressure flow-through experiments

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In porous sandstones, illite growth leads to significant modifications of the initial pore system. Reconstructing these changes provides information not only on the porosity-permeability evolution during diagenesis but also on the type, abundance and shape of illite particles that might be mobilized during fluid flow.

In the present study we present a comprehensive characterization of illite morphologies found in the Upper Rotliegend Flechtingen sandstone and investigate their behavior in flow-through experiments at differential pressures of up to 20 bars. Structures were analyzed using high-resolution SEM and 3D focused ion beam reconstructions. Polytype analysis and quantifications were conducted using TEM in combination with selected area electron diffraction (SAED) and powder XRD Rietveld analysis.

Based on Peltz et al. (2022), three different textural types of diagenetic illites can be recognized within the sandstone, which are: (1) altered and illitized feldspars including illite meshworks, (2) tangential illites and (3) pore-filling laths. However, it is mainly the youngest generation of lath-shaped crystals that are mobilized during high-pressure flow-through experiments. The dissolution of calcite likely enhanced this mobilization, which results in haystack-like illite accumulations and clogging of narrow pore throats. Particle size analyses of lath-shaped crystals show mean lengths of 4 μm and log-normal distributed widths that peak at 0.16 μm. TEM analyses further reveal that these laths are exclusively trans-vacant $1M_{tv}$ illite and contain no intercalated smectite layers as opposed to the disordered $1M_d$ illite that occurs as grain coatings and within altered feldspars.

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Sorption of diclofenac from aqueous solution using organo-smectites

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The widespread use of various pharmaceutical and drug compounds around the world is leading to serious environmental pollution of water resources. Clay minerals serve as a framework for the intercalation of various organic compounds. Interactions between clay minerals and organic substances lead to the formation of a dispersed organic and inorganic component formating organo-clays for preparation of sorbents with capability of the selective sorption for neutral, nonpolar organic compounds and anions, either they are contaminants or natural substances, not excluding pharmaceuticals. The objective of this work is design and preparation of different organo-smectites and the assessment of their ability for the removal of analgesics from aqueous solutions. The smectitic clays like montmorillonite (MMT), hectorite (HEC), beidellite (BEI) and nontronite (NAU) were used in both unmodified and cetylpyridinium bromide (CP) modified form as potential sorbent for diclofenac (DC). X-ray diffraction confirmed the intercalation of organic substance into interlayer by calculating the values of the basal spacing. The basal spacing of samples significantly increased indicating location of CP cations between layers. Thermal analysis exhibited, that organic modification generally caused changes of the temperatures of dehydratation, dehydroxylation and total melting processes during heat treatment. The adsorption of DC from aqueous solution according to smectite type follows the order MMT-CP > NAU-CP > SHC-CP> BEI-CP. Sorption experiments demonstrated excellent ability for DC removal up to 90 % for all smectites.

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Palygorskite and TiO_2 interactions by molecular simulations

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TiO_2 is frequently applied in photocatalysis applications because it is cheap and environmentally friendly material with very good photocatalytic properties. Nevertheless, the anatase (prefered crystal structure) nanoparticles have tendency to aglomerate which cause decreasing of catalysis efficiency. To avoid agglomeration we can use the fibrous clay minerals like palygorskite to anchor TiO_2 particles on its fibers. This cause that photocatalytic properties are preserved due to the strong mutual interactions between TiO_2 and clay.

Palygorskite–TiO_2 nanocomposites were prepared and characterized by various experimental techniques (X-ray diffraction, Fourier transform-infrared spectroscopy and transmission electron microscopy), while their mutual interactions including probable spontaneous bonding between clay and TiO_2 sphere were calculated by molecular simulation methods. Three various supercells of palygorskite with different type of surface were built, which were subsequently calculated with the TiO_2 sphere with suitable adjacent surfaces.

The simulations showed that optimal TiO_2-palygorskite connection takes place among the Ti atoms of the curved TiO_2 part of sphere with the O atoms from the surface of palygorskite via strong electrostatic interactions and the possible creation of covalent bonds. The results, calculated by molecular simulations, are in a good agreement with transmission electron microscopy data. Due to the simulation we can see the detailed curved part of anatase with Ti atoms which closely interact and are connected to the O atoms on various surfaces of palygorskite (Mavrikos et al., 2021).

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The mechanisms of V(V) interactions with Mg/Al and Mg/Fe LDH with various interlayer anions

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Layered double hydroxides (LDHs) have maintained enduring popularity in many areas of science. The multitude of possible applications makes the structure of these materials more and more studied. The brucite-like layers of LDHs and their interlayer show large variation in their chemistry. Thus, it is essential to get insight into layer-anion and surface interactions of LDH. Interactions between LDHs and the V(V) anionic form are important because of the LDHs application as adsorbents for the treatment of V(V)-containing industrial waters. Moreover, the V(V)-intercalated LDHs show promising activity as catalysts. Therefore, in this work, the mechanisms of V(V) adsorption on Mg/Al and Mg/Fe LDH with different interlayer anions (carbonates, sulfates) were studied.

The materials were obtained via the co-precipitation synthesis. Their maximum adsorption capacity and kinetics of V(V) removal were tested. Depending on the brucite-layer and interlayer chemistry, discrepancies of V(V) removal efficiency and rate were observed. However in all cases the results showed a good fit to the Langmuir isotherm and pseudo-second order equation indicating the chemisorption. The non-electrostatic model (NEM) was applied to the results of potentiometric titration of the materials and the adsorption edges calculations based on the pH-dependent adsorption experiment. The NEM model showed a different number of active sites for the materials and indicated formation of monodentate vanadium complexes. The latter dominated on the LDH surface after the adsorption process. Solid-state analyses confirmed the presence of V on the surface of the materials after experiments. In particular the XPS enabled to distinguish the oxidation state of vanadium and confirmed a partial dissolution of the materials which was in line with the chemical analysis.

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Bulk emplacement of high compacted Westerwald bentonite in a large-scale experiment for shaft sealings in underground mining

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In the Westerwald clay mining area, more than one million cubic meters of altered basaltic tuff stones and volcanic ashes overlay kaolinitic-illitic ceramic clays. These altered volcanic materials have been transformed into bentonites with smectite contents up to 90 percent. According to XRD analysis, the smectites are mainly dioctahedral. In spite of the low performance in swelling volume, recent studies show that the Westerwald bentonites in their natural calcium form are able to present an impressively high swelling pressure of up to 17.5 MPa by dry density of 1.84 t/m³ (Emmerich et al., 2019) which even exceeds the well-known Bavarian bentonites. Therefore, some bentonites with high smectite content were singled out, further developed and established as a new product under the brand **Secursol® UHP**. **Secursol® UHP** is used in several research studies for underground seals in mining industries and nuclear waste repository research. Laboratory research studies have shown that even by usage of 4 mol/l sodium chloride solution the swelling pressure is exceeding 1.0 MPa by dry density of 1.45 t/m³. This is the minimum swelling pressure required for shaft seals in potassium salt mining.

In 2020 two shafts in Saxony-Anhalt, Burggraf and Bernsdorf have been sealed in practice as a pilot project. Therefore, about 200 mt of **Secursol® UHP** have been produced and stowed pneumatically to emplace the material underground. Adjustment of production process was necessary to achieve residue moisture less than 11%. The grain size distribution of **Secursol® UHP** has been optimized close to the Fuller curve. Compacting the material underground was necessary. Finally, dry densities between 1.45 and 1.49 t/m³ have been realized in practice. Contrary to similar sealing projects with high density bentonite this was the first large scale project with pneumatically bulk emplacement of pure bentonite underground achieving such high densities.

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Ab initio thermodynamics study of the $MgCO_3$ formation

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The process of CO_2 capturing by advanced materials based on the clays and other inorganic structures has been intensively studied recently. Green technologies are an essential tool for the sustainability of a healthy environment.

Knowing the thermodynamic quantities (e.g., enthalpy, Gibbs energy) of the ongoing reactions at the formation of the final products for capturing CO_2 gas is crucial for the green technological processes.

Presented *ab initio* thermodynamics study of the $MgCO_3$ formation by theoretical approach uses DFT method in solid state implemented in VASP program package (Kresse&Hafner) to obtain these quantities and supply thus experimental study of $MgCO_3$ formation.

Theoretical results complement the experimental data of CO_2 sorption on porous clay-derived composites based on trioctahedral hectorite (Laponite RD) enriched into highly distributed nanostructured MgO species showing affinity to CO_2 molecules. The strength of developed basic centers and stability of the formed moieties will be discussed.

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10th Jubilee Mid-European Clay Conference

Argillitization mediated trace-element mobility during felsic tephra eogenesis

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Paleoenvironmental conditions of trace element enrichment or depletion during alteration of pyroclastic material in aqueous systems are readily preserved in marine and lacustrine bentonites. Considering a plethora of alteration assemblages in tuffs a careful comparison of fresh tephra with its alteration products may provide valuable clues on trace-element compositional variability. Sampling fresh and altered tephra from separate localities followed by a whole-rock geochemical analysis of collected material was heretofore a common approach in such investigations. This however involves relatively large amounts of material while failing to avoid artifacts of detrital contamination.

This contribution aims to reconstruct trace-element mobility trends by analyzing spatially linked fresh volcanic glass shards and clay minerals from a single sampling site (Badurina & Šegvić, 2022). Analyzed samples were sourced from partially altered Miocene tephra deposits of the Dinaride Lake System (Badurina et al., 2021). Representative material – thin-section glass shards and clay fraction concentrates – was analyzed by laser ablation inductively coupled plasma mass spectrometry. Resulting data revealed small volumes of clay fraction (i.e. ~50 mg) that successfully produced meaningful trace-element geochemistry, which was subsequently compared with the composition of glass shards to reconstruct trace-element mobility patterns.

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Application of Clay Minerals to Energy Storage

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The clay minerals as layered materials are being interesting candidates for many applications, where energy storage is one of the very advanced one. The silicate layers and interlayer gallery represent prototype for many advantageous modifications for utilization in various parts of battery components. 2D clays could provide sufficient intercalated sites and outstanding charge storage ability, which result in large contact area between the electrodes and electrolytes and short ion transportation pathways. The important physical properties of clays as separators and electrolytes are their ionic conductivity and porosity. The high ionic conductivity could boost the transportation of lithium ions and decrease the interfacial resistance. The superior porosity could increase the electrolyte uptake and maintain sufficient charge carriers between the electrodes, further improving the cycling stability. Application clays silicate layers and their properties are going to be described in spite of useful properties in relevance to environmental aspects (Martynková.et al.2022). The clay minerals represent materials that can be considered for green chemistry technologies in energy storage, since they are not harmful nature (Pakseresht.et al. 2022).

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Clay Conference

New aspects of kaolinite intercalation by NIR spectroscopy

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It is well known that only a few molecules such as hydrazine, DMSO, NMF, etc., spontaneously intercalate the interlayer space of kaolinite by disrupting the dense H-bonding network that holds the asymmetric neighboring layers together. The present work reviews the first systematic N-methylformamide (NMF) intercalation study of three kaolinites (KGa-1b, KGa-2 and Hywite) by vibrational spectroscopic monitoring as a function of temperature. Sealed slurries of kaolinite with 5x excess NMF were measured *in situ* by FT-NIR while intercalating over long time periods (up to 1 week) and in the 5-150 °C temperature range.

Kinetics studied in the 25-80°C range were symmetric sigmoidals in the logtime scale with steepness unique for each kaolinite. Interlayers/crystallites switched from the pristine to the fully intercalated state, as in XRD. The sigmoidals were attributed to the temporal distribution of intercalation events. The amount of non-reactive kaolinite was considerably larger than previously estimated (Andreou et al., 2021).

Increasing temperature accelerated the reaction but decreased the final NMF uptake, which almost vanished at temperatures above 100°C. Complementary thermogravimetric analysis (TGA) confirmed this unexpected trend. All kaolinites exhibited the same behavior, but the amount of inert material at any temperature was in the order: KGa-2>Hywite>KGa-1b. Subjecting the samples to stepwise temperature changes showed that once intercalated, NMF could not deintercalate and was removed from the equilibrium with the surrounding fluid.

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10th Jubilee Mid-European Clay Conference

Fixation of cesium by dioctahedral swelling clays

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The objective of the present study was to investigate the potential fixation of Cs by a set of dioctahedral clays having different mean layer charges and to evaluate the influence of the charges onto the fixation.

Over 20 clays including the Clay Minerals Society standards standards and natural soil clays were used in the study. Starting – (i.e. Na-pre-saturated clays) were first saturated with cesium (Cs) and split into two portions from which one was immediately (i.e. without drying) re-saturated with Na (CsNa-samples) while the second one was dried, re-dispersed and re-saturated with Na (CsdNa – samples). The degree of Cs fixation by the clays studied was evaluated using X-ray diffraction (XRD) and electron-induced X-ray energy dispersive spectrometry (EDS). Mean layer charges (LC) of studied samples were determined using OD – method.

All studied CsNa samples except for three montmorillonites having the lowest absolute LC values showed significant fixation of Cs under wet conditions (i.e. without drying of Cs-saturated samples). In the case of all studied soil clays and in the case of two beidellites more Cs was fixed in samples which were dried before being re-saturated with Na relative to the samples which were Na-re-saturated without drying. No significant change of Cs-fixation was observed between CsNa and CsdNa samples for other beidellites and for all studied montmorillonites. In most cases fixation of Cs caused reduction in the mean absolute LC values, as both CsNa and CsdNa samples gave lower absolute LC values than the starting Na-saturated clays. The degree of observed Cs-fixation seemed to be controlled by both the LC values and the LC location. Cs - fixation potential of high charge smectites and vermiculites is high enough to consider the clays as potential materials for decontamination of radio cesium-contaminated waters.

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Perchlorate pollutants adsorption by tetrahexylphosphonium-modified beidellite clay – theoretical and experimental research.

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Hexavalent chlorine, Cl(VI), belongs to the group of hazardous and toxic contaminants detected widely in many food products in surface and groundwater sources (Shi et al., 2007). Contamination by oxyanions consisting of Cl(VI), ClO_4^-, is caused due to the discharge of its salts, which are found in extensive applications (Motzer, 2001). In addition, inside the human body, ClO_4^- anions can affect the thyroid gland of mammals, disrupting thyroid hormone production and metabolism of the human body (Logan, 2001). Therefore, the presented work investigates the adsorption of toxic Cl(VI) oxyanion species into the interlayer space of tetrahexylphosphonium-modified beidellite (THP-Bd) with a theoretical (DFT-D3 method) and experimental approach.

This research aims to provide detailed information about the structure of studied systems, their stability and hydrogen bond interactions to anchor the toxic perchlorate anions into the interlayer space of the THP-beidellite system. Moreover, the calculated vibrational modes using *ab initio* molecular dynamic were analyzed in detail and compared with measured FTIR spectra. Finally, the calculated projected vibrational density of states was used to identify the individual vibrational modes and overlapped bands in the measured FTIR spectra.

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10th Jubilee Mid-European Clay Conference

Effect of silica fume - metakaolin combination on the thermal stability of cement pastes under hydrothermal conditions

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Stability of phases formed in cementitious systems at higher temperatures and pressures significantly influence the properties of materials, and thus the lifetime of geothermal wells. Besides external conditions (temperature, pressure, geothermal water), the composition of initial materials and especially the CaO/SiO_2 (C/S) ratio belong to the most important factors affecting an equilibrium state. The decrease of the C/S ratio is the possibility how to partially prevent undesired transformations of primary hydration products under hydrothermal conditions (Richardson, 1999).

In the present study, Portland cement Class G was substituted by 30 mass% of silica fume (SF) and metakaolin (MK) and submitted to hydrothermal curing (150 °C, 18 MPa, 7 days). Phase composition in relation to compressive strength (CS) was investigated by X-ray diffraction, Fourier Transform Infrared analyses in the mid-IR region, and thermogravimetric-differential scanning calorimetry.

The highest amount of C-(A)-S-H phases with the highest polymerization degree, including thermally stable tobermorite, hibschite, and katoite, and the highest CS were determined when SF and MK were used in the same amount. The higher content of MK led to the deceleration of reactions caused by the worse dissolution of MK due to the high content of Al^{3+} in pore solution and the availability of water-filled pores accessible for hydrates precipitation. Lower amounts of products resulted in the deterioration of CS. Hydration products of unblended paste underwent transformations resulting in the higher condensation degree and decreased CS.

Acknowledgments

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Study of hydration of alkylammonium and alkylphosphonium-based organo-montmorillonites using near-IR spectroscopy

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Organo-montmorillonites (O-Mts) are attractive inorganic-organic hybrid materials used in numerous industrial applications. In this work the adsorption of water on montmorillonite saturated with alkylammonium and alkylphosphonium cations, tetramethyl-(Me4-N/P$^+$), tetrabutyl-(Bu4-N/P$^+$) and tetraoctyl-(Oc4-N/P$^+$) was studied by NIR spectroscopy and gravimetric analysis.

With increasing degree of hydration a gradual increase of the intensities and broadening of the $2\nu H_2O$ and $(\nu+\delta)H_2O$ bands was observed. The combination band of water molecules $(\nu+\delta)H_2O$ near 5250 cm^{-1} provided information about the water content and the impact of the organic cations on the strength of H-bonds in the organo-montmorillonites. With increasing degree of hydration a shift of the $(\nu+\delta)H_2O$ band to lower wavenumbers indicated a growth of the water molecules bonded with stronger H-bonds.

Displacement of the $2\nu CH_3$ band to higher wavenumbers with increasing RH, observed for Me4-N/P-Mts and Bu4-N-Mt, provided the evidence that water molecules directly interacted with methyl groups of Me4-N/P$^+$ and Bu4-N$^+$ cations. NIR spectroscopy together with gravimetric analysis showed that the amount of adsorbed water decreased in the direction Me4-N/P-Mts ⟹ Bu4-N/P-Mts ⟹ Oc4-N/P-Mts due to the increasing hydrophobicity of the Mt surface after the exchange of the inorganic Na$^+$ cations with organic cations of different size. Both methods revealed a higher hydrophobicity for O-Mts saturated with alkyl-phosphonium cations compared to their alkyl-ammonium counterparts. Comparable results obtained by NIR spectroscopy and gravimetric analysis proved that the area of $(\nu+\delta)H_2O$ band reasonably reflected the hydration of the organo-montmorillonites. The obtained results showed that NIR spectroscopy is a very useful method for the characterization of the hydration of organo-montmorillonite.

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Characterization and application of glauconite as catalyst for the formulation of high octane fuels

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This research was focused on the catalytic conversion of low-octane fractions in gasoline using such natural catalyst as iron-rich (Fe = 11% wt.) glauconite.

Glauconite from a glauconite sand mine in Bystryca (Khmelnitsky region, Ukraine) has been applied in the study. The mineralogical composition of used sand was determined using X-ray diffractometry. The quantitative composition was estimated based on the relative intensities of the diffraction lines and on the results of the analysis of artificial mixtures of pure quartz and glauconite: glauconite - 75%; quartz - 20%; feldspar - 4%; carbonate - 1%. The catalytic conversion of low-octane fractions of gasoline on the thermally activated glauconite has been tested as a function of contact time by using a batch technique.

The main properties of gasoline octane number, vapour pressure and relative density were obtained by gas chromatography analysis using computing software „GAZOLIN”. A significant increase in the octane rate of treated fuels from 91.5 to 102.4 due to the catalytic conversion of olefins low-octane fractions using glauconite was found. Exhaust emissions for motor fuels were determined under different operating conditions of the engine using the Infrakar Vehicle Emissions Analyser. The obtained results for the active mode showed that CO emissions for motor fuels treated with thermally activated glauconite were reduced from 2.8 to 1.3% and CO_2 – from 13.4 to 10.2%. While in idle mode, CO emissions were reduced from 4.8 to 0.2% and CO_2 – from 12.8 to 8.6%.

The obtained results indicated that glauconite can be used as high efficiency catalyst in the production of high-quality motor fuels with lower toxicity, which will improve environmental safety.

Surface properties and thermal transformation of Al-ferrihydrite

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Ferrihydrite ($Fe_5HO_8{\cdot}4H_2O$) is a very poorly crystalline hydrous ferric oxyhydroxide common in various near-surface environments. Its high surface area, chemical reactivity and strong sorption properties make ferrihydrite an effective natural scavenger of many major and trace elements occurring in both cationic and anionic forms. Those impurities affect physical and chemical properties of the mineral including surface chemistry, thermodynamic stability and transformation pathways. One of the most common cationic admixture is aluminum. This work focused on the influence of Al for Fe substitution on surface chemistry and thermal transformation of synthetic ferrihydrite. A series of six ferrihydrites containing 0 to 50 mol% of Al were synthesized by rapid hydrolysis of Fe and Al nitrates followed by dialysis and freeze-drying. All the ferrihydrites were heated up to 1000°C in the air and both heated and unheated samples were characterized using powder X-ray diffractometry (XRD), scanning electron microscopy (SEM-EDS), simultaneous thermal analysis (STA) and infrared spectroscopy (FTIR). Specific surface area, porosity and point of zero charge were determined as well.

The results revealed relatively minor effect of Al substitution on ferrihydrite surface area and porosity, although pH_{ZPC} was shifted to more basic values. At the other hand, the increasing Al content distinctly increased temperature of ferrihydrite thermal transformation: Al-free ferrihydrite transformed to hematite (α-Fe_2O_3) below 400°C, whereas those containing Al remained unconverted at the temperature as high as ca. 500–750°C, depending on the Al/Fe molar ratio. Transformation pathways and the properties of the products were affected as well. Low-Al ferrihydrites (5–10 mol%) directly transformed to hematite, whilst transformation pathways of high-Al (20–50 mol%) ferrihydrites appeared more complex. In all cases the final product of thermal transformations was hematite, whose crystallite size and unit cell dimensions decreased with growing Al substitution. Heating of the high-Al ferrihydrites (20–50 mol%) resulted in crystallization of Fe-bearing corundum (α-Al_2O_3) and mixed $Al_2Fe_2O_6$-like oxides besides (aluminous) hematite.

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Molecular mechanisms of Ni and Lu adsorption on saponite edge surfaces

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Adsorption on clay minerals is a key process for the immobilization of hazardous metal contaminants in natural or constructed repository systems. Quantitative assessment of risks associated with it relies on a detailed understanding of the adsorption mechanisms and, hence, developing a robust and reliable predictive transport model. The existence of high- and low-affinity adsorption sites on smectites edge surfaces, responsible for metals uptake has been revealed in previous studies (Bradbury & Baeyens, 1997, Dähn et al., 2011). Despite decades of research, the exact molecular nature of these adsorption sites has not been fully resolved.

XAS characterization and ab initio MD modeling were applied to reveal Ni and Lu adsorption mechanism on saponite. Existence of strong and weak sites for both elements was confirmed. Nickel surface complexes resemble octahedral structural position at the edges of smectites. Lutetium occupy structurally different sorption sites requiring further characterization. At least two Li complexes were detected with with CN>6. Neoformation of Ni hydroxide like phase at the saponite edge surface was observed at the loading above 40 mmol/kg. Additionally, It was determined that Ni can be incorporated in the course of recrystallization, while Lu – can't.

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Mineral alterations in buffer materials from the 5th "hot bentonite" experiment in the Äspö Hard Rock Laboratory, Sweden

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The performance of bentonite barriers are currently being tested on pilot sites for sealing high-level radioactive waste repositories (Sellin & Leupin, 2014), but the degree of mineral stability under enhanced thermal conditions remains a topic of debate. In this study, we investigated the Alternative buffer material test-5 (ABM5) conducted by the Swedish Nuclear Fuel and Waste Management Company (SKB), which lasted for five years (2012 to 2017), and reached locally a maximum temperature of 250 °C (Kaufhold et al., 2021). Five bentonites were investigated by X-Ray diffraction (XRD) analysis and Rietveld refinement, Scanning electron microscopy (SEM) with Energy dispersive X-ray analysis (EDX), and by measuring the pH, cation exchange capacity (CEC) and exchangeable cations. Samples extracted from bentonite blocks at 0.1, 1, 4 and 7 cm away from the heating pipe showed various stages of alteration related to the horizontal thermal gradient. The bentonites near the contact that had lower CEC values exhibited smectite alteration with tetrahedral substitution of Si^{4+} by Al^{3+} and some octahedral metal substitutions. These alterations were probably caused by iron corrosion adjacent to the heater during oxidative boiling. Pyrite dissolution and increased acidity also occurred in some bentonite layers close to the contact. This alteration was furthermore associated with higher amounts of hematite and minor calcite dissolution. Despite these alteration features, the bentonite sealants are considered to have remained largely intact, as none of the bentonites showed any smectite loss and the documented reactions impacted only the heater–bentonite contact.

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Diagenetic reorganization of weathering hematite crystallites

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Hematite, a common component of sedimentary rocks and important carrier of magnetic signals, originates mostly from the erosion of lateritic tropical soils, and/or from the lateritic-type weathering of sediments *in situ*. During burial diagenesis this sedimentary hematite undergoes structural reorganization, recorded by significant changes of its powder X-ray diffraction (XRD) patterns. The aim of this study was to investigate mechanism of this process, using the Ediacaran rocks from the East European Craton as the main sample material.

The results indicate that hematite crystallizes during weathering, predominantly as plates ca. 10 nm thick and 40 nm across on average, with lognormal distribution of crystallite thicknesses. Evolution of XRD peak shapes of hematite in the course of diagenesis was explained by the growth of hematite crystals mainly in the [001] direction.

Along with the growth of crystallites, a decrease of micro-strain in [100] and [010] directions was observed. It can be related to a low micro-strain in the newly formed parts of crystallites, to the dissolution of part of older crystallites, and perhaps also to a decrease of micro-strain in older hematite.

Modelling of crystallite size distributions in [104] direction indicates that diagenetic growth mechanism is the surface/supply-controlled growth mixed with random ripening. Therefore, some hematite crystals from the weathering stage can be retained in the diagenetically altered rocks, preserving their original magnetic signals, and younger magnetic signals can correspond to the newly formed diagenetic hematite.

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Late diagenetic alteration of non-evolved glauconite from the Ediacaran and Cambrian sediments of the East European Craton

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The Ediacaran/Cambrian green globular particles suspected to contain glauconite were separated from the Ediacaran/Cambrian sediments of the western part of the East European Craton (Baltica) and characterized by XRD, in order to identify pure glauconite samples suitable for radiometric dating. All pure samples gave strongly rejuvenated, Paleozoic K-Ar ages, slightly older than ages of Proterozoic illite-smectites from the same area, investigated by Derkowski et al. (2021). The XRD characteristics, boron contents, and boron isotope compositions of pure glauconite samples were compared to younger glauconite samples of strictly stratigraphic ages, and also to younger glauconite samples with rejuvenated ages. It was established that the rejuvenated samples differ from the stratigraphic samples by XRD characteristics. Their 060 reflections are broader and displaced towards higher angles, an indication of chemical heterogeneity (layers with variable Fe contents). Other differences are lower boron contents and more extreme compositions of boron isotopes. These data combined are indicative of the mechanism of burial diagenetic alteration of glauconite: the growth of glauconite layers with lower iron contents at the expense of Fe-smectite layers present in the original glauconitic mineral crystallized during sedimentation. This mechanism is responsible for the chemical heterogeneity observed in many glauconite samples.

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10th Jubilee Mid-European Clay Conference

Correlation of illite Kübler indices and results of Raman spectroscopy of carbonaceous material from metasedimentary rocks from NW Croatia

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The Kübler index (KI), i.e. the width (in Δ°2θ) of the illite 001 diffraction peak, as determined by X-ray diffraction on the <2 μm clay fraction, and Raman spectroscopy of carbonaceous material (RSCM) were used to distinguish the peak metamorphic temperatures of rocks from NW Croatia, previously considered to be non-metamorphosed. The analyses were performed on the Late Paleozoic black shales belonging to the northwesternmost part of the Internal Dinarides sampled in the Samobor-Žumberak Mountains and the Marija Gorica Hills, and on the Triassic (Upper Ladinian) carbonaceous dolomites belonging to the post-Variscan Alpine overstep sequences of the Tisia Mega-Unit found in the western part of the Papuk Mountain. The study was carried out within the frame of a wider investigation of low-grade metamorphic rocks in northern Croatia to explain some inconsistencies in the KI values obtained so far.

A total of 12 rock samples, including 3 dolomite samples rich in organic carbon, were used to correlate the measured KI values with RSCM temperatures. XRD analysis of the Late Paleozoic black shales shows a dominance of illite, accompanied by chlorite. The KI values obtained range from 0.29 to 0.35 Δ°2θ, indicating that the black shales underwent anchizonal thermal alteration. The clay minerals in carbonaceous dolomites are illite and kaolinite. The KI value of 0.62 Δ°2θ indicates a diagenetic alteration.

Raman spectra of organic material extracted from black shales show an estimated peak temperature in the range 275-285 °C, consistent with the KI values. In contrast, the Raman data from dolomite samples (285°C) contradict the diagenetic KI value, implying that the organic material in carbonaceous dolomites could be detrital. However, the KI of the surrounding rocks in the western part of Papuk are in agreement with the anchizonal metamorphism. Further analyses are required for a better understanding of the thermal history of the studied area.

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Bentonite, perlite and kaolinite-rich zones in the Lutila I bentonite deposit, the Western Carpathians, Slovakia

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With an annual production of about 250 kt of bentonite, Slovakia belongs to the TOP 10 world producers. The most important bentonite deposits in Slovakia are in the Central Slovakia Volcanic Field, where they associate with rhyolite volcanics in the southern part of Kremnické vrchy Mts. The aim of the contribution is to characterize samples from recently discovered perlite and kaolinite-rich zones from one of the largest bentonite deposits in Slovakia - Lutila I and compare the mineralogy and chemical properties of mined bentonites from the Kremnické vrchy Mts. (15 samples from 6 deposits). A detailed lithological-petrographic analysis found that perlite is the dominant parent rock for bentonites. The highest Al-Mg montmorillonite content in bentonite from the Lutila I deposit, and two other deposits is from 70 to 80 wt.%. Admixtures of perlite and kaolinite decrease the quality of the bentonite. On the other hand, presence of high volume of both could be interesting as source of the other industrial minerals. Bentonite, perlite and kaolinite-rich zones are clearly bounded without a significant gradual transition between these three phases in the Lutila I deposit. Perlite was described as light grey, crumbly, porous glassy rocks with porphyritic texture containing 70-80 wt.% of volcanic glass, about 20 wt. % sum of non-clay minerals (feldspars>quartz) and 4-0.3 wt.% of clay minerals (montmorillonite>kaolinite). The higher number of phenocrystals in the primary perlite has a partial limitation for the quality of the perlite itself and also for the bentonite due to the dominant alteration of the volcanic glass only. Kaolinite-rich zones contain 40-50 wt.% of kaolinite, 30 wt.% of opal-C/CT and again about 20 wt. % of feldspars and quartz.

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FT-IR spectroscopy and TG/DTA as a tool for characterization of clay mineral mixtures

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Clay minerals belong among the most widespread minerals in the earth's crust rock system. Clays, and in particular mixed layered or interstratified clay minerals, are generally mixtures of predominantly clay mineral together with a minor amount of other clay minerals, wherein the ratio of the components determines the final properties of these materials. The widely common method used for the qualitative and quantitative phase analysis is X-ray powder diffraction. Whereas the mineral identification is quite simple and unambiguous, accurate quantitative analysis, especially for clay minerals, is still rather complicated due to varying chemical composition and frequent structural defects together with very small particle size. Therefore, the aim of this study is focuses on FT-IR spectroscopy and thermal analysis and their contribution to the identification of clay minerals in clay mixtures. From the results of both methods is evident, that kaolinite is the most reliable detectable mineral. FT-IR spectroscopy allows detection of 1 wt.% of kaolinite in admixture with chlorite, while thermal analysis allows detection of 3 wt.% of kaolinite in admixture. In case of montmorillonite and chlorite, the identification by FT-IR spectroscopy shows detection limit only 30 wt.% in contrast to TG/DTA with the detection limit of 5 wt.% for montmorillonite and 5 wt.% or 10 wt.% for chlorite. The differences in detection limits for all tested minerals are attributed to both more or less overlapping absorption bands in the infrared spectra for clay minerals and overlapping thermal effects of clay minerals or thermal effects related to accessory minerals (calcite, quartz etc.) in DTA curves. The obtained results can be effectively used to solve problems in identification of clay minerals in sedimentary rocks, which is very important for subsequent applications in geological, geochemical and geomechanical mining activities.

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Inorganically modified smectites for environmental applications

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Smectites represent promising starting nanomaterials for the design and preparation of multifunctional eco-friendly clay composites with predefined properties and a wide range of environmental applications. In this work, composite materials based on montmorillonite/manganese dioxide (MMT/MnO_2) were synthetized by chemical treatment of clay matrix. Advanced techniques including XRD, XRFS, FT-IR, TG/DSC, SEM and N_2 adsorption/desorption were used for detailed physico-chemical characterization of obtained composites. The MMT/MnO_2 composites exhibited specific surface area ranging from 80 to 116 m^2/g and mesoporous texture. MnO_2 component formed in a presence of a clay matrix appeared as cryptomelane with a tunnel structure. The prepared materials were tested for their potential use as effective catalysts for the oxidation of volatile compounds and also for their application as effective sorbents for the removal of pharmaceuticals from wastewater. The obtained MMT/MnO_2 composites showed catalytic activity on model compounds of ethanol and toluene, sorption properties on selected antibiotics (ampicillin and amoxicillin) and higher thermal stability. Textural properties of MMT/MnO_2 samples facilitated the dispersion of the catalyst active phase and their high specific surface area enhanced their catalytic effects. Sorption experiments have demonstrated the ability to remove up to 90% of ampicillin and amoxicillin.

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Talc modified by milling and alkali activation: physico-chemical characterization and application in base catalysis

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Due to the ever-growing pressure to develop new, more environmentally benign materials for industrial purposes, solid base catalysts gained attention as an alternative for presently used liquid bases. The concept of using cheap and abundant natural silicate minerals as a source of solid bases represents a particularly attractive and cost-effective option. Talc, a 2:1 phyllosilicate, with structure built of layers consisting of an octahedral Mg-based sheet sandwiched between two tetrahedral Si-based sheets, is a magnesium-rich silicate with base properties. However, talc is characterized by a very low specific surface area (SSA), which limits its potential in catalysis. It is known that appropriate grinding of talc results in an increased SSA. Further modification of talc-derived ground materials with alkaline media should cause leaching of silicon from talc structure, the effect expected to enhance both the basic properties and the SSA, features important for catalytic applications.

Thus, activation of talc by means of grinding in a planetary mill cojoined with, or followed by treatment with alkaline reagents was investigated, with aim to manufacture novel solid base materials. Insight into the evolution of talc composition, structure, texture and acid/base properties upon mechanochemical activation was provided by a number of physico-chemical characterization techniques. Talc-derived materials were tested as catalysts in aldol condensation of acetone and Baeyer-Villiger oxidation of cyclohexanone to ε-caprolactone.

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Influence of polymer treatment on the swelling capacity of bentonite

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Clays are widely used in various industries and for environmental protection. The most common clays used as engineering barriers are bentonites. The insulating properties of bentonite are due to the ability to swell, high sorption capacity, and low hydraulic conductivity. However, prolonged exposure to aggressive solutions can reduce swelling and increase permeability deteriorating the insulating properties. It is proposed to modify bentonites to overcome this problem. One of the most promising materials is bentonite modified with anionic polymers.

Ca-bentonite from the Cherkasy deposit of bentonite and palygorskite clays containing up to 85% of montmorillonite was used for the experiments. The clay was treated with polymers such as anionic polyacrylamide and carboxymethylcellulose (1–5% by dry weight). Modification of the clays was performed as follows. First, the bentonite suspension was activated with sodium carbonate, and then an aqueous solution of the polymer of the appropriate concentration was added, and the mixture was stirred for half an hour. Then it was dried at 120 °C and ground. The fraction of the clays of $\leq$ 100 μm was used for experiments.

A swell index test was carried out to evaluate the swelling capacity of the bentonites. 2g of bentonite were placed in a 100 ml graduated cylinder filled with 90 ml of deionised water or sodium chloride solution. Then additional part of deionised water or the solution was poured to fill the cylinder to the 100 ml. After 24 hours, the volume of swollen bentonite was measured. Experimental results have shown that the volume of swollen bentonite increases with increasing polymer content. A comparison of bentonites modified with polyacrylamides and carboxymethylcellulose showed that the latter exhibit higher swelling capacity. For example, the swell index for bentonite was 6 ml/2g, bentonite modified with polyacrylamide – 21 ml/2g, and bentonite treated with carboxymethylcellulose – 28 ml/2g. The content of the polymer was 5% by dry weight. The advantage of carboxymethylcellulose treated bentonite compared to natural bentonite was also observed in salt solutions.

Optimizing of the basic properties of porous heterostructured composites derived from laponite for CO_2 sorption

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Progressing industrialization and the development of new technologies are not inert to the environment in which we live. Accumulating evidence indicates that industrial combustion of fossil fuels has raised the greenhouse gas emission in the atmosphere, predominantly CO_2, which has been pointed to as the main cause of the gradual warming of the Earth. As a consequence, the development of new technologies for CO_2 capture, storage, and utilization will become increasingly important. Concerns about our future have stimulated us to study CO_2 capture using easily accessible layered silicates, assembled by templating method into porous heterostructured clay composites (PCH). Trioctahedral hectorite - Laponite RD - layered hydrous magnesium silicate, with a small basic character, was used as a platform for the assembled composite formation and treated with iron nitrate solution during „top-down approach" impregnation to evoke the structure rearrangement. Our previous studies showed that an acidic environment influences the release of magnesium ions from the octahedral sheet of clay minerals. The aim of this work was to modify the PCH by combining Fe doping with mechano-chemical activation (MA) and hydrothermal (H) or sequential-microwave (SM) treatment to increase the sorption properties of the parent material and generate the new basic centers with high affinity to CO_2.

XPS study supported by FTIR analysis revealed bulk/surface migration of the Mg species and changes of the structural O-H groups vibrations in Mg_3OH within octahedral sheets of Laponit due to functionalization. SM treatment contributed to the formation of highly dispersed, nanostructured moieties of MgO capable of absorbing CO_2 in two distinct coordinations. It was evidenced by the appearance of new CO_2 desorption maxima at around 110 and 180 °C on TPD CO_2 profiles attributed to the development of the weak basic centers with the strength higher than coming from the intrinsic basicity of the Laponite. The nanocrystalline character of α-Fe_2O_3 distributed on PCH due to SM radiation contributed to the CO_2 capture with strength and stability higher than MgO. This study shows that appropriate treatment of layered hydrous magnesium silicate may result in the development of the surface basicity eightfold higher than the parent material.

Influence of fulvic and humic acids on the undrained shear strength of clayey soils

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Mineral surfaces in soils and sediments, in particular those of clay minerals, are often coated with natural organic matter (OM). Such associations will affect the soil mechanical behaviour of clayey soils. For example, an increasing compressibility of different with humic acid reconstituted clays was found, based on consolidation tests (e.g., Varghese et al., 2021). Another important geotechnical property of (clayey) soils is the shear strength. The influence of OM on the shear strength, however, is hardly investigated (e.g., Plötze 2018). Additionally, previous research on this topic focused little on the composition of OM itself and the influence of the pH and electrolytes in the pore water. In this study, we prepared mixtures of two main components of OM, humic acid (HA), soluble fulvic acid (FA), and raw illite, kaolinite, Na- and Ca-bentonite. Shear strengths of the mixtures were measured with a vane shear apparatus. Results show that shear strength increases with the HA mixtures of Ca-bentonite and illite. On all other mixtures, the addition of HA or FA reduced the shear strength, mostly in a non-linear fashion. This effect cannot be explained by changes in pH or ionic strength alone. Neither can this be explained by changes in the grainsize and void ratio. At the current state of the project, we hypothesis that overall FA has a dispersive effect because of steric hindrance, probably dependent on the adsorbed amount of FA. In the case of HA, our data suggests that the type of clay mineral and their interaction with carboxylic group of HA have a deceive role on the shear strength.

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