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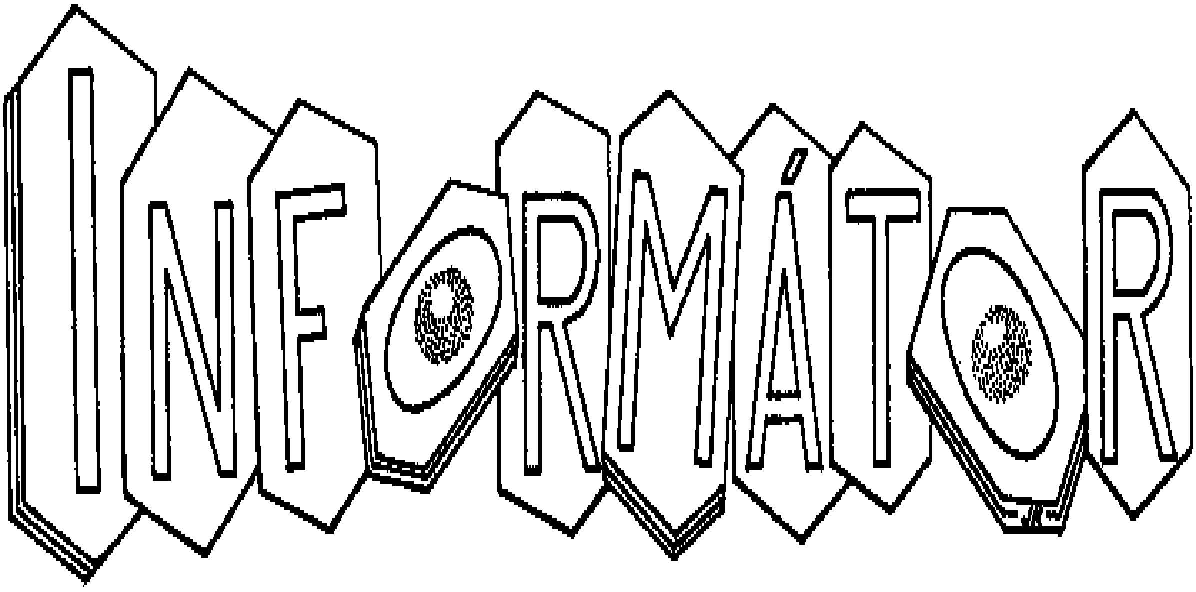

INFORMÁTOR

Book of Abstracts

Martin Šťastný and Miroslav Pospíšil (eds.)

11th Mid-European Clay Conference (MECC´24), September 15-20, 2024, Pilsen

Czech National Clay Group, Plzeň

Book of Abstracts, 11th Mid-European Clay Conference (MECC 24), Plzeň, September 15-20, Czech Republic, M. Šťastný and M. Pospíšil (eds.)

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Content

Plenary lectures

THE GEORGE BROWN LECTURE

ENGINEERED BARRIERS, THE SANDWICH SEALING SYSTEM AND THE SWELLING OF BENTONITES

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Deep geological disposal of high-level radioactive waste by applying the multi-barrier concept is a widely international consensus. The components of the engineered barrier system (EBS), that comprises buffer and backfills as well as sealings, are designed in most national concepts containing compacted bentonite. The particularities of the safety relevant properties depend on the position in the EBS. Therefore, the thermo-hydro-mechanical-chemical (THMC) behavior of bentonites has been studied since about five decades now and a lot about water in smectites and the swelling of bentonites is known. However, the swelling pressure of compacted bentonite can hardly be accurately measured or predicted. In addition, new research results require a continuous reassessment of the current state of knowledge, whereby it must be ensured that know-how from previous research is not lost.

The sandwich sealing system was developed by KIT as part of drift and shaft seals for hydraulic separation of aquifers and to block potential pathways of radionuclides between a nuclear waste repository and the biosphere. It consists of sealings segments (DS) sandwiched by equipotential segments (ES). DS are built of a binary mixture of bentonite pillows and bentonite granular material (BGM). The ES are characterized by a higher hydraulic conductivity than the DS and preferential flow paths of fluid during hydration are interrupted in ES. Fluid is evenly distributed over the cross section of the seal in the ES and available for hydration of adjacent DS resulting in homogenous hydration, swelling and sealing. The functionality of the system has been demonstrated in semi-technical tests, and an in-situ experiment is performed at the Mont Terri rock laboratory (CH) to investigate the interaction between the sandwich sealing system and a potential clay host rock. The in-situ experiment is accompanied by laboratory experiments and numerical simulations. The laboratory program includes a variety of experiments on different scales and with different model geometries that are used for development, parametrization, and evaluation of material models in numerical simulations.

The lecture gives an overview of the current state of knowledge on the structure-function relationship of bentonite swelling. The relation between fundamental smectite properties and parameters that influence the swelling of bentonite and the resulting swelling pressure will be presented based on experimental results and molecular modeling.

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STRUCTURAL EVOLUTION OF HALLOYSITE-(10Å) UPON DRYING

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Widely used halloysite nanotubes (HNTs) are derived from the dehydration of halloysite-(10 Å), the only naturally hydrated member of the kaolin sub-group. Dehydration is essentially a deintercalation reaction which takes place irreversibly at ambient temperature and relative humidity conditions. The collapse of the interlayers of dehydrating halloysite is subjected to constraints imposed by the cylindrical or polygonal nano-roll morphology of the -(10Å) parent mineral (Gray-Wannell et al., 2023).

This is a study of the 10Å to 7Å transition of cylindrical and polygonal halloysite based, for the first time, on *in situ* infrared spectroscopic monitoring over a range of relative humidities at ambient temperature. H/D exchange is employed to distinguish the various types of H_2O and OH species by their different accessibility and improve the resolution of overlapping features, also during the rehydration of the 7Å form. Infrared is combined with XRD and thermogravimetric analysis.

Analysis puts emphasis on the systematics of at least two 'defect' H_2O species which emerge upon drying and characterize the 7 Å material. One is the well-known 'hole' H_2O (Constanzo, Giesse, 1985) which persists up to ~250 ˚C, the other is assigned to H_2O in lens-shaped cavities (crevices or slits) formed amidst packets of collapsing layers. Drying splits the originally uniform in-plane Si-O stretch of halloysite-(10 Å) in two components: one with kaolinite-like ordering and the other very disordered. As a result, the as-formed halloysite-(7 Å) has an open imperfect structure. Both types of domains are present in polygonal halloysite, whereas the latter predominates in cylindrical samples. The recovery of the original ordered and expanded structure depends on 'unlocking' the kaolinite-like domains by re-intercalation: Re-expansion is possible by formamide, N-methyl formamide, and other small organic molecules, but not H_2O.

References

Costanzo P.M., Giese F.F. Jr. (1985): Dehydration of Synthetic Hydrated Kaolinites: A Model for the Dehydration of Halloysite(10Å). *Clays and Clay Minerals* **33**, 415-423.

Gray-Wannell N., Cubillas P., Aslam Z., Holliman P.J., Greenwell H.Ch., Brydson R., Delbos E., Strachan L.-J., Fuller M., Hillier S. (2023): Morphological features of halloysite nanotubes as revealed by various microscopies. *Clay Minerals* **58**, 395-407.

Strachan L-J., Fuller M., Hilier S. (2023): Morphological features of halloysite nanotubes as revealed by various microscopies. *Clay Minerals,* **58**(4), 395-407.

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ABOUT THE IDENTIFICATION OF FIXED CATIONS IN SMECTITES

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Smectites are amongst those clay minerals with an extraordinary high cation exchange capacity, also in praxis compared to higher charged minerals such as vermiculites. Exchangeable cations are mainly located in the smectitic interlayer region. The cation exchange takes place upon exposure to an excess of cations in aqueous solutions of a different type or by already adsorbed cations (e.g. McBride, 1979) such as K^+ and NH_4^+, which may be specifically adsorbed or fixed. Other typical cations in non-acidic solutions (Na^+, Mg^{2+}, and Ca^{2+}) are usually assumed as fully reversibly adsorbed.

Analytically, the cation exchange capacity (CEC) is often determined using metal-organocomplexes such as Cu-triethylenetetramine (Cu-trien) or similar complexes which are selectively bound to the surface such as Co-hexamine, silver-thiourea, or Ni-ethylenediamine (e.g. Dohrmann et al., 2012). Some smectites, however, contain interlayer cations which are not exchanged by routine CEC measurements. The concept of such “fixed cations” was introduced about hundred years ago to understand processes in soils related to agricultural use (e.g. Schachtschabel, 1937 and citations within). Schachtschabel (1941) observed that K^+ was not fixed in soil clay fractions after saturation with K^+-rich solution, however fixation started after drying, and fixation was enhanced by several drying cycles of temperatures up to 70°C.

Kaufhold et al. (2010) showed on different bentonites that some of the previously exchangeable cations (Na^+, K^+, and Ca^{2+}) could be fixed by extensive thermal treatment confirming the work of Schachtschabel who studied soil clay minerals. In 2023, the same authors tried to reverse the effect by trying to liberate some naturally present fixed cations from bentonites by extensive hydrothermal treatment (Kaufhold et al., 2023). The amount of liberated cations, such which were not exchangeable before the hydrothermal treatment, was low but measureable. Upon liberation of these cations, however, the index cation CEC values decreased which was not expected and was explained by a partial destruction of the smectite structure. This result indicates that fixed cations may be strongly bound to the smectite surface and cannot be simply liberated by hydration.

In a further attempt to investigate fixed cations, a couple of pure smectite samples were selected and three times exchanged by Cu-trien. After washing and dialysis the treated samples were investigated with respect to their chemical composition, particularly with respect to remaining Na^+, Ca^{2+}, and K^+. The highest contents of fixed cations were found for exchangeable K^+ which is not surprising because K^+ fixation is well known from illitisation experiments and explained by its´ low hydration energy which allows the K^+ to sink into the ditrigonal holes. In addition, some exchangeable Ca^{2+} was found in some samples which hence is assumed to be fixed (without knowing their exact position of residence). Analysing pure Cu-trien exchanged smectite is, therefore, one option to identify fixed cations. As in the case of the determination of the structural formula, however, possibly present minor components in the apparently pure fraction can cause a significant error. The accurate quantification of fixed cations, e.g. in bentonites, is therefore still challenging and further efforts are needed for quantification of fixed cations.

References

Dohrmann R., Genske D., Karnland O., Kaufhold S., Kiviranta L., Olsson S., Plötze M., Sandén T., Sellin P., Svensson D., Valter M. (2012): Interlaboratory CEC and ex-changeable cation study of bentonite buffer materials: II. Alternative methods. *Clays and Clay Minerals*, **60**, 176-185, https://doi.org/10.1346/CCMN.2012.0600207

Kaufhold S., Dohrmann R. (2010): Effect of extensive drying on the cation exchange capacity of bentonites. *Clay Minerals,* **45**, 4, 441-448.

Kaufhold S., Dohrmann R., Gröger-Trampe J. (2023): About the possibility to liberate naturally present fixed cations from dioctahedral smectites by hydrothermal treatment. *Applied Clay Science,* **244** 107115.

McBride M.B. (1979): An interpretation of cation selectivity variations in M^+-M^+ exchange on clays. *Clays and Clay Minerals*, **27**, 417-42. https://doi.org/10.1346/CCMN.1979.0270604

Schachtschabel P. (1937): Aufnahme von nicht-austauschbarem Kali durch die Pflanzen. *Bodenkunde und Pflanzenernährung*, **3**, 107-133. https://doi.org/10.1002/jpln.19370030105

Schachtschabel P. (1941) Die Bestimmung des Kalibedarfs im Boden. *Bodenkunde und Pflanzenernährung,* **24**, 371-384. https://doi.org/10.1002/jpln.19410240606

SERPENTINIZED ULTRAMAFIC ROCKS FROM CABEÇO DE VIDE (PORTUGAL) - LINKING GEOLOGICAL PROCESSES ON EARTH AND MARS

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Serpentines hold significant importance for the study of life on Mars as they provide evidence of past water activity, offer potentially habitable environments for microbial life, preserve organic compounds and biosignatures, and guide future exploration and sample return missions. Understanding the role of serpentines in the Martian geological and astrobiological context is crucial for unraveling the mysteries surrounding the potential existence of life on the Red Planet. Due to its accessibility and active serpentinization, the hydrothermally altered mafic-ultramafic complex of Cabeço de Vide (CdV), Portugal, provides a unique opportunity to investigate continental serpentinized rocks on Earth. CdV ultramafics are not ophiolites but are associated with the intrusion of mafic/ultramafic plutons. Our main objectives are the mineralogical and chemical analysis, as well as the bio-signatures contained in CdV serpentinized rocks and comparison of the obtained data with those of Jezero Crater, Mars. The findings of this work will provide greater context on the serpentine bodies on Earth as an important approach to understand the geochemical processes on Mars.

For this work we studied 22 core samples obtained (between 30 and 124 meters deep) from a borehole drilled on CdV. Their textural, mineralogical and crystallochemical features allowed to put forward a genetic model for the serpentinization process. Moreover, a metagenomic approach was applied targeting 16S rRNA gene in selected drill cores to identify taxonomical groups belonging to Bacteria and Archaea preserved in CdV serpentines. For this study, the following techniques were used: X-ray diffraction, petrographic microscopy, scanning electron microscopy, fluorescence microscopy, and the extraction, treatment, and analysis of the 16S rRNA gene. The obtained results confirmed the similarities in lithology between CdV and Jezero Crater, Mars, both predominantly composed of serpentinized ultramafic rocks and authigenic carbonates. The study also verified, for the first time, the presence of preserved Archea in the serpentinized rocks CdV. The exploration of serpentinization environments like CdV underscores the importance of understanding the role of serpentinization in the formation of organic compounds and the support of potential microbial life. This study stands out from all previous ones as it is the first time that the presence of the 16S rRNA gene in rock samples collected in a continental serpentinization environment at significant depths has been confirmed.

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COMBINING MOLECULAR SIMULATIONS WITH DIFFRACTION EXPERIMENTS OF INTERCALATED CLAY MINERALS

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The organization of interlayer water, cations, and organic molecules in the interlayer space of clay minerals remains a key topic in clay science. X-ray diffraction (XRD) is a commonly used methodology that allows to probe distribution of interlayer atoms. However, due to the inherent disorder of clay minerals, especially intercalated ones, this method is indirect and relies mainly on relative intensities of basal 00l reflections. Molecular simulations are thus a complementary technique that provides possible distributions of interlayer molecules, which can then be verified using XRD. Conversely, XRD can serve as a testing probe for various input parameters (force fields), which are used in molecular simulations.

Molecular simulations of intercalated water molecules in smectites have led to the exclusion of certain models used in X-ray diffraction, where water molecules were considered to occupy one or more very well-defined positions. Instead, the organization of water molecules is described using higher temperature factors, which does not correspond to the vibration of atoms (like in XRD models of crystals), but is related to their distribution in the interlayers.

Molecular simulations have been also used to describe the interlayer organization of organic molecules intercalated in smectites, such as ethylene glycol, glycerine, Co-hexammine, or Cu-triethylenetetramine. The main results were consistent with those observed for water: distributions of atoms should be described by higher temperature factors, with positions of atoms varying depending on variable basal spacing around optimal values (e.g. 17Å for ethylene glycol, and 18Å for glycerine). Additionally, molecular simulations can be used to evaluate a number of interlayer molecules. For instance, in the case of N-Methylformamide (NMF) intercalated in kaolinite, the introduction of NMF molecules leads to a decrease of the intensity of 001 reflection. Thus, it was possible to evaluate a number of interlayer molecules by combining the results of the two methods.

XRD results are also frequently used as probes of different force fields. For example, testing various organic and clay mineral parameters for studies of ethylene glycol intercalated in smectites confirmed the necessity to modify force field of clay minerals (CLAYFF). These modifications were especially related to Lennard-Jones parameters of basal oxygens, leading to their bigger effective sizes, because organic and water molecules were too close to the smectite surface without this corrections.

In this study, several applications of combining XRD and molecular simulations were examined, including either the explanation of the interlayer atoms' distribution or the XRD use as a testing probe of various molecular models.

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PERLITES, BENTONITES, AND ZEOLITES FROM SLOVAKIA - GEOLOGY, PROPERTIES AND USES

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Bentonite, perlite and zeolite are useful industrial minerals with several common features. Their origin relates to volcanic fields and they all contain significant amount of water. All of them can be used for protection and reclamation of the environment, for example they can be use as supplementary cementitious materials. They also have a long-term tradition in mining of the industrial minerals in Slovakia. They belong to the most perspective, despite their significantly lower extraction volume compared to carbonates and construction materials. The production of bentonite and zeolite increases every year and Slovakia belongs to world producers. Lehôtka pod Brehmi and Jastrabá represent exploitable perlite deposits in the Slovakian part of the Western Carpathians. Perlite water content is in range 3.0–6.0 wt.%. Slovak crude perlites include a higher amount of loosely bound, a lower amount of strongly bound water, and contain a higher ratio of K/Na when compared to other world perlites. These can be important factors that cause lower expansion of Slovak perlites. On the other hand, due to the same reason, the Slovak perlites have a better mechanical stability. In 2022, the Slovak Republic for the first time reached the annual production of bentonite over 300 kt and it has ranked among the 10 largest producers in the world. The highest-grade Slovak bentonites, containing 70-85 wt.% Ca-Mg montmorillonite, are found in the Central Slovak Volcanic Field, specifically in the Jastrabá, rhyolitic, Fm. Bentonite deposits of the Jastrabá Fm. were created mostly by bentonitization of a marginal glassy/perlitic carapace of extrusive domes/flows and cryptodomes. In addition to common bentonite deposits also the K-bentonite Dolná Ves (DV) deposit is located in the Jastrabá Fm. The major minerals are mixed-layered illite-smectite (I-S) and quartz. In the 90‘s, a sample was sent to the Clay Minerals Society (ISCz-1; illite-smectite, former Czechoslovakia) as a Special clay by V. Šucha. A more recent study confirmed that the expandability of studied DV I-S samples is between 10 and 35 %. The most important Slovak zeolite deposits occur in rhyodacite volcanoclastic rocks in the East Slovak Neogen Basin (e.g., Nižný Hrabovec, Kučín). The major mineral is clinoptilolite (60–80 wt.%). Zeolite from Nižný Hrabovec was successfully tested for use as a zeoponic substrate.

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Geology and mineralogy of clays
Oral presentation

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CHARACTERIZATION OF FLUVIAL-LACUSTRINE SEDIMENTS AND SILICEOUS SINTER SEDIMENTS AT THE LUTILA I BENTONITE DEPOSIT (KREMNICKÉ VRCHY MTS., SLOVAKIA)

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Our contribution focuses on the characterization and spatial delineation of the positions of limnosilicites (siliceous sinter), lacustrine sediments, and accompanying rocks at the Lutila I bentonite deposit, located in the southwestern part of the Kremnica Mountains. Earlier works indicate that the formation of limnosilicites (Upper Sarmatian to Lower Pannonian) at the Stará Kremnička – Kotlište deposit is associated with the infiltration of high SiO_2 solutions into marshy to lacustrine environments and suggest a connection between the formation of limnosilicites, bentonites and the alteration products of rhyolitic volcanism with the Kremnica hydrothermal system (e.g. Kraus et al., 1994; Lexa and Bartalský, 1999). The thickness of the bentonite zones ranges from meters to tens of meters and occurs at depths from the surface down to over 50 m. In some cases, limnic silicite accumulations are present alongside products of rhyolitic volcanism at bentonite deposits.

The occurrence of silicites, lacustrine sediments, associated bentonites, and other rocks at the Lutila I deposit was mapped on the surface of quarry benches and in four vertical profiles. Rock samples were collected during mapping and analyzed using quantitative X-ray diffraction analysis, the internal standard method, and RockJock 11 software (SAS, Banská Bystrica). The results of the mapping and X-ray analyses of the samples were visualized using QGIS and Leapfrog Geo software.

X-ray diffraction analysis of accompanying rock samples indicates varying degrees of bentonitization characterized by the presence of smectite, increased quartz content, and variable amounts of opal-CT, cristobalite, and volcanic glass. Analyses indicate the presence of high-temperature muscovite 2M in the sediments, suggesting a non-volcanic material admixture.

Mapping results was used to refine the detailed geological map of the Lutila I deposit, reambulate the geological map of the area of interest to a scale of 1:10000/1:5000, and address the spatial variability and genesis of the bentonite deposit. Paleohot spring within the siliceous sinter layer and their chemical composition point to the connection with the Kremnica hydrothermal system.

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References

Kraus I., Šamajová E., Šucha V., Lexa J., Hroncová Z. (1994): Diagenetic and hydrothermal alterations of volcanic rocks into clay minerals and zeolites. (Kremnické vrchy Mts., the Western Carpathians). *Geol. Carpath*., **45**, 3, 151-158.

Lexa J., Bartalský B. (1999): Low-Sulphidation Epithermal Gold Deposit at Kremnica. In: Molnár F., Lexa J. & Hedenquist J. W. (eds.): Epithermal mineralization of the Western Carpathians. Society of Economic Geologists, *Guidebook Series*, **31**, 265-273.

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VARVE-LIKE SEDIMENTS IN CAVES FROM THE NORTHERN RIM OF THE DACHSTEIN MASSIF (AUSTRIA)

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Fine-grained clastic sediments with bright and dark laminae, informally called "Bright Cave Loam" (BCL) are present in caves of the Dachstein Massif below an altitude of about 1700 m a.s.l. The Dachstein Massif, with an areal extent of 580 km^2, is one of the largest karst massifs in Austria. The BCL represents the topmost layer in a number of caves of the area and has a maximum thickness of 6 m.

In the past, the mm- to cm-thick laminations of the BCL were assumed to be glacio-lacustrine varves caused by seasonal or longer climatic rhythms. To investigate this theory, samples were taken from two different caves, Hirlatzhöhle (from c. 1000 m a.s.l.) and Dachstein-Mammuthöhle (c. 1400 m a.s.l.).

Sedimentological methods used were grain size analysis and X-ray diffraction (XRD) for the bulk- and clay mineralogy. Wherever possible, individual laminae of the BCL were analysed separately.

The results of the bulk mineralogy show that darker laminae mainly consist of calcite (32–75%) with secondary amounts of quartz (2–5%), dolomite, ankerite, and traces of K-feldspar and goethite. In the dark laminae clay minerals are more abundant (11–60%) than in the bright laminae. Overall, the bright laminae have the same mineralogical constituents, but show slightly higher amounts of calcite and quartz. Clay mineralogy shows a laminae dependent pattern for all clay minerals except smectite. Illite is the most abundant clay mineral and is, together with kaolinite and chlorite, slightly enriched in the darker laminae.

The bright and dark laminae can also be distinguished by grain size analysis. The dark laminae have a higher percentage of clay-sized particles. The maximum grain size of both lamina types is coarse silt. Components up to medium silt are very well sorted.

In conclusion, the BCL was likely formed under conditions of slack-water facies and can be interpreted as a result of glacial backflooding in the Pleistocene. This also explains the altitude control of the BCL. The bright, carbonate-rich, and coarser-grained laminae originate from more energetic meltwater during spring and summer; in winter there is lower discharge, the remaining clay minerals are sedimented and result in the thin, darker laminae. The studied sediments can thus be interpreted as varves.

CHARACTERIZATION OF SMECTITE IN BENTONITE BEDS FROM LAGO PELLEGRINI, NEUQUEN BASIN, ARGENTINA

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The bentonites around Pellegrini Lake, Neuquén Basin, Argentina belong to the Cenomanian transitional marine-continental sedimentary sequences and correspond to the Allen Formation (Malargüe group, Upper Cretaceous). The bentonites are related to the volcanic activity associated with the Andean chain uplift during the Late Cretaceous, at the time of deposition of Allen Formation. The two main bentonite beds are 0.21–0.8 m thick (0.60 m average thickness), are intercalated with mudstones, siltstones and heterolithic rocks and are easily identifiable due to their lighter colors, the lower being green and the upper white. Twenty samples were collected from four profiles ~3 km apart from each other, in the two beds. Three of the profiles (PL1, PL2 and PL4) are aligned in a N-S direction, whereas PL3 profile was sampled 3 km east of PL2. Quantitative mineralogical analysis was performed with the Rietveld method. The layer charge of smectite was determined with the modified K-saturation method and the charge localization was estimated with the Greene-Kelly test after Li saturation.

In addition to Al-smectite the bentonite beds consist of quartz, feldspars (plagioclase and sanidine), biotite, zircon, apatite, ilmenite, monazite, pyrite, hematite, celestite and barite. Zeolites (heulandite-clinoptilolite and mordenite), halite and gypsum are also present as cement or replacement. The green bentonite is more homogeneous and richer in smectite (74-83 wt%), whereas the white bentonite contains less abundant smectite and displays a gradual increase in smectite content from bottom to the top of the bed (56-82 wt%). Beidellite dominates over montmorillonite in both beds, but the distribution of the two smectites is random without particular trends. In the green bentonite the PL1 and PL4 profiles contain only beidellite, the PL2 profile contains montmorillonite in the bottom that changes to beidellite in the top, whereas in the PL3 profile beidellite and montmorillonite alternate in the different samples. In the white bentonite the PL2 profile contains montmorillonite in the bottom grading to beidellite at the top, whereas in the PL3 profile the opposite trend is observed. In all profiles beidellite and montmorillonite have a low layer charge (0.28-0.42 e/huc). The transition from one smectite type to the other is associated with differential leaching of silica during alteration of the volcanic glass. Since alteration is not controlled by temperature, the distribution of the different smectites might reflect alkalinity gradients along the different profiles during alteration.

DISTRIBUTION OF SMECTITE AND SMECTITE LAYER CHARGE IN THE AGGERIA BENTONITE DEPOSIT, MILOS ISLAND, GREECE.

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The Angeria bentonite deposit in Milos Island Greece, is a world-class deposit with >100 Mt reserves of high-quality material. The deposit has an E-W strike and consists of three sectors, the Koufi, Angeria and Agia Irene from east to the west. In this contribution we examined the mineralogy and geochemistry of a ~150 x 45 m (length x height) bentonite profile from the Angeria sector. Eighty-seven (87) bentonite samples were collected from the profile. Quantitative mineralogical analysis was performed with the Rietveld method (BGMN code, Autoquan© 2.80 software). The layer charge of smectite was determined with the modified K-saturation method. The mineralogical data were processed with geostatistical analysis using the Matlab code to draw conclusions for spatial variation and trends of the major mineral phases. The samples are composed of Ca-Mg-smectite (45-86.8%, average 70%), calcite (1.3-43.9%, average 12%) quartz (0.5-2.7%, average 0.8%), plagioclase (1.8-11.5%, average 5.6%) and K-feldspar (0-12.9%, average 2.4%), with traces of illite, jarosite, alunite, gypsum, anatase and pyrite. High-charge smectites (>0,480 e/huc) were recorded in the middle and higher parts of eastern and western sectors of the profile, whereas most central sectors have intermediate-low layer charge. Those central sectors with intermediate-low layer charge are located in a structurally controlled area that has been affected by alteration of the bentonite, due to the activity of acidic hydrothermal fluids.

A geostatistical analysis by means of Regression Kriging method was implemented employing depth of blocks as auxiliary information. Cross-validation analysis showed that the spherical variogram was the most appropriate model to determine the samples' spatial dependence. The geostatistical analysis showed that smectite content is maximized in the central and the western sectors of the profile. The sectors of the smectite minima contain abundant calcite (eastern sectors) and gypsum (western sectors), both showing a vertical distribution. The distribution of smectite is not characterized by a particular trend of layer charge, since low- and high-charge smectites are distributed throughout the profile. The gypsum-bearing sectors are closely related to the structurally controlled zone, suggesting that gypsum is a product of the acidic alteration of the bentonite. By contrast, the vertical distribution of calcite is interpreted to reflect deposition from a channelized flow. In conclusion, the use of geostatistics provides useful information about the spatial distribution of smectite content and crystal-chemical properties of smectite in bentonites, thereby optimizing bentonite processing including Na-activation and classification of bentonite deposit in blocks of variable properties.

Identification of clay minerals
Oral presentation

Book of Abstracts, 11th Mid-European Clay Conference (MECC 24), Plzeň, September 15-20, Czech Republic, M. Šťastný and M. Pospíšil (eds.)

INTERSTRATIFIED ILLITE-HYDROXY-INTERLAYERED SMECTITE – A DISORDER STRUCTURE MODEL FOR QUANTIFICATION USING RIETVELD REFINEMENT

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Hydroxy-interlayered minerals (HIM) are known for a long period of time. They are formed in soils during the acidic weathering of commonly dioctahedral 2:1 layer silicates such as white mica, smectites or interstratified mica-smectites. In this acidic environment Al^{3+} is dissolved from easily weatherable silicates such as feldspars or chlorites and then intercalated into swellable clay minerals such as smectite or vermiculite by exchanging hydrated interlayer cations, which are subsequently removed and often washed out of the soil horizon. Al^{3+} polymerizes in the interlayer forming an oligomer “island structure”, which cannot be exchanged anymore. This is accompanied by deterioration of essential soil properties including soil fertility, water or cation buffering capacity, organic matter storage capacity, or retention of contaminants. With increasing degree of weathering, non-expandable (e.g. micaceous) layers transform to expandable (e.g. vermiculitic or smectitic) layers which in turn are hydroxy-interlayered. X-ray diffraction (XRD) in combination with Rietveld refinement is a powerful tool to quantify HIM in complex mixtures such as soils. Although disorder structure models for hydroxy-interlayered smectite (HIS) exist, they can only be used to a limited extent in real soils, as usually interstratifications like illite-hydroxy-interlayered smectite (Ill-HIS) instead of pure HIS is formed. Ill-HIS combines micaceous (e.g., illitic) unit structures with swellable smectitic and/or vermiculitic unit structures as well as hydroxy-interlayered smectitic and/or vermiculitic unit structures. The ratio of swellable to hydroxy-interlayered unit structures can be expressed by the parameter "degree of hydroxy-interlayering". In the present study, disorder structure models for Ill-HIS were created including these types of unit structures for the Reichweite values R0, R1, and R3, typically present in soils. These disorder structure models can be used with the software BGMN and/or Profex to quantify these phases in complex mixtures such as soils. For each Reichweite value, two different states, air-dried or ethylene-glycol saturated, were considered, as well as two different degrees of rotational disorder: n*120° or n*60°. Due to the lack of natural Ill-HIS samples with sufficient purity to verify the structure models, the models were tested on synthetically hydroxy-interlayered samples (ISCz-1 as R1, illitic clay from Király-hegy near Sárospatak, Hungary as R3). Where no sufficient sample was available (R0), the models were verified by comparison with independently calculated/simulated diffraction patterns using the software DIFFaX. After the successful test, some of the samples were mixed with a known amount of corundum as an internal standard and measured to verify the quantification result of the models. A measurement uncertainty of 5 % w/w was assumed as a quality criterion. The presence of X-ray amorphous phases due to the unpreventable precipitation of $Al(OH)_3$ during the Ill-HIS synthesis had to be taken into account in the quantitative estimation. Independent measurements such as Fourier-transformed infrared spectroscopy (FTIR) and simultaneous thermal analysis (STA-MS) were included and checked for plausibility. Consistent with the findings of HIS formation, for both natural samples (R1 and R3) the hk lines did not differ significantly with increasing Al treatment indicating no significant change of the stacking and ordering. Hence, the *hk* model of non-hydroxy-interalyered phases such as interstratified illite-smectite can be used also for Ill-HIS. For user-friendliness, most structural parameters are automatically fixed as soon as the respective proportion of the unit structure is refined to values below 5 % mol/mol. E.g., layer thicknesses and occupation parameters of swellable (smectitic) layers are fixed to physically reasonable values as soon as the proportion of swellable (smectitic) layers falls below 5 % mol/mol during the refinement. This mechanism is intended to reduce the problem of strong over-parameterization of the models, excessive correlation between parameters with little influence on the diffractogram, and the resulting large measurement uncertainties of individual parameters.

Modification of clay minerals and materials science

Oral presentation

Book of Abstracts, 11th Mid-European Clay Conference (MECC 24), Plzeň, September 15-20, Czech Republic, M. Šťastný and M. Pospíšil (eds.)

SURFACE-FIXATION INDUCED EMISSION IN HYBRID SYSTEMS OF LAYERED SILICATES AND ORGANIC DYES

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Interaction of organic dyes with layered silicates can cause various changes in dye properties, such as metachromasia, fluorescence quenching, resonance energy transfer, or even fluorescence enhancement. These phenomena are caused by the molecular aggregation or adsorption of dye molecules on silicate nanolayers.

This study investigates the interaction between organic dyes and layered silicates, emphasizing the photophysical properties of dyes from the groups of cyanine dyes, metalloporphyrins, and dyes from the group of benzothiazoles. Using a various type of layered silicate and dye/layered silicate ratio (ndye/mLS) enables control of the dye aggregation and the photophysical properties of the hybrid systems.

At low silicate/dye ratios of all the systems, we observed a significant increase in the fluorescence. This phenomenon can be explained using the phenomenon of adsorption induced emission. Adsorption-induced emission is caused by the planarization of dye molecules on the layered silicate surface. This planarization suppressed the non-radiative deactivation of molecules, leading to a significant fluorescence increase. As the silicate/dye ratio increases, the effect of adsorption-induced emission decreases, which is probably due to the increase in dye aggregation as identified by MCR analysis.

The work brings a combination of experimental spectral methods, chemometric methods, and methods of theoretical computational chemistry.

Overall, these findings provide insights into optimizing photophysical properties in organic dyes immobilization on solid carriers, which could have significant implications for the development of new applications in various fields, especially in photoactive materials.

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CLAY NANOCOMPOSITE THIN FILMS IMPARTING ANTIMICROBIAL PROPERTIES TO POLYMER SURFACES

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Nanocomposites based on clay minerals and organic polymers represent a relatively new and diverse class of materials applicable across various industries. The dispersion of clay particles within a polymer matrix introduces novel properties, leading to new possibilities for their application. However, a drawback of such composites is the loss of certain properties typical of pure polymer materials. In the preparation strategy of bioactive nanocomposites, attention is focused on carriers of bioactive molecules. Traditional composites often suffer from the limitation that most active components within the polymer matrix are inaccessible to the polymer surface. This study introduces a novel strategy for preparing active polymer surfaces. The approach involves the fusion of active thin layers of organically modified saponite (Sap) particles with liquid polymer precursors or polymer melts. During fusion, a thin film of active nanocomposite is formed, with a thickness of only a few micrometers, firmly bound to the polymer matrix through the intercalation of organic polymer chains into the silicate layer. The surface properties are governed by the thin composite films. In this presentation, procedures for preparing two types of materials containing antimicrobial and photosensitizing molecules, namely phloxine B (PhB), will be presented. One type of material was prepared by fusing liquid polyurethane precursors with Sap followed by *in situ* polymerization. The second type was produced by combining a Sap film with a poly(caprolactone) melt. Both types preserved the photoactivity of PhB to some extent and did not significantly affect the mechanical properties of the polymer matrix. The structure, physicochemical properties, photoactivity, and antimicrobial characteristics of both types of materials will be discussed in the presentation. The surfaces exhibited promising antimicrobial properties, as evidenced by the inhibition of biofilm growth.

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CATION EXCHANGE CAPACITY MEASUREMENT FOR BENTONITE-CEMENT REACTIONS IN A NUCLEAR WASTE DISPOSAL

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Bentonite barriers in repositories for high-level radioactive waste disposal are expected to react with Portland cement used during the underground construction of a repository. The reaction runs at very high pH (>12) and produces amorphous phases along with newformed zeolites and feldspathoids. The cation exchange capacity (CEC) is one of the major parameters and analytical tools which can be applied to determine the ability of bentonite to swell and adsorb cationic specie released from the waste over its lifetime after the reaction with cement. Besides, CEC may be the indication for the newformed zeolites. However, an extremely high pH produced by the material once in contact with water and an excess of Ca^{2+} cations released from the unreacted portion of cement or the reaction products, strongly affect the CEC measurement invalidating its applicability.

In this study, testing the CEC in both reacted and unreacted bentonite-cement mixtures was performed using hexamminecobalt(III) ($[Co(NH_3)_6]^{3+}$) solution and a spectrophotometric method (Derkowski, Bristow, 2012), under natural pH of the suspension. The as-is fresh bentonite-cement mixtures did not return realistic CEC values due to the too high suspension pH, beyond the stability of ($[Co(NH_3)_6]^{3+}$. Extended washing of the material by dialysis enabled the pH to be decreased to a level acceptable for CEC measurement and reduced the excess Ca^{2+} cations. The measured CEC value, however, of the reacted bentonite-cement mixture is not straightforward to interpret, as it is a combination of the exchange by interlayer cations in the residual smectite, including smectite crystallite edges, the cement-$[Co(NH_3)_6]^{3+}$ interaction, and the contribution from new-formed zeolites. The CEC of zeolite strongly depends on the actual index cation used in the CEC measurement (Derkowski et al., 2006). In the samples studied, the $[Co(NH_3)_6]^{3+}$ probes only the external surfaces of the zeolite crystallites.

References

Derkowski A., Bristow T.F. (2012): On the Problems of Total Specific Surface Area and Cation Exchange Capacity Measurements in Organic-Rich Sedimentary Rocks. *Clays and Clay Minerals*, **60**, 348-362.

Derkowski A., Franus W., Beran E., Czimerová A. (2006): Properties and possible applications of zeolitic materials produced from fly ash by a simple synthesis method. *Powder Technology*, **166**, 47-54.

THERMALLY-INDUCED Fe^{2+} AND Mg^{2+} FIXATION IN SMECTITE INTERLAYERS UNDER DRY- AND WET-HEATING CONDITIONS

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Smectite present in bentonites serving as barriers in repositories for high-level radioactive waste disposal (HLRW) will undergo strong cation exchange, both with the ambient pore fluid and the cations released from waste metal containers (Wersin et al., 2021; Dohrmann, Kaufhold, 2017). The observed alterations and decrease in cation exchange capacity in barrier bentonites with increasing temperature at contacts with the canister surface requires an understanding of the long-term mechanism (Kanik et al., 2024) potentially challenging the bentonite stability.

Using the layer charge (LC) measurement and interlayer probing by the “O-D method” (Kuligiewicz et al., 2015), we tested a working hypothesis that Mg^{2+} cations (present in the smectite interlayer in untreated bentonites and in formation waters) and Fe^{2+} cations (released from the metal heater/canister) enter the smectite interlayer and become fixed due to the high temperature. These cations may partially neutralize LC and thus alter the long-term barrier properties of the bentonite.

Three homoionic smectite-rich mineral fractions containing high-charge and low-charge montmorillonite, and beidellite, respectively, were tested under hydrothermal and dry conditions at 100 °C and 200 °C (temperature as predicted for RWD barriers) for several months. Under wet (hydrothermal) conditions Fe^{2+}-saturated smectites showed immediate cation fixation and further mineralogical alterations at 200 °C but none at 100 °C, whereas Mg^{2+} fixation was not observed. In contrast, drying caused strong Fe^{2+} fixation, even at 100 °C whereas strong interlayer Mg^{2+}fixation was observed at 200 °C, but not near 100 °C. The fixation was found more reversible upon cation exchange in beidellite than montmorillonite. All LC measurements were verified against Ca^{2+}-saturated smectites.

The results are discussed considering the temperature, water saturation and smectite interlayer cation composition in long-term pilot experiments of RWD barrier bentonites.

References

Dohrmann R., Kaufhold S. (2017): Characterization of the Second Package of the Alternative Buffer Material (ABM) Experiment — II Exchangeable Cation Population Rearrangement *Clays and Clay Minerals*, 65, 104-121

Kanik et al. (2024) *Applied Clay Science*, submitted

Kuligiewicz A., Derkowski A., Emmerich K., Christidis G.E., Tsiantos C., Gionis V., Chryssikos G.D. (2015): Measuring the Layer Charge of Dioctahedral Smectite by O—D Vibrational Spectroscopy, *Clays and Clay Minerals*, 63, 443-456.

Wersin P., Hadi J., Jenni A, Svensson D., Grenèche J.-M., Sellin P., Olivier X., Leupin O.X. (2021): Interaction of Corroding Iron with Eight Bentonites in the Alternative Buffer Materials Field Experiment (ABM2). *Minerals,* 11(8), 907. https://doi.org/10.3390/min11080907

PHOTODEGRADATION OF ZEARALENONE WITH KAOLINITE NANOTUBES-BASED PHOTOCATALYSTS: MECHANISMS AND PATHWAYS

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With over 500 mycotoxins known, their number is still rising. Mycotoxins, produced by fungi as secondary metabolites, frequently contaminate agricultural products, especially animal feed. Zearalenone (ZEN) is one of the most commonly detected. Despite its low acute toxicity, it can mimic estrogen-like effects, disrupt normal estrogen levels, and lead to reproductive disorders. Another troubling feature of ZEN is its weak polar nature, making adsorption ineffective for its removal. Therefore, the present study is focused on the photodegradation, which allows for the complete decomposition of harmful substances while being sustainable, fast, and effective.

Photocatalysts based on calcined kaolinite nanotubes (MNC) impregnated with TiO_2 (MNC-T), g-C_3N_4 (GCN) (composite MNC-AG), or their 1:1 mixture (MNC-T-AG) were used to investigate the kinetics of ZEN removal. For all the experiments, an initial ZEN concentration of 10 ppm was set. The experimental setup contained a 35 W UV lamp with a peak emission wavelength of 365 nm and a radiation power density adjusted to approximately 10 mW/cm^2.

The experiments conducted under visible light allowed for the removal of 18.1-39.4% of ZEN, while the use of UV light resulted in the removal of 88% of ZEN with the MNC-T and over 99.9% with the MNC-AG and MNC-T-AG. Among the tested pH conditions (pH ~2/6/10), the fastest photodegradation was achieved at the highest pH. In an alkaline medium, deprotonated ZEN has high molar absorption coefficients and reacts faster than its undissociated form. The use of tap water as a matrix accelerated the photodegradation with the MNC-T and MNC-AG materials. Simultaneous photodegradation of ZEN and deoxynivalenol (DON) mycotoxins showed almost no degradation of DON and reduced efficiency of ZEN removal. Scavenger tests indicated the significance of $O_2^{\bullet-}$ radicals in the photodegradation of ZEN. In the case of the MNC-AG, the major influence of e^- was also observed. The use of electrospray ionization tandem mass spectrometry (ESI-MS/MS) showed that all the materials led to similar ZEN photodegradation pathways, and the plausible products of ZEN photodegradation were proposed. Future research will focus on the photocatalytic removal of DON and the determination of its photodegradation pathways.

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SYNTHESIS CHALLENGES OF LDH/GCN HETEROSTRUCTURES FOR THE PHOTODEGRADATION OF ESTRONE

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Layered double hydroxides (LDH) and graphitic carbon nitride (GCN) are both promising visible-light-active photocatalysts for environmental remediation. LDH materials in particular offer chemical flexibility in terms of introduced metal cations and interlayer anions. However, they suffer from limited visible light absorption and fast charge recombination. On the other hand, GCN has a suitable band gap and high chemical stability, yet is hindered by relatively rapid charge recombination and limited surface area. The formation of LDH/GCN heterostructures combines the advantages of individual components, enhancing light absorption and charge separation efficiency.

Herein, we obtained Zn-Cr LDH/GCN heterostructures using 1) coprecipitation, 2) adsorption-coprecipitation, and 3) hydrothermal methods. The first method involved adding Zn(II) and Cr(III) salts to a GCN suspension while maintaining a pH of 10. In the second method, Zn(II) and Cr(III) salts were mixed with the GCN suspension for 0.5 h before raising the pH to 10. In the third synthesis route, Zn(II) and Cr(III) salts were added to the GCN suspension, then the pH was raised to 10, and the suspension was heated at 100°C for 24 h. The morphology, structure, and electronic properties of the formed heterostructures were analyzed and compared. Most importantly, their photoactivity was assessed in reactions with 1 ppm of estrone (steroid hormone) under visible light emitted by a 150 W LED lamp.

All of the formed heterostructures exhibited complex charge transfer mechanisms and reduced recombination rates, in comparison to the pristine GCN and LDH materials. In particular, their electronic properties differed, which influenced their photocatalytic activity towards estrone degradation. The material obtained via the hydrothermal route and containing 50% wt. of the GCN exhibited the highest efficiency in estrone photodegradation. After 1 h of the reaction, 99.5% of estrone was degraded. This work highlights the importance of proper synthesis parameters to obtain heterostructures with superior photocatalytic activity.

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PHYLLOSILICATES FOR SAFE ENERGY STORAGE MATERIALS

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Safety for the devices used for common life is a very important challenge for technology, science and producers. Li-ion/LiPo batteries have emerged in recent years as the most popular secondary batteries due to the advantages that include light weight, higher energy density, low memory effect, and longer life span. However, the lithium is considered as the dangerous part in the combination with liquid electrolyte causing very fast reaction related to the explosion and noncontrolled fire. Progress of solid-state electrolyte (SSE) is a key to the fabrication of all-solid-state batteries that are safer.

Natural minerals having unique architecture, adsorption capability, and rich active sites have captured numerous attentions with remarkable innovations. Recently, composites with the minerals containing all dimensionally variable components 1D (halloysites, attapulgites, sepiolite), 2D (montmorillonite, vermiculite,) and 3D (feldspar, zeolites), have been applied in plenty of key elements of batteries. Aiming at their energy-storage applications, the significant utilizations in electrodes, separators, electrolyte, and metal-protection were detailed reviewed in lithium-ions battery, lithium-sulfur battery, solid-state battery and other types of batteries.

Providing features of fire retardancy and chemical resistance to the main parts of the battery is possible to improve all safety. Discussion regarding current knowledge of phyllosilicates related to the safety and environment is given.

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ADVANCES IN DETERMINING SMECTITE COMPOSITIONS AND THEIR LAYER CHARGE PROPERTIES BY TRANSMISSION ELECTRON MICROSCOPY - ENERGY DISPERSIVE X-RAY (TEM-EDX)

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Smectites are notoriously sensitive to electron beam damage and as a result, determining their crystal chemistry by electron microscopy is challenging. In this study, we use transmission electron microscopy* - energy dispersive X-ray analysis (TEM-EDX) for improved compositional and layer charge determinations by i) reducing cation migrations to a minimum by using <5 pA/cm^2 beam current density, ii) maximizing acquisition intensities to >10.000 cps by measuring in parallel beam TEM mode and iii) calibrating with appropriate Cliff-Lorimer Factors (k) using phyllosilicate of known composition and similar particle thicknesses. Based on TEM-EDX area analyses, the composition of Wyoming montmorillonites (SWy sample series) was studied in its natural and Ca-saturated form for < 50 nm thick particle aggregates lying on lacey carbon films. The heterogeneous charge distributions of montmorillonite at the particle and sample levels were confirmed by the TEM-EDX results with an average composition per formula unit of

$$(Na_{0.12}Ca_{0.04}Mg_{0.03}K_{0.02})(Si_{3.91}Al_{0.09})(Al_{1.57}Mg_{0.27}Fe_{0.19})_{2.03}\ O_{10}(OH)_2 \cdot nH_2O$$

and tetrahedral and octahedral layer charges of -0.09 and -0.19 per $O_{10}(OH)_2$, respectively. The total layer charge ranges from -0.25 to -0.30 per $O_{10}(OH)_2$ (mean of -0.28) and the charge distribution was very similar to that determined by the alkylammonium method (mean also -0.28). News insights into the natural heterogeneities of smectite chemistry can be determined by TEM-EDX as long as adequate calibration and specimen damage control procedures are implemented. The results presented in this talk will soon be available in a *Clays and Clay Minerals* publication (Warr et al., in press).

**This study used a JEOL 2100 Plus TEM microscope, which was financed by the Deutsche Forschungsgemeinschaft (DFG project number 428027021 https://gepris.dfg.de/gepris/projekt/428027021).*

Reference

Warr L.N., Thombare B.R., Sudheer Kumar R., Peltz M., Podlech C., Grathoff G.H. (in press). Determining the stoichiometric composition of Wyoming montmorillonite using improved transmission electron microscopy - energy dispersive X-ray (TEM-EDX) techniques. *Clays and Clay Minerals*.

NANOSTRUCTURED MINERAL-BASED HYBRID COMPOSITES FOR ENERGY-RELATED APPLICATIONS

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Clay-derived composites are starting to play an increasingly important role in energy-related applications. They are a convenient choice due to their abundance, susceptibility to modification, and specific properties resulting from their layered, sandwich-like structure. In particular, the small intrinsic basic character resulting from the presence of Mg in the octahedral sheets of clay structure places them in the group of promising starting materials.

In this study, nanostructured porous clay mineral-based hybrid composites and mesoporous silica supports were compared as catalysts, in a steam reforming reaction of bio-ethanol for H_2 production.

All supports were treated by wet soaking with Fe^{3+} cations followed by thermal treatment or hydrothermal assistance to facilitate the growth of nanocrystalline α-Fe_2O_3 or to develop the sub-surface Fe species embedded into silica lattice triggered by the interaction with the applied siliceous or composite supports and delivered condition (time, temperature, and pressure). All catalysts were active in bio-ethanol decomposition but a different distribution of reaction products was strongly dependent on the speciation of iron moieties developed on the support surface and related to the acidic or basic properties of the used supports.

The composition of the parent clay mineral, in particular the presence of Mg cations in the octahedral sheets of the used smectite/hectorite structure, and their mobility played a crucial role in the shift of the reaction balance towards hydrogen formation, simultaneously limiting the dehydration of ethanol to ethylene which further polymerization resulted in the formation of carbon deposits. The creation of the weak basic sites was evoked by the forced migration of Mg^{II} from the octahedral sheet of the smectite to the composite surface. Mg markedly hindered the coke deposit formation facilitating the dehydrogenation pathway. The dehydration of ethanol to the ethylene was conducted on the acid centers particularly developed on the surface of mesoporous silica, where the formation of coke deposits was confirmed by X-ray Photoelectron Spectroscopy. The different distribution of reaction products indicated a strong interaction of the support in the creation of active nanostructures during the synthesis of catalysts. The role of clay components in H_2 production, the nature and distribution of nanostructured Fe-O moieties formed on the surface of porous supports were investigated by X-ray diffraction method (XRD), scanning electron microscopy (SEM), temperature-programmed reduction with the hydrogen (H_2-TPR), CO_2 temperature-programmed desorption (CO_2-TPD), and advanced X-ray photoelectron, and ^{57}Fe Mössbauer spectroscopies. Our studies have shown that nanostructured clay-based hybrids can serve as promising catalysts active in H_2 production, more resistant to coke contaminants than mesoporous silica.

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Physicochemical evaluation of clays
Oral presentation

Book of Abstracts, 11th Mid-European Clay Conference (MECC 24), Plzeň, September 15-20, Czech Republic, M. Šťastný and M. Pospíšil (eds.)

WESTERWALD AND BAVARIA BENTONITES FROM GERMANY. A MINERALOGICAL AND GEOTECHNICAL STUDY

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This study examines the fundamental mineralogical, geotechnical, and physico-chemical properties of two naturally occurring Ca/Mg bentonites from Germany and their homoionic sub-fractions. The two bentonites are Secursol UHP® from the Westerwald region (Stephan Schmidt Gruppe SSG) and Calcigel® from Bavaria (supplied by Clariant). These natural bentonites were delivered as compacted and crushed with granules sizes between 0 and 4 mm. Both bentonites are currently considered in the Sandwich sealing system concept developed by the Karlsruhe Institute of Technology (KIT). This system is designed for the hydraulic sealing of shafts and drifts in underground waste repositories, comprising sealing segments (DS) made of bentonite, alternating with equipotential segments (ES) that have higher hydraulic conductivity. Such setup ensures uniform hydration of the sealing segments.

In this study, we present the results of a comprehensive suite of characterization techniques that examine the mineralogy, chemical properties, morphology, and geotechnical classification of Calcigel and Secursol UHP. The exchangeable cations results confirmed the successful homoionic transformation of the <2 μm sub-fractions into four homoionic forms: Na-, K-, Ca-, and Mg-bentonite. We also investigated the hydration properties and the effect of heating temperature on bentonite water content using conventional geotechnical methods coupled with Simultaneous Thermal Analysis (STA). Additionally, the results of Cationic Exchange Capacity (CEC) and water adsorption isotherms enabled us to determine the quantity of adsorbed water and the number of water molecules per interlayer cation for the smectite phase in both the raw and homoionic forms across a broad range of relative humidity values. Our findings also demonstrated an expected increase in the smectite phases in the smaller size fractions. This phase was identified as pure dioctahedral smectite, with no evidence of mineralogical interstratification. Chemical analysis allowed us to derive the unit formula for the smectite phase, revealing the presence of montmorillonitic beidellite with significant octahedral iron content in both bentonites. Moreover, the layer charge of the smectite phase was determined, and the morphology and average sizes of individual smectite layers were examined via Atomic Force Microscopy (AFM).

The main focus of our presentation will be to compare these properties between the two bentonites, and to highlight the evolution of these properties with particle size. The outcomes of this work provide a foundational repository for ongoing investigations (not presented here) that explore the kinetics of cationic exchange and swelling pressure heterogeneity as a function of different interlayer cations, and due to the accompanying cationic exchange processes.

ACIDIFYING CLAYS: KINETICS OF FE(II) OXIDATION AND MINERAL CONTRIBUTIONS

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Clays from different sources differ in their mineralogical composition and several chemical and physical properties, challenging a reliable assessment of the clay's performance in specific applications. The actual quality is commonly determined by several different tests, but here is still a lack of information to provide optimum clay products. Open questions still exist for acidification reactions triggered by oxidation of Fe(II)–containing minerals, which are present in (i) the predominant stable clay minerals, where Fe(II) is located in the octahedral sheet, and (ii) heavy minerals, which contain elements such as Fe, Mn and S in the reduced oxidation state. The presence of free O_2 induces oxidation of Fe(II), going along with proton release and in consequence carbonate dissolution, CO_2-degassing and neoformation of Fe oxides. Mass loss, modified surface reactions of clay minerals and internal degasification can cause unexpected behavior.

In the investigations two bentonites, which showed in previous experiments degassing reactions, were included and compared with a translocated clay containing pyrite. Heavy minerals were separated from the light fraction using a sodium polytungstate solution with a density of 2.9 g cm^{-3}. Mineral turnover of bulk clays was determined in batch experiments up to 1500 h for 20 and 60°C treatments. In another approach the oxidizing agent H_2O_2 was added in amounts of 0.1, 0.5, and 1.0 %. The pH, electrical conductivity, and dissolved cations and anions were determined during the runtime of the experiment of 1500 h. In the solid phase Fe oxidation state was determined by photometric analysis and DCB extractable Fe was quantified. Degassing issues / bubble formation were determined by in situ microtomography.

Acidifying mechanisms, were traceable in the light and heavy fraction of the clays as well as in the surrounding solution. Decisive parameters are the oxidation of Fe(II), the content of DCB soluble Fe and the transfer of S from the solid phase to the surrounding solution. Increase of temperature or the addition of the oxidizing agent H_2O_2 increased Fe(II) oxidation rate and improved traceability of turnover. Nucleation of CO_2 bubbles, their growth, and coalescence induced pressure built-up and decreased stability of the clay matrix, traceable by the circularity of bubbles. Despite proton buffer reactions by carbonates, exchange sites and silicates, a distinct decrease in pH was obtained. This shift in pH towards slightly acidic conditions can be useful in technical applications.

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USING FTIR SPECTROSCOPY TO ESTIMATE SMECTITE CONTENT IN BENTONITIC BINARY MIXTURES

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X-ray diffraction (XRD) is often deemed to be the most effective method for quantitative clay mineralogy. However, its superiority needs to consider the time factor. In contrast, infrared spectroscopy (IR) is one of the fastest, simple, non-destructive, and reliable analytical techniques available; this makes it a potentially valuable tool for quantifying clay minerals, although its practical applicability needs to be tested pragmatically.

Therefore, in this study, we aimed to evaluate its effectiveness by creating controlled mixtures with simple bentonite components (binary mixture) and applying the linear spectral unmixing technique to recalculate the proportion of these components based on the measured spectra by Fourier-Transform Infrared (FTIR) spectroscopy in the near-Infrared (NIR) spectral region.

Two separate sets of binary mixtures were prepared using pure dioctahedral smectite with quartz for the first set, and with feldspar for the second one. Pulverized samples (less than 250 µm) were mixed to produce various percentages of smectite with other nonclay endmembers (quartz, feldspar), ranging from 10% to 90%. Near-Infrared (NIR) reflectance spectra were obtained using a Nicolet 6700 (FTIR) spectrometer.

Encouragingly, the obtained results were promising, with a deviation of less than five percent of the smectite content used to prepare binary mixtures in the laboratory.

Acknowledgement

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ENHANCED QUALITY CONTROL OF BENTONITES IN THE BAVARIAN MINING DISTRICT ACHIEVED BY SMECTITE LAYER CHARGE DETERMINATION

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Bentonite is mined globally for is use in commercial and industrial applications, including as a geotechnical barrier material in contaminant remediation and nuclear waste storage. In these applications quality control of the bentonite material produced is paramount, however, the properties of bentonites can vary significantly over a large mining district or within a single mine. Properties that may vary include: mineral composition, exchangeable cation population, and smectite content. The differences in bentonite properties locally or over a spatial area stems from the different geological settings present throughout bentonitization.

The aims of this study were to: 1) determine the variation in layer charge (LC) of smectites over the Bavarian mining district and within individual mines in the area and 2) assess the error of smectite content calculations based on cation exchange capacity (CEC) data resulting from the actual range of experimentally determined LC values. This information has been missing in the scientific literature, as previous LC methods were laborious or subject to assumptions, making a comprehensive study over a large spatial area impractical.

This study employed the use of the recently developed spectroscopic “O-D method” by (Kuligiewicz et al., 2015), which is accurate and efficient hence enabling the LC of a large number of samples to be measured relatively quickly. Analysis of LC was performed for 40 samples from eight different mines in the Bavarian bentonite mining district, covering an area of 250 km^2, within the North Alpine Molasse Basin. Results of the LC measurements showed LC values generally ranged between 0.29 and 0.30 eq/FU, with only 10 % of samples showing LC values slightly above 0.31 eq/FU. This narrow LC range has positive implications for the accuracy of determining smectite content calculated from CEC data, which is routinely done during quality control of Bavarian bentonites. The remaining error of the CEC based smectite contents resulting from LC variations accounts on average for ± 3 mass %.

Reference

Kuligiewicz A., Derkowski A., Emmerich K., Christidis G. E., Tsiantos C., Gionis V., Chryssikos G. D. (2015): Measuring the layer charge of dioctahedral smectite by O-D vibrational spectroscopy. *Clays and Clay Minerals*, **63**(6), 443-456.

NEAR-INFRARED AND X-RAY DIFFRACTION *IN SITU* STUDIES OF SMECTITE REHYDRATION KINETICS

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Understanding smectite-water interactions is of prime importance as it impacts application of smectites in several industrial fields. The ability of smectite to rehydrate is controlled by its structure and depends on the type of interlayer cation, the relative humidity (RH), and the temperature. Several types of water in smectites can be distinguished, e.g., water molecules coordinating interlayer cations or adsorbed at the external surface sites, among others. In this study, Near-Infrared spectroscopy (NIR) and X-Ray Diffraction (XRD) were employed to study the kinetics and mechanism of smectite rehydration. Experiments were carried out on SCa-3 ("Otay") smectite (California, USA) which was exchanged with K^+, Na^+, Ca^{2+}, Mg^{2+} to obtain four homoionic forms. Each experiment was performed *in situ*, with controlled temperature and humidity. Both NIR and XRD experiments were carried out under the same scheme that included equilibration at 40 °C and RH=30%, dehydration at 100 or 200 °C and RH<5%, cooling to 40 °C (RH<5%) and rehydration at 40 °C and RH=30%. The evolution of the $(\nu+\delta)H_2O$ combination band at ~5250 cm^{-1} in the NIR spectra showed an increase in area and intensity as the rehydration progressed. The progress was slower for samples dehydrated at 200 °C, which pointed to the potential collapse of the smectite interlayers during dehydration at higher temperature and their slower reopening during rehydration. The layer charge of smectites exchanged with divalent cations showed a decrease with an increasing dehydration temperature, which implies a collapse of high-charge smectite layers, whereas partial fixation of interlayer cations probably occurs at lower temperatures. The complex profile of O-H overtones in the region 7500-6700 cm^{-1} showed changes in the position and relative intensity of the component bands during rehydration. These changes also dependent on the type of interlayer cation. The XRD results showed a shift in d(00l) reflection towards lower 2θ values with progress of rehydration that indicated reopening of the interlayer. However, samples exchanged with cations of different hydration enthalpy showed different extent of recovery of the basal reflection. The d(001) reflection for K and Na-exchanged smectite after rehydration did not reach their original position. For the sample exchanged with Ca, the position of d(001) was fully recovered, however, its intensity was still lower after 3h. The position of the d(001) of Mg-exchanged sample exceeded the original position after 10 min of rehydration. All of the changes indicated that the rehydration of smectites with different interlayer cations depends on their structural changes during dehydration.

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IN-SITU H/D EXCHANGE IN CLAY MINERALS

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The protium (H)/deuterium (D) exchange in clay minerals performed either under vapor or with liquid D_2O, depends on the accessibility of various OH species. In smectites, for example, H/D exchange experiments performed at room temperature (RT) and over long reaction times showed that only the bands of adsorbed H_2O shift to lower frequencies as D_2O, whereas the structural OH signature remains unaffected (Kuligiewicz et al, 2015). Under the same conditions neither the inner-surface OH nor the inner OH groups of kaolinites showed any measurable deuteration. This study reports on the H/D exchange of kaolinite at high temperatures.

Three kaolinite samples of different structural order, KGa-2, KGa-1b and Keokuk, were used for the real-time study of deuteration kinetics, under D_2O-wet gas, in the temperature range 125 - 275 °C by Near Infrared spectroscopy (NIR). A diffuse reflectance setup was employed, based on a bifurcated optical fiber bundle probe which was attached to a controlled high-temperature stage. The NIR kinetics were based on the integrals of the 2νO-D envelope in the 5480-5180 cm^{-1} range. Besides strong kinetically-controlled dependence on temperature, the reaction progress showed dependence on the structural order of the kaolinite crystallites. At any temperature, the exchange was highest in the most disordered KGa-2 (e.g. ~55% after 45h at 250 °C) and almost not observed in the most ordered Keokuk sample. The results obtained have been extrapolated to H isotope exchange in natural fluid-kaolinite reactions (Derkowski et al, 2024). Surprisingly, both the inner-surface and the inner-OH groups were exchanged simultaneously and the two reaction pathways could not be separated.

In order to distinguish between the two pathways, fully N-methyl formamide-intercalated kaolinite KGa-1b was flush-deintercalated by D_2O. This treatment yields a stable ~7Å phase which maintains the original inner OH but has (partially) exchanged inner-surface OH. Three isothermal experiments were performed (175, 225, 275 °C for ~ 5d, 20h and 6h, respectively) with real-time NIR monitoring of the redistribution of D under a flow of dry N_2. At fixed total H/D mineral ratio, the reactions lead to the appearance of the inner 2νOD at 5253 cm^{-1}, at the expense of the original inner 2νOH (7077 cm^{-1}, H/D=1.347). Inner-surface 2νOH and 2νOD showed an opposite trend.

References

Derkowski A. et al. (2024): Geochimica et Cosmochimica Acta, submitted.

Kuligiewicz A., Derkowski A., Szczerba M., Gionis V., Chryssikos G.D. (2015): Revisiting the Infrared Spectrum of the Water—Smectite Interface. *Clays and Clay Minerals,* **63**, 15-29.

POTENTIOMETRIC TITRATIONS OF CLAY MINERAL SUSPENSIONS

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As with oxide minerals, protons and hydroxyl ions are identified as charge determining ions for clay minerals. In order to determine the amount ad-/desorbed and the corresponding point of zero charge, potentiometric titrations are performed. These consist of measuring the proton activity as a function of pH in a suspension and subtracting these values from a blank titration, both at given concentration of a background electrolyte. The surface excess of protons/hydroxyls obtained in this way, is then translated to a surface charge density and commonly interpreted in terms of surface complexation models. These models use reversible reactions between surface groups and protons/hydroxyls as a common starting point.

Regarding the available experimental data on clay minerals, one must note that points of zero charge and other characteristic quantities scatter widely for a given mineral (see for instance Ganor et al. (2003) and Duc et al. (2005) for reviews). Even more alarming is the fact that titration curves for clay mineral suspension show a pronounced hysteresis, i.e., the surface excess apparently depends on the direction of the titration (e.g., Tombácz and Szekeres (2006), Duc et al. (2005a)). Although hysteresis not always checked for, such behavior is in direct conflict with the application of surface complexations models, since it hints towards the non-reversibility of surface reactions. As the reported non-reversibility can have various experimental reasons, the presentation will focus on experimental aspects of potentiometric titrations and present ways to minimize hysteresis in such experiments. Both blank titrations and titrations of clay mineral suspensions will be presented and sources of inaccuracies and common experimental mistakes will be discussed.

References

Duc M., Gaboriaud F., Thomas F. (2005): Sensitivity of acid-base properties of clays to the methods of preparation and measurement: 1. Literature Review. *Journal of Colloid and interface Science*, **289**, 139-147.

Duc M., Gaboriaud F., Thomas F. (2005a): Sensitivity of acid-base properties of clays to the methods of preparation and measurement: 2. Evidence from continuous potentiometric titrations. *Journal of Colloid and interface Science*, **289**, 148-156.

Ganor J. Cama J., Metz V. (2003): Surface protonation data of kaolinite – reevaluation based on dissolution experiments. *Journal of Colloid and Interface Science*, **264**, 67-75.

Tombácz E., Szekeres M. (2006): Surface charge heterogeneity of kaolinite in aqueous suspensions in comparison with montmorillonite. *Applied Clay Science*, **34**, 105-124.

Application of clays in industry, medicine and environment

Oral presentation

LONG-TERM ANTIMICROBIAL EFFECT OF POLYLACTIDE-BASED COMPOSITES SUITABLE FOR BIOMEDICAL USE

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Polylactic acid excels in its properties such as easy processability, low toxicity, lower carbon footprint, mechanical and thermal strength, biodegradability, bioabsorbability and biocompatibility over other biodegradable polymers. Therefore, it attracts high attention for industrial and biomedical applications. In this study, composite materials with antimicrobial effects based on polylactide enriched with fillers such as silver and hexadecylpyridinium or hexadecyltrimethylamonium cations anchored on graphene oxide and vermiculite were prepared. Their degradation and antimicrobial effects on selected microorganisms, bacteria and yeast, were studied after immersing the composites in buffer solutions of pH 7 and 9 for six months to simulate the environment in different parts of the human body. As a result, this confirmed our hypothesis that when storing composites at the above-named pH, there will be a gradual degradation of these composites and thus a gradual release of antimicrobial fillers. In addition, antimicrobial effects increased over time. This caused a long-term inhibition of bacteria that could be involved in biofilm formation on the surface of biomedical products. In conclusion, after six months of immersion, all composites showed the highest antibacterial activity against the tested antimicrobial strains, and the polylactide/vermiculite+hexadecylpyridinium composite was also effective against *C. albicans*. During aging, the composites lost their surface integrity, which allowed the antimicrobial fillers to be active and prevent colonization of the composite surface by these microorganisms. This shows the suitability of PLA-based composites for biomedical purposes, e.g. for use as stents or implants.

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References

Stachurová T., Rybková Z., Škrlová K., Malachová K., Havlíček M., Plachá D. (2022): Biocompatibility and biocidal effects of modified polylactide composites. *Frontiers in Microbiology,* **13,** 1031783. DOI: 10.3389/fmicb.2022.1031783

Škrlová K., Rybková Z., Stachurová T., Zagora J., Malachová K., Měřinská D., Gabor R., Havlíček M., Muñoz-Bonilla A., Fernández-García M., Plachá D. (2022): Long-term antimicrobial effect of polylactide-based composites suitable for biomedical use. *Polymer Testing*, **116**, 107760.

ADVANCED SMECTITE ALTERATION AND THE ROLE OF ACCESSORY REACTANTS AT 180°C: NEW EXPERIMENTAL CONSTRAINTS ON THE STABILITY OF BENTONITE

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Despite the broad recognition of bentonite as having excellent hydrodynamic sealing properties, concerns about the long-term stability of this barrier material in underground radioactive waste disposal sites persist. The current experimental study investigated the advanced smectite illitisation of Bavarian bentonite at 180 °C, with a solid to liquid ratio of 300 mg:40 ml for 31 days. The experiment was conducted in the presence of different concentrations of K-oxalate or KCl and included accessory minerals such as pyrite and calcite.Using Rietveld refinement and transmission electron microscopy, the formation of mixed-layered illite-smectite was quantified and its elemental composition analyzed. The study revealed the neocrystallisation of celadonitic illite-smectite (up to 63 % illite layers) after treatment with K-oxalate, showing increased Al^{3+} in the tetrahedral sheets, reduced amounts in the octahedral locations, and greater fixation of non-exchangeable K^+ ions due to increased layer charges. K-oxalate's complexation of Al^{3+} and enhanced smectite dissolution led to a possible intermediate amorphous phase and illite-smectite crystallites with additional vacant sites, as indicated by the lower number of octahedral ions (< 2 per formula unit). Adding accessory minerals affected the degree of alteration noticeably in the presence of KCl, but had minimal impact on the illitisation when reacted with K-oxalate, which further accelerated illitisation by up to 6.4 times. These findings suggest that claystone host rocks low in organic matter should be preferred over organic-rich lithologies that likely contain oxalate ligands or similar catalyzing compounds. The results presented are currently in press as a journal article in Applied clay sciences (Sudheer Kumar et al, In Press)

Acknowledgment

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Reference

Sudheer Kumar R., Warr L. N., Grathoff G., Thombare B. R. (in Press): Advanced smectite alteration and the role of accessory reactants at 180°C: New experimental constraints on the stability of bentonite, *Applied Clay Science.*

EFFECT OF MAGNESIUM-BASED CEMENTITIOUS BINDER ON SMECTITE FOR EARTH CONSTRUCTION

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To achieve carbon-neutral construction, (sub)soils used as earth concrete offer a promising solution (Van Damme, Houben, 2018). Soils are infinitely recyclable and do not require energy-intensive processing. However, adding a cementitious-based binder is still necessary because dried soils do not exhibit the same strength as concrete. Additionally, soils with a high content of the clay mineral "smectite" are unsuitable for construction due to their shrinkage and cracking upon drying (Van Damme, Houben, 2018). In this study, a potential solution is presented: Magnesium-based cementitious binder (MB), which is produced with a low-to-negative CO_2 emission (Bernard et al., 2023). Different bentonites were mixed with MB and characterised at different curing times. Results show that adding MB transforms smectite into a chlorite-like clay mineral within hours. This newly formed clay mineral is known as hydroxy-interlayered smectite (HIS). In a HIS, the smectite interlayer is exchanged by oligomeric Mg-hydroxyl. Compared to common smectite, HIS has strongly reduced cation exchange capacity, reduced specific surface area, and, most important, reduced swelling capacity. Therefore, MB has the advantage to stabilise smectite-rich soils as a cement, and additionally reduce the shrinkage by altering the fundamental properties of smectite. Furthermore, this study shows a simpler method to transform smectite into HIS than in previous studies, e.g. (Xeidakis, 1996), and its constraints.

References

Bernard E., Nguyen H., Kawashima S., Lothenbach B., Manzano H., Provis J., Scott A., Unluer C., Winnefeld F., Kinnunen P. (2023): MgO-based cements – Current status and opportunities. *RILEM Tech. Lett.*, **8**, 65-78. doi: 10.21809/rilemtechlett.2023.177.

Van Damme H., Houben H. (2018): Earth concrete. Stabilization revisited. *Cem. Concr. Res.*, **114**, 90-102. doi: 10.1016/j.cemconres.2017.02.035.

Xeidakis G.S. (1996): Stabilization of swelling clays by Mg(OH)2. Factors affecting hydroxy-Mg-interlayering in swelling clays. *Eng. Geol.*, **44**, 1-4, 93-106. doi: 10.1016/s0013-7952(96)00046-4.

Computational methods in clay science

Oral presentation

HALLOYSITE AS A DRUG CARRIER FOR DICLOFENAC; A COMPUTATIONAL STUDY

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Halloysite (HNT), is an aluminosilicate clay mineral of kaolin group, with spiral-shape nanotubular morphology. The tetrahedral sheet (SiO_2) composes the outer surface of the nanotube giving it a negative charge, while the octahedral sheet ($Al(OH)_3$) composes the inner surface of the tube giving an opposite positive charge. Its particularity is based in its structure and charges, while it is extensively investigated for its use in a variety of fields due to the creation of interactions with a wide range of molecules. Thus, halloysite has the potential to be used in pharmaceutical applications, mainly as drug delivery system.

Diclofenac (D) is a non-steroidal, anti-inflammatory analgesic finding application mainly in inflammation and pain treatment (Zhao et al., 2013). As it is a commercial active substance, it is widely investigated for the preparation of new formulations aiming to targeted release. Halloysite mineral has been investigated as a drug carrier of diclofenac with promising results and a loading capacity of 20.52 mg/g (Lei et al., 2023). However, there is a gap in the explanation of mechanisms behind the loading process.

The present study aims to fill this gap by the investigation of mutual interactions between halloysite nanotubes and two different forms of diclofenac; the neutral one (D^0) and the anionic one (D^-). Classical molecular simulations methods and especially Forcefield (FF) calculations were used. By explaining the sorption mechanisms through theoretical investigation, there is the possibility of optimization of real scale sample from a perspective of enhancing the loading capacity and controlling the drug release.

HNT-D^0 and HNT-D^- models were built, geometrically optimized and run with molecular dynamics. The results showed that HNT has a tendency to stronger attract the neutral form of the active substance. Both forms preferably interacted with the alumina octahedral sheet ($Al(OH)_3$ unit) of HNT, while the sorption mechanism acted among initial components is mainly based in electrostatic interactions. Chlorine atoms of D were strongly interacted with the halloysite sheet.

From computational point of view, when the anionic form of the drug interacted with HNT the composite can be effectively used for drug delivery applications, as the releasing process from the carrier will be faster than in the case of neutral diclofenac. The faster release is required when the active substance is given in a cream form, as it remains in contact with the skin for a short period of time while swelling quickly upon contact with water (Tiemessen et al., 1988).

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References

Lei X., Zhou Y., Liu X., Kong L., Liao L., Li Y., Liu M., Tian L., W. Rao, Lv G. (2023): Effective pH-responsive nanocarrier based on the anisotropic surfaces of halloysite nanotubes for controlled drug release. *Applied Clay Science,* **232,** 106799.

Tiemessen H.L.G.M., Boddé H.E., van Mourik C., Junginger H.E., in: K. Hummel, J. Schurz (Eds.), (1988): Dispersed Systems, Steinkopff, Darmstadt, 131-135.

Zhao Y., Abdullayev E., Vasiliev A., Lvov Y. (2013): Halloysite nanotubular clay for efficient water purification. *Journal of Colloid and Interface Science,* **406**, 121.

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HALLOYSITE AS A POTENTIAL SORBENT OF IRINOTECAN DRUG

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The presence of antitumoral drugs is dominant in hospital or municipal wastewater, but unfortunately, it significantly impacts the natural environment. One of them, irinotecan (IRI), a chemotherapeutic agent used for various cancer types, is a commercial medicinal substance widely studied in recent years. Many materials for drug removal by adsorption have been studied regarding the low initial cost, operational simplicity and absence of harmful byproducts. Clay minerals are considered superb compared to other commercial adsorbents for organic pollutants since they are abundant materials, cost-effective, and have significant sorption capacities. Halloysite is a clay mineral extensively tested for its sorption properties for organic pollutants.

In the present study, the adsorption energy and interactions between halloysite and all forms of IRI (cationic, neutral and anionic) were investigated by *ab initio* Density Functional Theory (DFT) method for the potential use of the halloysite mineral as a sorption medium for this drug removal from wastewaters (Gianni, Scholtzová, 2022). The *in silico* method implemented in the VASP program also involved corrections of dispersion interactions (Tkachenko-Scheffler).

The analysis of the calculated results showed the suitability of halloysite mineral for immobilisation of the IRI from wastewater. All forms of IRI form stable complex systems with halloysite, and the most stable system IRI-halloysite was with the cationic form of the drug.

Acknowledgements

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Reference

Gianni E., Scholtzová E. (2022): Theoretical investigation of halloysite as potential sorbent for pharmaceutical wastewaters. SUSTENG 2022. 1st International Conference on Sustainable Chemical and Environmental Engineering, 31 Aug - 04 Sep 2022, Rethymno, Crete, Greece, p. 172-173. ISBN 978-618-86417-0-9.

ACTINYL ADSORPTION ON CLAYS IN THE PRESENCE OF ORGANICS – A MOLECULAR DYNAMICS STUDY

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High-level radioactive waste is due to be stored underground in geological disposal facilities. In France, the chosen area is rich in Callovo-Oxfordian clay rock, which is itself rich in montmorillonite, illite, and interstratified illite-smectite. As the waste canisters eventually degrade, the radioactive contents may migrate into the surrounding environment. Thanks to their adsorptive properties, clay minerals will act as a barrier to prevent such radionuclide migration. However, the effectiveness of this barrier may be affected by the presence of additional species, such as carboxylic acids and carbonate ions. These anionic ligands form complexes with radionuclides which may result in reduced retention by the clay barrier. As such, an atomistic understanding of the interaction mechanisms in these systems is needed. We investigate these mechanisms using classical molecular dynamics. Our radionuclides of interest are two actinyls – $U^{VI}O_2^{2+}$ and $Np^{V}O_2^{+}$, our chosen organic molecule is malonate and the clay model is a *cis*-vacant smectite. Our chosen analysis methods include radial distribution functions, atomic density profiles, surface density profiles, diffusion coefficients and and potentials of mean force. Preliminary results indicate the importance of these ligands on the adsorption affinities and mobilities of these actinyls due to the formation of various malonato and carbonato complexes. Results also highlight the difference between the two actinyls on adsporption and complexation affinities. Ongoing work is focused on understanding how such complexes affects adsorption site preference, actinyl mobility, and adsorption free energies.

Book of Abstracts, 11th Mid-European Clay Conference (MECC 24), Plzeň, September 15-20, Czech Republic, M. Šťastný and M. Pospíšil (eds.)

IRON IN DIOCTAHEDRAL SMECTITES: A QUANTUM CHEMICAL COMPUTATIONAL VIEW ON DISTRIBUTION, STABILITY AND REDOX BEHAVIOR

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Iron as a common substituent in dioctahedral smectites affects various of their properties, like layer charge, cation exchange capacity, and swelling ability directly and via its redox capability (Stucki, 2006). The distribution and site dependent redox properties of structural iron are only partially known. To contribute to the understanding of structural iron substitutions in iron-poor dioctahedral smectites we use the quantum chemical density functional approach as implemented in the parallel software VASP (www.vasp.at). The generalized gradient approximation of the exchange-correlation potential is applied together with corrections for dispersion interactions (D3) and iron d-electron localization (DFT+U). We calculate in this way structures and energies of octahedral Fe(III) and Fe(II) substitutions in dioctahedral smectites.

We determine relative energies of Fe(III) and Fe(II) for trans- and cisvacant lattices in dependence of the distance to other substitutions for pyrophyllitic, montmorillonitic, and beidellitic sodium smectite models. These models are either charge neutral or carry layer charges of -0.25 *e* and -0.5 *e*. The energy results reproduce the known preference of montmorillonite for a cisvacant lattice and the trend of Fe(III) to stabilize transvacancy (Kaufhold et al., 2017). Fe(III) prefers sites distant from octahedral Mg(II) and Fe(II) substitutions, but close to tetrahedral Al (III) substitutions. For Fe(II) substitutions we occasionally obtain a metastable state (≈ +120 meV) with a slightly more compact first coordination shell than the ground state.

From the energies or Fe(III) and Fe(II) substitutions, relative redox potentials are derived assuming an arbitrary electron source and employing Na^+ ions for charge compensation. Cis- and transvacant sites and lattice variants affect the relative redox potential of iron by up to 100 mV. Neighboring charged substitutions lead to sites harder to reduce and yield the main effect of 300-400 mV of the variation of the redox potential. Thus, depending on the site of an Fe(III) substitution the reduction potential varies in smectites of low charge by up to 400 mV in qualitative agreement with experiment (Gorksi et al., 2013). Comparison of Fe(III) and Fe(II) in pyro-phyllite, montmorillonite, and beidellite models yields easier reduction for favorable sites in charged models. This result is supported by preliminary calculations of structural iron reduction in smectites by hydrogen.

References

Gorksi C., Klüpfel L.E., Voegelin A., Sander M., Hofstetter T.B. (2013): Redox Properties of Structural Fe in Clay Minerals: 3. Relationships between Smectite Redox and Structural Properties. *Environ. Sci. Technol.* **47**, 13477.

Kaufhold S., Kremleva A., Krüger S., Rösch N., Emmerich K., Dohrmann R. (2017): Crystal-chemical composition of dioctahedric smectites: An energy-based evaluation of empirical relationships. ACS Earth *Space Chem* ,1, 629-636.

Book of Abstracts, 11th Mid-European Clay Conference (MECC 24), Plzeň, September 15-20, Czech Republic, M. Šťastný and M. Pospíšil (eds.)

DENSITY FUNCTIONAL THEORY STUDY ON STABILITY OF SATURATED Na-, K-, Ca- AND Mg-MONTMORILLONITE

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Keywords: Density Functional Theory, saturated montmorillonite, interlayer cations, cis and trans-vacant structures.

The Density Functional Theory (DFT) method with van der Waals dispersion correction (DFT-D3) was used to determine the most stable Na-, K-. Ca- and Mg- saturated montmorillonite structures, each with a layer charge of 0.5 e. The trans-vacant (tv), cis-vacant 1 (cv1) and cis-vacant 2 (cv2) structures of the octahedral sheet were selected to be studied. Optimization of these structures was performed in a simplified model unit cell, focusing on interlayer cations (Na^+, K^+, Ca^{2+}, and Mg^{2+}), octahedral vacancy type, and d_{001} basal spacing. The purpose of this research is to obtain the most stable structures (the smallest total energy is the most stable structure) for each of these parameters. The results show that Na-saturated montmorillonite is more stable than K-saturated montmorillonite in one unit cell (1 x 1 x 1 model), and Ca-saturated montmorillonite is more stable than Mg-saturated montmorillonite in two-unit cells (1 x 2 x 1 model). The type of vacancy affected the d_{001} of the most stable structure and the structure stability. Cis-vacant structures are more stable than the trans-vacant structure in all of structures with different interlayer cation.

DYNAMIC PROPERTIES OF CLAY BASED NANOMATERIALS DESCRIBED BY COMPUTATIONAL METHODS

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Clay-based nanomaterials have earned a lot of attention for their dynamic properties, particularly in the fields of drug delivery and water dynamics. Computational methods, such as molecular dynamics simulations and density functional theory, have been recognized as well established tools to understand these properties on molecular scale. These methods allow the detailed analysis of the interactions between clay nanoparticles and drug molecules, revealing insights into drug encapsulation, release mechanisms, and stability. Additionally, the study of water dynamics within clay matrices provides crucial information on hydration, diffusion, and the overall behavior of water molecules in confined spaces. This knowledge is crucial for optimizing the design of clay-based nanomaterials for efficient drug delivery systems and enhancing their performance in various biomedical applications. Selected used cases will be shown regarding achieved results especially connected to Layered Double Hydroxides (LDHs) and Halloysites intercalated or loaded by various organic molecules.

MODELING STUDY OF ADSORPTION OF HALOGENATED BENZENES ON MONTMORILLONITE

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Halogenated benzenes (HBs) are hydrophobic organic chemicals and persistent organic pollutants. Owing to their persistence they represent a serious problem in case of environmental contamination, specifically of soils and sediments. One of the most important physical processes determining the fate of HBs in soils is adsorption to main soil components such as soil organic matter and soil minerals. Smectites, layered clay minerals of the 2:1 type, are common minerals in clay-rich soils, of which montmorillonite (Mnt) is a typical representative.

This work focuses on a systematic modeling study of the adsorption mechanism of selected HBs interacting with the basal (001) surface, which is the dominant surface of Mnt particles. HBs-Mnt interactions were studied by means of a quantum chemical approach based on the density functional theory method. HBs were represented by five molecules, particularly C_6F_6, $C_6Cl_3F_3$, C_6Cl_6, $C_6Br_3Cl_3$, and C_6Br_6. Since montmorillonite has a permanent negative layer charge due to isomorphic substitutions, which is compensated by interlayer cations, the key HBs interaction with Mnt is of the cation-π type. Thus, the effect of a different cation type on adsorption using M^+/M^{2+-}Mnt models with cations from alkali group (M^+: Li, K, Na, Rb, Cs) and alkaline earth metal group (M^{2+}: Mg, Ca, Sr, Ba) was investigated. Adsorption energies were calculated as a measure of the adsorption strength. Distances of the main molecular plane from the Mnt surface and from M^+/M^{2+} cation were measured as well. The results showed that the strongest adsorption is for Na^+-Mnt and Ca^{2+}-Mnt surfaces. The strongest affinity was observed for hexabromobenzene, while the weakest adsorption was found for hexafluorobenzene. The calculated adsorption energies showed a good correlation with experimentally determined $\log K_d$ values (adsorption coefficients, K_d, were achieved from Henry adsorption isotherms).

General session
Oral presentation

TEMPERA PAINTS BASED ON GREEN EARTH AND YOLK

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In contrast to the oil painting technique which supplanted it at the end of the 15th century, *tempera* painting[a)], practiced on wood panels, walls or canvas has received little attention on the physico-chemical scale. This painting technique, which has been practiced since Antiquity, is characterized by pigments applied in a water-based binding-medium, often egg-yolk. In order to understand the properties and appeal of this mixture on a molecular scale, we reproduced 15th century recipes which a Tuscan painter Cennino Cennini had consigned to paper, using egg-yolk and two clay-based pigments, green earth (*terra verde mainly composed of celadonite and glauconite)* or red earth (kaolinite and hematite). Rheological properties were investigated. The spreading and covering properties of the paint are enhanced due to a better internal cohesion of both pigments in the presence of the binder. The formation of a network between the proteins of the egg-yolk, the water molecules and the clay particles of the pigment which renders the mixture more viscoelastic was probed by low field NMR. The drying of these tempera paints was subsequently monitored for the first time, showing an initial stage of water evaporation followed by long term chemical processes (reticulation of the lipidic part).

This study at the very boundary of materials science and art history contributes to a better understanding of the materials chosen by painters, with the prospect of enhancing the conservation and restoration of works executed with this technique.

a) or in glue-size. *www.grandpalais.fr/fr/article/tempera-ou-detrempe*

Book of Abstracts, 11th Mid-European Clay Conference (MECC 24), Plzeň, September 15-20, Czech Republic, M. Šťastný and M. Pospíšil (eds.)

GREEN CLAYS AS COLORING AGENTS IN GEMSTONES: AN LA ICP-MS PERSPECTIVE OF NI- AND CR-BEARING CLAY MINERALS IN SILICA ROCKS

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Green microcrystalline silica rocks are known in the gem trade as “chrysoprase” or “chrome or chromium chalcedony” if colored by nickel or chromium, respectively. More rarely, opaline varieties of both exist. These green gemstones used since Antiquity generally occur in silicified laterites developed on ultramafic rocks. While the presence of Ni-bearing 2:1 clay minerals as pigments have been established for chrysoprase, the colorant phases of chromium-bearing chalcedony are yet unknown. Here, we present a geochemical mineralogical study using laser ablation inductively coupled plasma mass spectrometry in combination with X-ray diffraction analysis and scanning electron microscopy to determine the colorant phases of the green silica-rich gem materials from ten deposits and to gain insights into their origin. Due to the inhomogeneous distribution of the colorant phase, the correlation of Ni or Cr with other minor elements from multiple analyses and crystal chemical constraints allow an attribution of analyzed elements to the green chromophore, to the silica phase, to fluid inclusions or evaporated pore fluids, or to ancillary inclusion minerals, such as iron oxides. X-ray diffraction data help to identify the structure of the silica and clay minerals. Our new data show that chrysoprase and prase opal are colored by nano-sized willemseite (Haneti, Gumigil, Sarykulboldy) or Ni-bearing talc (Szklary, Golesh), rarely with additional Ni-bearing sepiolite (Golesh). The green rocks formed by co-precipitation of Ni-rich clay minerals with silica phases in open fractures probably during dry climatic phases in a lateritic environment. In contrast, chromium-bearing chalcedonies mostly originate by replacement of ultramafic rocks as evidenced by residual Cr-rich spinel inclusions, high immobile trace element contents, and field evidence. Three distinct types of green clay mineral inclusions are encountered: 1) Cr-bearing muscovite/illite (Newman, Dikmen), 2) Mg-rich, Fe-Al-poor volkonskoite (Mtoroshanga, Ricón del Tigre), and 3) various Cr-Fe-rich smectites (Eskişehir). A hydrothermal origin is indicated for chromium-bearing chalcedony with Cr-rich mica inclusions by unusual REE patterns and in part, large crystal size of the phyllosilicates, while a supergene lateritic environment is envisaged for the two types of chrome chalcedony with Cr-rich smectites. The results of this study can be applied in origin determination of gem materials in archeological objects.

WEATHERING OF FELDSPARS IN PLEISTOCENE DUNES ALONG THE OREGON COAST, USA

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Pleistocene paleodune, composed of a variety of feldspars together with quartz, make up a large area along the central Oregon coast. Secondary cementation from feldspar weathering products within these deposits provides some stability, allowing for near-vertical sea cliffs, roadcut outcrops but also cause frequent landslides. Weathering in dunal soils is accelerated by a lack of carbonates causing a high Al mobility within the last 100,000 years to precipitate several authigenic Al phases including: allophane, gibbsite, vermiculite and halloysite resulting in a degree of stability. This study aims to investigate the variability in the type and degree of cementation and weathering of feldspars in these deposits using XRD, SEM, TEM and water chemistry.

Results of the mineralogical analyses reveal cementing agents consist of hydrated minerals including Al-phases such as gibbsite, allophane, vermiculite, and halloysite. Vermiculite, and halloysite typically form a discontinuous coating on the sand grains in organic poor sections, while allophane occurs in organic rich areas. Fe-phases such as goethite, ferrihydrite, and Fe-/Mn-oxides were identified as well but are not included in this study. Results of groundwater analyses indicate the Al mobility but only to an extent, particularly under lower pH conditions. The total range of pH conditions is narrow. Furthermore, waters associated with the deposits are generally poorly buffered, due to the lack of carbonates, and thus are susceptible to significant changes in pH. Further TEM observations will give us information about the morphology, crystal structure and chemistry of the vermiculites, halloysites and allophane.

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STIMULI-INDUCED OPTICAL MODULATION

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Layered silicates offer unique confined environments for organic molecule intercalation, leading to novel heterostructures with tunable properties. This study explores the confinement-induced changes in 4,4'-(2,6-naphthalenediyl)dipyridine dication intercalated within the interlayer space of synthetic saponite, with a focus on excimer formation and stimuli-responsive behavior. The interlayer space of synthetic saponite provides a microenvironment capable of manipulating the optical properties of intercalated organic molecules either by varying the density of organic species or by expanding the interlayer space via swelling with aprotic solvents, resulting in stimuli-responsive clay-organic hybrid materials.

A combination of spectroscopic techniques, statistical analysis, and theoretical methods facilitates the identification of distinct spectral features corresponding to different spatial arrangements of the intercalated species. Moreover, this study reveals how the application of dimethyl sulfoxide affects the re-orientational behavior and the relative distribution of the intercalated organic species. The presented findings contribute to the fundamental understanding of clay-organic interactions and pave the way for optimizing and developing novel functional materials based on clay minerals for potential optoelectronic applications.

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30 YEARS' EXPERIENCE IN CLAYS AND BENTONITES FOR HIGH QUALITY SHAFT SEALINGS IN UNDERGROUND MINING – A HISTORICAL OVERVIEW

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Due to their sealing properties, clays and bentonites are well-known construction materials in geotechnical construction sites like landfills, dams and dykes. The usage of clays as a sealing segment for closing structures in underground mining on the other hand is more or less only a point of interest in the scientific discussion on nuclear waste disposals. This contribution gives an overview of the requirements and clay-based solutions in closing structures for potassium and anthracite coal mining for more than 3 decades.

During these years the requirements for sealing segments developed dramatically. While as in the 80s and beginning of the 90s of the last century earth moist clays in lumps have been dumped directly into the shaft without any further requirements, there has been a rapid development of requirements with different targets due to the specific characteristics of the construction sites. The presentation gives an overview on different concepts like self-compacting sealing clays for shaft and gallery sealings in coal mines (Wolters et al., 2015) sealings in potassium mines with low permeability, high swelling pressure towards tap water and sodium saturated brines (Schellhorn et al., 2022). Different sealing concepts are shown in development and in practice on site.

References

Schellhorn M., Diedel R.,Emmerich K., Christ F., Bodenstab D., Pöthig S., Baille W. (2022): Usage of Westerwald bentonites in a large-scale experiment for high swelling pressure shaft sealings in underground mining and nuclear waste deposits. 8th international conference on clays in natural and engineered barriers for radioactive waste confinement. Nancy 2022.

Wolters F., Baille W., Emmerich K., Schmidt E., Wolters C., Königer F., Kunz J., Krase V., Schellhorn M. (2015): High-density bimodal bentonite blends for hydraulic sealings at the Ibbenbüren coalmine. *Clay Minerals*, **50**, 391-403.

Geology and mineralogy of clays
Poster presentation

Book of Abstracts, 11th Mid-European Clay Conference (MECC 24), Plzeň, September 15-20, Czech Republic, M. Šťastný and M. Pospíšil (eds.)

MINERALOGY OF PELITIC QUATERNARY SEDIMENTS ON THE SLOPES OF MEDVEDNICA MT. (CROATIA)

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Quaternary sediments on the slopes of Medvednica Mt. belong to the Bistra Formation which consists of gravely, sandy, silty and clayey poorly sorted sediments. They were deposited in an alluvial environment in the area of sheet flows, crevasse splays, longitudinal bars and flood plains (Grizelj et al., 2017).

Mineralogical analysis of clayey silty sediments included X-ray powder diffraction analyses on random mounts of bulk samples and oriented mounts of the <2 µm fraction. Oriented mounts of the <2 µm fraction were recorded after the following treatments: a) air drying, b) ethylene-glycol solvation, c) saturation with K^+ and Mg^{2+}, d) K^+ saturation and ethylene-glycol solvation, e) Mg^{2+} saturation and ethylene-glycol solvation, f) K^+ saturation and DMSO solvation, g) Mg^{2+} saturation and glycerol solvation, h) heating to 400°C and 550°C. Geochemical analysis on same samples included determination of major and trace element compositions using inductively coupled plasma emission spectroscopy (ICP-ES) and inductively coupled plasma mass spectrometer (ICP-MS).

The main mineral components of clayey sediments are quartz, feldspar, swelling clays (vermiculite and/or smectite), illite/muscovite and in a lesser quantity kaolinite. Chlorite is present only in some samples. Analyses of the provenance of the coarser clastic sediments of the Bistra Formation point to their local origin from Medvednica Mt. They contain fragments of different types of shists and minerals derived by their weathering, and are also rich in quartz and chert (Grizelj et al., 2017). The ratios of elements that are critical for studying the provenance of pelitic sediments (LREE/HREE, Eu/Eu*, La/Sc, Th/Sc, Th/Co, Th/Cr and La/Co) confirm that their source was from several different rock types, but predominantly acidic (silicic) rocks. On the other hand, some investigated localities show a dominant source from basic rocks, which additionally confirms the strong influence of local material on the composition of these clastic rocks. However, it had no major influence on the composition of clay minerals in them. Clay minerals present in clayey silt sediments are typical for an intermediate weathering intensity, and the chemical index of alteration (CIA) generally confirms these results.

Acknowledgments

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References

Grizelj A., Bakrač K., Horvat M., Avanić R., Hećimović I. (2017): Occurrence of vivianite in alluvial Quaternary sediments in the area of Sesvete (Zagreb, Croatia). *Geol Croat*, **70**, 41-52.

THE CATION FIXATION IN BCV 2017 BENTONITE AFTER HEATING; LABORATORY EXPERIMENTS

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Bentonites are considered to be usable materials for the barrier system of high-level radioactive waste (HLRW) repositories. Černý vrch bentonite (BCV) has been proven as a representative of Czech Ca-Mg bentonites, and hence this material is included in the Czech Radioactive Waste Repository Authority (SÚRAO) research and development programme. The aim of this study was to characterize the mineralogical reactions that take place in BCV 2017 Ca-Mg bentonite following short (1 day) and long-term (47 months) heating in air at 200°C in laboratory (dry, aerobic conditions). Most concepts consider the temperatures up to 100°C in the deep geological repositories of spent nuclear fuels. The aim of this research is to investigate the potential to increase the temperature limit. Laboratory experiments can correspond to the conditions soon after placement of spent fuel canisters in the HLRW repository, with higher temperatures, the lowest humidity, and an aerobic environment.

A laboratory procedure of interlayer cation exchange by the Cu-trien complex with subsequent ethylene glycol solvation and the full-profile X-ray diffraction pattern modelling was used for the comparison of the original and heated bentonites. Heat treatment of the BCV 2017 bentonite at 200°C in the air led to a decrease in cation exchange capacity (CEC) and exchangeable Mg^{2+} (ex. Mg^{2+}) content accompanied by an increase of 10 Å layers (smectite layers with fixed Mg^{2+}) and $Sm_{Cu\text{-}trien}2g$ layers (low-charged smectite layers with interlayer Cu-trien complex and two ethylene glycol layers) and the decrease of $Sm_{Cu\text{-}trien}$ layer (high-charged smectite layers with interlayer Cu-trien). The predominance of the fixation of Mg^{2+} over the release of Ca^{2+} following heating was accompanied by the CEC decrease from an initial value ca. 58 meq/100g of original bentonite to ca. 48 meq/100g of bentonite heated for 47 months.

PROPERTIES OF VARIOUS TECHNOLOGICAL TYPES OF K-BENTONITE FROM DOLNÁ VES DEPOSIT (KREMNICKÉ VRCHY MTS., SLOVAKIA)

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The Dolná Ves K-bentonite deposit represents one of a few known economic accumulations of illite-smectite in the world. The main goal of the present study was to perform mineralogical and physico-chemical characterizations of various technological types of K-bentonites from the Dolná Ves deposit to better understand the relationships between the various qualitative types and their properties which may result in various possible applications of K-bentonites from the Dolná Ves deposit. A further goal was to compare the results obtained in the present study with the data for the Special clay ISCz-1 (illite-smectite from the Dolná Ves deposit) which has been part of the Source Clays Repository of The Clay Minerals Society Source Clays since the 1990s. The results showed that high-grade (type I) K-bentonite contains 88 – 91 wt.% of illite-smectite. The low-grade (type II) K-bentonite contained less illite-smectite, typically between 37 and 63 wt.%. The illite-smectites isolated from the high-grade K-bentonites displayed greater expandability, contained more octahedral Mg and less octahedral Fe, had greater cation exchange capacity (CEC), smaller thickness of fundamental particles, and thinner illite-smectite crystals in comparison with illite-smectites from the low-grade K-bentonites. The LOI (loss-on-ignition) and Al_2O_3 content increased with increasing amount of illite-smectite. The increase in the expandability by 10% corresponded to an increase in CEC by ~10 meq/100 g. Special clay ISCz-1 illite-smectite displayed properties similar to the high-grade K-bentonite. The best tilemaking performance was expected for the high-grade K-bentonite, with potential applications in pharmaceutical, cosmetic and food industries. Overall, the results showed that the studied technological types of K-bentonites from the Dolná Ves deposit differ not only in illite-smectite contents but also in the nature of the illite-smectites.

Book of Abstracts, 11th Mid-European Clay Conference (MECC 24), Plzeň, September 15-20, Czech Republic, M. Šťastný and M. Pospíšil (eds.)

CLAY MINERALOGY AND K/Ar GEOCHRONOLOGY OF PHYLLOSILICATE-RICH ROCKS OF THE PĂIUŞENI COMPLEX (HIGHIŞ MOUNTAINS, SW APUSENI, ROMANIA)

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The Highiş Mountains (HM) form the southwesternmost segment of the Apuseni Mountains (Romania), an Alpine orogeny located between the Pannonian and Transylvanian Basins. The major parts of the HM are built up by the Biharia nappe system which is composed of the Highiş Complex and the Păiuşeni Complex (PC) in the study area. The PC is intimately related to the Highiş–Biharia Shear Zone which represents a Variscan shear zone with Alpine overprint (Dallmeyer et al., 1999; Pană et al., 2002). As a result, the PC is comprised of different types of mylonites with heterogeneous protoliths, including felsic and mafic igneous and sedimentary rocks. Based on muscovite ^{40}Ar/^{39}Ar geochronological data, multiphase shear activity is proven with an Albian climax (Dallmeyer et al., 1999). In the present study, phyllosilicate-rich rocks of the PC were collected from two localities. The representative samples were examined by petrography, X-ray powder diffractometry-based phyllosilicate mineralogy, Mössbauer spectroscopy and K/Ar geochronology to investigate the geological evolution of the PC.

According to the observations, the studied PC rocks are (proto)mylonites with differently developed foliation. The clay fraction of the felsic phyllonites is predominated by illite ± muscovite + kaolinite + quartz + albite ± paragonite. The metabasites have diverse composition with overall presence of chlorite, illite ± muscovite and different clay minerals with vermiculitic component. Esquevin-index values indicate a heterogeneous composition of mica controlled by octahedral Fe-substitution. Kübler-index data and estimated main apparent crystallite size values prove anchi-to-epizonal metamorphic conditions. The Mössbauer spectra indicate a wide variety of chemical environments both for ferrous and ferric ions in the different clay minerals. The K/Ar geochronological data highlight the importance of the mid Cretaceous event related to the main shearing episode in the area.

References

Dallmeyer, R.D., Pană, D., Neubauer, F., Erdmer, P. (1999): Tectonothermal Evolution of the Apuseni Mountains, Romania: Resolution of Variscan versus Alpine Events with40Ar/39Ar Ages. *Journal of Geology*, **107**, 329-352.

Pană, D., Heaman, L.M., Creaser, R.A., Erdmer, P. (2002): Pre-Alpine Crust in the Apuseni Mountains, Romania: Insights from Sm-Nd and U-Pb Data. *Journal of Geology*, **110**, 341-354.

EVIDENCES FOR CRETACEOUS METAMORPHISM IN THE ZEMPLINICUM: ILLITE 'CRYSTALLINITY' AND GEOCHRONOLOGICAL DATA FROM THE PYROCLASTIC ROCKS OF THE CARBONIFEROUS ŠIMONOV VRCH FORMATION (SLOVAKIA)

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Permocarboniferous rocks of the Zemplinicum (Western Carpathians) are exposed in SE Slovakia and surrounded by the Cenozoic filling of the East Slovakian Basin. The sequence is predominated by various siliciclastics incuding conglomerates, sandstones and pelitic rocks. The Upper Carboniferous formations contain intercalations of anthracite and show anchizonal metamorphic overprint Cretaceous in age (Kobulský et al., 2012). Moreover, the coaliferous sequence is overlaid by the Šimonov vrch Formation (SVF) which is composed of, according to Kobulský et al. (2012), alternation of different pyroclastic rocks, quartzite and 'sericite schist'. Based on geochronological data of Vozárová et al. (2019), tuffs of the SVF have an eruption age of 308.5 ± 3.4 Ma (Late Carboniferous, Moscovian). In this study, SVF was sampled in the type locality and investigated by means of petrography, X-ray powder diffraction (XRPD)-based phyllosilicate mineralogy and K/Ar geochronology to trace the metamorphic grade and age.

Based on micropetrography, the studied SVF pyroclastics are predominantly vitric tuffs with poorly foliated, sericitized matrix of abundant nondeformed glass and pumice shards and opaque minerals. Crystal fragments are represented by quartz, feldspar, altered biotite and zircon. According to the XRPD measurements, the clay fraction is predominated by illite±muscovite with minor quartz, albite and kaolinite. Results of specific measurements, including determination of $d_{00,10}$ and Esquevin-index, indicate significant octahedral Fe-substitution without paragonite and/or margarite component in the K-white mica. Kübler-index data and estimated main apparent crystallite size values show anchizonal metamorphic conditions, while the K/Ar geochronological data suggest a Cretaceous (~120–140 Ma) thermal event during the evolution of the studied felsic pyroclastic rocks.

References

Kobulský J., Gazdačko Ĺ., Németh Z. (2012): New knowledge about the geological setting of Zemplinicum in the Zemplínské vrchy Mts. *Mineralia Slovaca*, **44/1, Appendix** 16-20.

Vozárová A., Larionov A., Šarinová K., Rodionov N., Lepekhina E., Vozár J., Paderin I. (2019): Clastic wedge provenance in the Zemplinicum Carboniferous–Permian rocks using the U–Pb zircon age dating (Western Carpathians, Slovakia). *International Journal of Earth Sciences*, **108**, 115-135.

Identification of clay minerals
Poster presentation

X-RAY PHOTOELECTRON SPECTROSCOPY REVEALS THE CHEMICAL ENVIRONMENT OF AL AND SI IN SECONDARY SILICATES

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Weathering of primary aluminosilicates generates secondary silicates that control important environmental processes such as binding of contaminants and organic matter. Possible products of aluminosilicate weathering comprise short-range ordered aluminosilicates (SROAS; imogolite / allophane group), clay minerals (phyllosilicates) and amorphous silica ($SiO_{2(am)}$). Those phases form at narrow mineral-water interfaces that are difficult to analyse, limiting our mechanistic understanding of weathering reactions. We tested whether X-ray photoelectron spectroscopy (XPS) can differentiate secondary silicates. This technique allows for evaluation of binding energies of photoelectrons ejected from Al and Si atoms located at the outermost region of particles. We analysed four vitreous volcanic rocks (two obsidians and two pyroclastics), two clay minerals (kaolinite and illite), three SROAS (proto-imogolite, Si-rich SROAS, SROAS formed in the presence of organic matter) and $SiO_{2(am)}$. The positions of the Al 2s and Al 2p peaks were located at lower binding energies for volcanic rocks than for secondary silicates, possibly due to the predominance of tetrahedral Al in vitreous phases. Secondary silicates contained mainly octahedral Al with variable contribution of tetrahedral Al; up to 29% of Al in Si-rich SROAS was fourfold-coordinated based on solid-state ^{27}Al nuclear magnetic resonance (NMR) analyses. However, the effect of Al speciation on Al 2s and Al 2p binding energies remained ambiguous for secondary silicates. The binding energies of Si 2s photoelectrons were lowest for SROAS (153.2–153.5 eV) and increased in the order volcanic rocks (153.7–153.8 eV), clay minerals (154.2 eV) and $SiO_{2(am)}$ (155.2 eV). The same trend was observed for Si 2p photoelectrons. Solid-state ^{29}Si NMR spectra of SROAS evinced single Si tetrahedra bound to three Al octahedra (local imogolite-like configuration) and poorly ordered Si in SROAS. Hence, the Si 2s and Si 2p binding energies correspond to the polymerization degree of Si as the number of Si-O-Si linkages per Si tetrahedron increases from SROAS to clay minerals to $SiO_{2(am)}$. Our findings suggest that gradients of the polymerization degree of Si in alteration layers on mineral surfaces could be analysed by depth-dependent XPS. Moreover, XPS measurements could reveal trajectories of mineral and glass transformation as a function of primary aluminosilicate structure and weathering conditions.

FTIR AND RAMAN SPECTROSCOPY OF ASBESTOS MINERALS

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The contribution is devoted to the identification of asbestos minerals in rock samples from various locations in the Czech Republic using FTIR and Raman spectroscopy. This spectral study was carried out within the framework of project No. SS01010257, Development of tools for minimizing the risks of air contamination by respirable asbestos fibers released by human activity from the rock environment, financially supported by the Technology Agency of the CR and also supported by the programme Dynamic Planet Earth of the Czech Academy of Sciences – Strategy AV21. Thanks to the ability to reflect the internal structure and chemical composition of the investigated substances, vibrational spectra represent an effective tool in their characterization and identification. The aim of the study was to identify and differentiate individual asbestos minerals, both from the serpentine and amphibole groups. The main focus was mainly on chrysotile, tremolite and anthophyllite. Based on the similarity with all hydrous silicates, the vibrational spectra of asbestos minerals were investigated mainly in the spectral region of the higher wavenumber region (4000–3000 cm^{-1}), where OH–stretching vibrations of hydroxyl molecules dominate, and in the lower wavenumber region (<1200 cm^{-1}), where the internal *vibrations* of *tetrahedral skeleton Si-O-Si*, cation-oxygen polyhedral (M-O), or bending/libration modes, are found. The interpretation of vibrational spectra of amphibole asbestos was more complicated than serpentine asbestos due to their extremely wide ranges of chemical composition. The mutual complementarity of infrared and Raman spectra significantly helped to obtain reliable interpretation results.

Modification of clay minerals and materials science

Poster presentation

SURFACE CHARACTERIZATION AND BULK PROPERTIES OF THE MECHANICAL TREATED ZINC OXIDE/VERMICULITE POWDER

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The surface activation of clay materials to change the physical or chemical properties of their surfaces is a common practice. Especially fine clay powdered materials have surface characteristics that influence their common behaviour (agglomeration) and, at the same time, their subsequent use, for example as fillers in polymer matrices. The modification of the surface properties of silicate layers using organic coatings (e.g. chlorhexidine/vermiculite) or growing inorganic nanoparticles on the surface (e.g. zinc oxide/vermiculite), helps not only to change their surface charge and energy, but also to significantly influence their role in the interfacial interaction between the clay (nano) filler and the polymer matrix in nanocomposites.

One of the possibilities of surface activation of clay (vermiculite) nanostructured materials is mechanical treatment in a nitrogen atmosphere. It was demonstrated that the protective atmosphere preserves the nanostructured character of the original material and also contributes to the formation of new nanostructured fractions while at the same time preserving the original vermiculite fractions. This fact was confirmed by evaluation of the increased values of the specific surface area (SSA), surface conductivity and ζ-potential values. New peaks were detected as a result of an enlarged interlayer of vermiculite using X-ray diffraction in samples containing an organic component.

Mechanical treatment in a protective nitrogen atmosphere reduces the effect of milling on the structure deformations of the vermiculite nanostructured materials, is suitable for large-scale processing, is economically undemanding, and effectively replaces the need to use chemicals for surface activation of the clay materials.

Acknowledgments

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PHOTODEGRADATION OF ZEARALENONE WITH KAOLINITE NANOTUBES-BASED PHOTOCATALYSTS: MECHANISMS AND PATHWAYS

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With over 500 mycotoxins known, their number is still rising. Mycotoxins, produced by fungi as secondary metabolites, frequently contaminate agricultural products, especially animal feed. Zearalenone (ZEN) is one of the most commonly detected. Despite its low acute toxicity, it can mimic estrogen-like effects, disrupt normal estrogen levels, and lead to reproductive disorders. Another troubling feature of ZEN is its weak polar nature, making adsorption ineffective for its removal. Therefore, the present study is focused on the photodegradation, which allows for the complete decomposition of harmful substances while being sustainable, fast, and effective.

Photocatalysts based on calcined kaolinite nanotubes (MNC) impregnated with TiO_2 (MNC-T), $g\text{-}C_3N_4$ (GCN) (composite MNC-AG), or their 1:1 mixture (MNC-T-AG) were used to investigate the kinetics of ZEN removal. For all the experiments, an initial ZEN concentration of 10 ppm was set. The experimental setup contained a 35 W UV lamp with a peak emission wavelength of 365 nm and a radiation power density adjusted to approximately 10 mW/cm^2.

The experiments conducted under visible light allowed for the removal of 18.1-39.4% of ZEN, while the use of UV light resulted in the removal of 88% of ZEN with the MNC-T and over 99.9% with the MNC-AG and MNC-T-AG. Among the tested pH conditions (pH ~2/6/10), the fastest photodegradation was achieved at the highest pH. In an alkaline medium, deprotonated ZEN has high molar absorption coefficients and reacts faster than its undissociated form. The use of tap water as a matrix accelerated the photodegradation with the MNC-T and MNC-AG materials. Simultaneous photodegradation of ZEN and deoxynivalenol (DON) mycotoxins showed almost no degradation of DON and reduced efficiency of ZEN removal. Scavenger tests indicated the significance of $O_2^{\bullet-}$ radicals in the photodegradation of ZEN. In the case of the MNC-AG, the major influence of e^- was also observed. The use of electrospray ionization tandem mass spectrometry (ESI-MS/MS) showed that all the materials led to similar ZEN photodegradation pathways, and the plausible products of ZEN photodegradation were proposed. Future research will focus on the photocatalytic removal of DON and the determination of its photodegradation pathways.

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Book of Abstracts, 11th Mid-European Clay Conference (MECC 24), Plzeň, September 15-20, Czech Republic, M. Šťastný and M. Pospíšil (eds.)

THE POLYELECTROLYTE GEL-LIKE MODEL OF CLAY SWELLING

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The so-called long-range or osmotic swelling of bentonite clays in aqueous solutions is traditionally considered to be a result of electrostatic repulsion between diffuse double layers at the surface of silicate platelets whose strength is governed by the surface charge, and the valence and concentration of neutralizing electrolyte ions (Gouy-Chapmann theory, GC-EDL). This is in accord with the relationship between the X-ray-determined clay interlayer spacing and the inverse square root of concentration of ions, $c^{-1/2}$, measured directly by Keith Norrish´s in 1954 on homoionic montmorillonites (Norrish, 1954). However, our measurements reveal the equilibrium sediment volume and the Einstein intrinsic viscosity factor of bentonite dispersions (both quantitative measures of free or unrestricted swelling extent) to depend on the ionic activity according to the power law with −3/5 rather than −1/2 exponent. This has also been confirmed by re-analysing newer X-ray diffraction data for montmorillonites. Therefore, we suggest that the anomalous swelling of bentonites is markedly influenced by the presence of three-dimensional polyelectrolyte gel-like layers (in some conjunction with the GC-EDL theory) representing amorphous polymeric clay hydrolytic dissolution products, as the latter value of the exponent has been predicted in the approximate power scaling law for polyelectrolyte gels (Flory, 1953).

References

Norrish K. (1954): The swelling of montmorillonite. *Disc. Faraday Soc.*, **18**, 120-134.

Flory P. J. (1953): Principles of Polymer Chemistry, Cornell University Press, Ithaca and London, 672 pp.

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COMBINED EFFECT OF CLAY MINERALS AND CALCIUM CARBONATE PRECIPITATION AT WET-DRY CYCLES ON AGGREGATE FORMATION AND STABILITY

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Different organic and inorganic binding agents have been suggested to be crucial for aggregate formation and stability in soils (Totsche et al., 2018). Microbial-derived organic matter favors the formation of aggregates by their gluing nature, while small-sized inorganic soil compounds such as clay minerals and metal (hydr)oxides as well as carbonates and siliceous phases precipitated from the liquid phase could act as cements (Totsche et al., 2018). The location and function of these binding agents is strongly related with water meniscii present. The clay minerals have high ability to retain calcium ion. Thus, the level of calcium carbonate formation and their micromorphology might be different compared to the sandy soil without the clay content. Here we want to determine in which way carbonates in presence/absence of clay contributes to stable aggregation of sand in wet-dry cycles.

Polished glass beads (200-250 μm) and bentonite were used in model experiments on sandy soil and clay mineral, respectively. The bentonite was added to the glass beads at 1 wt%. Calcium carbonate was added as both nanoparticle and saturated solution. The treatments with SiO_2 nanoparticle or suspension instead of bentonite were also prepared. Partly saturation of the pore space was adjusted by solution/water addition. After solution addition samples were kept at room temperature for 2 hrs and stored at 35 °C for 24 hrs as dry cycle, followed by a rewetting. This drying condition was adequate to dry out the solution added. Wet-dry cycles were repeated up to five times. The micromorphology of cementing of the glass beads was determined by both digital- and confocal-laser-scanning-microscopy focussing on the contact point of glass beads. Surface coverage degree, surface roughness and the number of heights were quantified by confocal laser scanning microscopy.

Marked assemblages of precipitates were found at or close to the contact point of the glass beads. Their formation is strongly related with the shape of water meniscii. In presence of SiO_2 nanoparticles, indicated by surface roughness, precipitation occurred undifferentiated on the total surface of glass beads, in contrast to the H_4SiO_4 solution, efficently binding glass beads to each other. The presence of bentonite resulted in wall-like precipitations connecting the glass beads in marked distance to the contact point. Surface charge, size exclusion at contact points of glass beads and the formation of stable flocculated structures of bentonite affected micromorphology of the cements. The knowledge on micromorphology of different cementing agents in the pore space is important to enhance this process for engineering applications because the aggregation formation and their stability might depend on the cementing agents.

References

Totsche K.U., Amelung W., Gerzabek M.H., Guggenberger G. (2018): Microaggregates in soils. *J. Plant. Nutr. Soil Sci.* **181**, 104–136.

THE STABILITY OF SMECTITE TO THERMOCHEMICAL TREATMENT AS ONE OF THE CRITERIA FOR SELECTING BENTONITES FOR RADIOACTIVE WASTE DISPOSAL.

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The concept of high-level radioactive waste disposal in crystalline rocks involves the creation of an engineered barrier system, one component of which is based on bentonite materials. After the closure of a deep geological repository (DGR), various processes can lead to the degradation of barrier materials, which could affect long-term safety. The concept of radioactive waste disposal currently under development in the Russian Federation, considers the use of bentonites in various locations, primarily in the buffer zone. In order to justify the choice of bentonite for the buffer zone, complex studies are conducted on the influence of various negative factors on the composition, structure, and properties of bentonites and their insulation properties under conditions imitating the underground disposal site.

The study of the transformation mechanisms of montmorillonite particularly and bentonite in general, and their behavior under DGR conditions, is an important task for assessing the safety of underground disposal in the short and long term. One can use both highly negative scenarios that that are less probable, and scenarios similar to the expected conditions, to obtain data for modeling the evolution of the repository system.

The thermochemical treatment was performed using solutions of acids (13 M HNO_3) and alkalis (0.5 M KOH and 0.5 M NaOH) and a solution simulating the groundwater of the Nizhnekansky crystalline rock massif, at different pH values and high temperatures. The acid and alkali treatments were carried out for 1 and 5 hours at 90 °C. Experiments with artificial groundwater lasted 6 months at the same temperature. Bentonite clays were selected from different deposits that differed in the structural features of smectites, such as 10th Khutor, Zyryanskoe, Dashkovskoe (Russian Federation), Taganskoe (Kazakhstan), Dash-Salakhli (Azerbaijan), Trebia (Morocco). Changes in the structure of smectites in treated bentonites were analyzed using a set of techniques, including XRD, XRF, DTA/TG, and FTIR.

The conducted studies revealed several factors that determine the stability of smectite clays under thermochemical treatment. These factors include the predominance of cis-vacant octahedral sites, the layer charge and the average density of charge, as well as the fraction of tetrahedral charge. However, there was no clear correlation found between the stability of smectites and the amount of isomorphic substitution of Fe, Al and Mg. It can therefore be argued that, in each individual case, certain structural characteristics have the greatest influence on the stability, and may differ for the same bentonite in different conditions.

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MICROCELLULAR CORDIERITE CERAMICS TO ADDRESS ENVIRONMENTAL ASPECTS OF ENERGY STORAGE MATERIALS

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Cordierite-based ceramics represent one of the very interesting engineering materials. The properties of final ceramic product depend on the starting materials and processing conditions used to the preparation. The focus of this study was to produce cordierite ceramics with different porosity with possible application in energy storage. The basic pre-ceramic mixtures were composed of natural minerals – kaolinite, talc and vermiculite combined with technical alumina. The clay minerals including kaolinite and talc were used in their natural forms in the pre-ceramic mixtures. The vermiculite was used either in its natural, milled form or organically modified with dodecylamine. At first, four pre-ceramic mixtures were carefully homogenized and afterwards two of them were immediately sintered at 1300 °C (Fig. 1a). The remaining two mixtures were exposed of the effect hydrogen peroxide to prepare ceramic foams (Fig. 1b) and increase the porosity of ceramic materials. This process was followed by sintering at the same temperature as in the previous case. The chemical and phase composition, microstructure and other properties were characterized by several techniques.

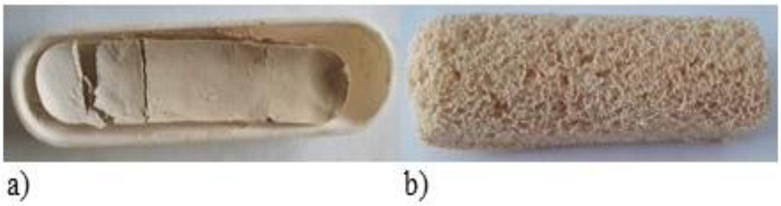

Fig. 1. Porosity changes of cordierite-based ceramics: a) after sintering and b) after foaming process followed by sintering.

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FORMATION AND PROPERTIES OF TRIMETHYL CHITOSAN/SMECTITE NANOCOMPOSITES

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N,N,N-trimethyl chitosan (TMCH) is an antibacterial, biocompatible, biodegradable and highly bioadhesive polymer compared to chitosan (CH). TMCH or CH and two smectites with different cation exchange capacity (CEC) were used for preparation of hybrid systems by layer-by-layer (LBL) method. The objective of the work was to study the influence of the smectite layer charge on the resulting properties of hybrid systems. TMCH was prepared by two-stage quaternization reaction of CH with iodomethane. The success of reaction was controlled by H-NMR and IR spectroscopy in the mid and near IR regions. Two smectites were used for preparation of hybrid films: Sumecton SA (S; CEC = 0.72 mmol/g) and montmorillonite Lutila from new Slovak deposit (Lu; CEC = 1.04 mmol/g). The polypropylene glass (PP), used as substrate for LBL films, was activated by DCSBD plasma for 20 s at ambient air and put into TMCH, resp. CH solution. After the activation, the PP was immersed in stock solutions of S, or Lu and again TMCH or CH and it was marked as the first layer of LBL film. Films were prepared by alternating layers of cationic CH and TMCH molecules and negatively charged S and Lu until reaching a total of 20 layers of LBL film. Infrared spectra were measured by ATR method after the deposition of each layer. The most significant changes were observed in the 950 – 1100 cm^{-1} region. These changes were attributed to Si-O stretching vibrations of smectites and C-O stretching vibrations of CH or TMCH. As the number of layers increased, the following trend was observed in the intensity of the band region: CH-S < TMCH-S < CH-Lu < TMCH-Lu. This indicates that films prepared with Lu (higher CEC) were thicker than those with S. Additionally, the TMCH-based films were thicker than the CH-based films. The prepared samples were also tested for stability of LBL films in water. The samples were immersed in water, shaken for 24 h and again analyzed by IR spectroscopy. The most intense decrease of the mentioned band area was observed for the TMCH-Lu (28.8 %) and least significant for the TMCH-S (8.9 %). The antibacterial activity of prepared samples was also tested. The most pronounced bacterial inhibition was observed for the TMCH-Lu sample and confirmed the substantial influence of layer charge on the resulted properties of the materials.

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PHOTODEGRADATION OF ZEARALENONE WITH KAOLINITE NANOTUBES-BASED PHOTOCATALYSTS: MECHANISMS AND PATHWAYS

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With over 500 mycotoxins known, their number is still rising. Mycotoxins, produced by fungi as secondary metabolites, frequently contaminate agricultural products, especially animal feed. Zearalenone (ZEN) is one of the most commonly detected. Despite its low acute toxicity, it can mimic estrogen-like effects, disrupt normal estrogen levels, and lead to reproductive disorders. Another troubling feature of ZEN is its weak polar nature, making adsorption ineffective for its removal. Therefore, the present study is focused on the photodegradation, which allows for the complete decomposition of harmful substances while being sustainable, fast, and effective.

Photocatalysts based on calcined kaolinite nanotubes (MNC) impregnated with TiO_2 (MNC-T), g-C_3N_4 (GCN) (composite MNC-AG), or their 1:1 mixture (MNC-T-AG) were used to investigate the kinetics of ZEN removal. For all the experiments, an initial ZEN concentration of 10 ppm was set. The experimental setup contained a 35 W UV lamp with a peak emission wavelength of 365 nm and a radiation power density adjusted to approximately 10 mW/cm^2.

The experiments conducted under visible light allowed for the removal of 18.1-39.4% of ZEN, while the use of UV light resulted in the removal of 88% of ZEN with the MNC-T and over 99.9% with the MNC-AG and MNC-T-AG. Among the tested pH conditions (pH ~2/6/10), the fastest photodegradation was achieved at the highest pH. In an alkaline medium, deprotonated ZEN has high molar absorption coefficients and reacts faster than its undissociated form. The use of tap water as a matrix accelerated the photodegradation with the MNC-T and MNC-AG materials. Simultaneous photodegradation of ZEN and deoxynivalenol (DON) mycotoxins showed almost no degradation of DON and reduced efficiency of ZEN removal. Scavenger tests indicated the significance of $O_2^{\bullet-}$ radicals in the photodegradation of ZEN. In the case of the MNC-AG, the major influence of e^- was also observed. The use of electrospray ionization tandem mass spectrometry (ESI-MS/MS) showed that all the materials led to similar ZEN photodegradation pathways, and the plausible products of ZEN photodegradation were proposed. Future research will focus on the photocatalytic removal of DON and the determination of its photodegradation pathways.

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BEHAVIOR OF ENGINEERED BARRIER SYSTEM MATERIALS IN THE CONDITIONS OF RUSSIAN DEEP GEOLOGICAL REPOSITORY

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Currently, the Russian Federation is developing a concept for the construction of a deep geological repository (DGR) of radioactive waste in crystalline rocks on the periphery of the Nizhnekansky granitoid massif. The concept proposes to use bentonite clays as a buffer material. Bentonites of the buffer layer will be affected by pore waters of the massif and other barrier materials such as concrete and steel. To ensure the safety of the repository, it is important to obtain numerical data on changes in the engineered barrier system (EBS) materials, particularly buffer clays (Krupskaya et al., 2023).

A series of experiments were conducted to identify patterns in the changes of composition, structure and properties of bentonites, as well as the changes in the structure of smectites, at simulated conditions of the DGR using solutions simulating pore waters of the “Yeniseisky” site with different pH and in interaction with concrete and steel. Bentonites from the deposits of 10th Khutor (Russian Federation) and Taganskoe (Kazakhstan Republic) were studied.

The results of experiments with artificial pore water solutions at different pH and temperature of 90 ^{o}C showed high stability of smectites for up to 6 months. Under these conditions the mineral composition changed insignificantly.

In the experiments on the interaction between bentonite and steel, iron (Fe) incorporation into the octahedral sheets of smectite was observed as the layer charge increased. In experiments with the 10th Khutor bentonite and steel in artificial pore water, there was a reduction in Fe in the octahedral layer. However, in experiments with concrete leachate solution, Fe oxidation occurred.

In the experiments on the interaction of bentonite from Taganskoe deposit with steel, there was reduction in the smectite content, according to XRD quantitative mineral analysis and infrared spectroscopy. In all conducted experiments, no synthesis of other clay minerals, such as either chlorite and illite, or trioctahedral forms of smectite, was observed. However, under the same conditions, the studied bentonites showed different resistance to the influence of solutions with different compositions at high temperatures. This was manifested in structural changes of smectites and their partial destruction.

References

Krupskaya V.V., Tyupina E.A., Zakusin S.V., Ilina O.A., Saveleva E.A. (2023): On the feasibility assessment of clay material application in the development of engineered safety barrier designs for deep geological RW disposal at the Yeniseiskiy site. *Radioactive Waste*, 2 (23), 98-112

Morozov I., Zakusin S., Kozlov P., Zakusina O., Roshchin M., Chernov M., Boldyrev K., Zaitseva T., Tyupina E., Krupskaya V. (2022): Bentonite–Concrete Interactions in Engineered Barrier Systems during the Isolation of Radioactive Waste Based on the Results of Short-Term Laboratory Experiments. *Applied Science*, **12**, 6, 3074.

LUMINESCENCE ENHANCEMENT IN HYBRID MATERIALS COMPOSED OF BENZOTHIAZOLE-BASED DYES AND LAYERED SILICATES

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The study focuses on the development of photoactive hybrid materials composed of organic dyes and layered silicates aiming to enhance photoactivity. These hybrid systems combine the photoactive properties of benzothiazole-based cationic dyes and the stabilizing properties of synthetic saponite (Sap) nanoparticles. Two new dyes were investigated: 2-(4-(diphenylamino)styryl)-3-methylbenzothiazole-3-ium iodide (SIG373) and 2,6-bis{(E)-2-[4-(diphenylamino)phenyl]vinyl}-3,7-dimethylbenzo[1,2-d;4,5-d']bisthiazole-3,7-diium diiodide (AC111). Dispersions of these dyes with Sap were prepared in ten different dye/Sap ratios to study their optical behavior. Various spectroscopic techniques, including UV-VIS spectroscopy, fluorescence spectroscopy, time-resolved fluorescence spectroscopy, and quantum yield measurements, were employed to analyze the photophysical properties of both the pure dye solutions and the hybrid dye dispersions. Our findings indicate that the adsorption of both dyes on Sap particles significantly stabilizes the systems against absorbance changes (bleaching) and enhances emission intensity, particularly in the systems with SIG373 dye. This enhancement is attributed to surface-fixation-induced emission (S-FIE) phenomenon. The most substantial increase in emission was observed at a dye/Sap ratio of 0.01 mmol/g. Over time, the hybrid systems exhibited further enhancement in emission intensity, reaching optimal fluorescence quantum yields of 1.9 % for AC111/Sap and 3.1 % for SIG373/Sap after 7 days. Overall, this research underscores the potential of dye/Sap hybrid systems in creating advanced photofunctional materials with improved photoactivity and stability, paving the way for their application in various photochemical technologies.

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SMECTITE COMPOSITES FOR WATER DECONTAMINATION FROM PHARMACEUTICAL MICROPOLLUTANTS

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Due to increasing occurrence of drugs in wastewater associated with their consumption, it is necessary to pay attention to finding new accessible types of sorbents for effective drug removal. Smectite composite materials can represent low cost and eco-friendly sorbents. The aim of this study was the comparison of ability of prepared organo-smectite composites for the removal of the most used analgesics from water environment. Montmorillonite, beidellite, hectorite and nontronite were modified with benzalkonium and cetylpyridinium chloride. X-ray powder diffraction and FT-IR spectroscopy were used to evaluate the intercalation process of organic cations into the clay structure. The enhancement of the basal spacing confirmed the intercalation process of surfactants. The simultaneous thermogravimetry and differential thermal analysis showed that the organically modified smectites generally exhibited lower values of temperatures related to releasing of structural water as well as the higher temperatures of total melting process. Adsorption experiments were carried out in a batch mode with different mass of sorbents and initial concentration and volume of ibuprofen and diclofenac solutions. The removal of diclofenac and ibuprofen from aqueous solution reached up to 95% sorption efficiency for all smectite composites in the following order montmorillonite > notronite > beidellite> hectorite.

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PREPARATION AND CHARACTERISATION OF MONTMORILLONITE/POLY(2-ETHYL-2-OXAZOLINE) NANOCOMPOSITES

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Poly(2-oxazoline)s are an important class of non-ionic polymers which are biostable and biodegradable. They have structural similarities to poly(ethylene oxide) and polypeptides. Poly(2-ethyl-2-oxazoline) (PEtOx) have similar hydrophilicity, biocompatibility and blood circulation times as poly(ethylene oxide). Composites of clay minerals with non-ionic polymers, such as poly(ethylene glycol), poly(vinyl alcohol), and polyvinylpyrrolidone are frequently and systematically studied systems. On the other hand, composites of montmorillonite (Mnt) and PEtOx were prepared for the first time and the effect of increasing $n_{\text{PEtOx}}/m_{\text{Mnt}}$ ratio on the adsorption and structural characteristics was examined. For adsorption experiments a colloidal dispersion of Mnt with various loadings of PEtOx were prepared, for infrared and X-ray diffraction (XRD) analysis, solid samples with various loadings of polymer were prepared. Adsorption isotherm of PEtOx revealed a sharp increase in adsorption at low polymer loadings. When the surface of Mnt was saturated with the PEtOx, on the adsorption isotherm we can observe a plateau that does not change significantly with the increasing loading of polymer. The maximum adsorption capacity of PEtOx adsorbed on Mnt was 3.86 $\text{mmol}\cdot\text{g}^{-1}$. XRD is the most widely used method for the characterization of clay minerals. The most intense diffraction reflex with ~ 7° 2θ in smectite XRD records belongs to the first basal reflection 001 and it corresponds to d value, which represents the layer height together with the interlayer space. We used this method to monitor the changes in the size of the interlayer space during the intercalation of PEtOx into Mnt. The interlayer space increased significantly with increasing loading of PEtOx in the interval from 0.5 to 5.0 $\text{mmol}\cdot\text{g}^{-1}$. When the loading of PEtOx was higher than 5.0 $\text{mmol}\cdot\text{g}^{-}$, interlayer space did not change practically with increasing loading of polymer. The prepared nanocomposites were also studied FT-IR method. The intensities of the absorption bands related to the vibrations of the C=O and CH groups increased with rising amounts of polymer. A slight shift of the CH bands position reflected the transition from disordered to more ordered polymer arrangement. Study and understanding the interaction between PEtOx and Mnt is needed for designing novel organically modified Mnt composites for environmental and industrial applications based on these components.

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PHYSICOCHEMICAL ASPECTS AND NEAR-IR STUDY OF HYDRATION PROPERTIES OF POLY(2-ETHYL-2-OXAZOLINE) AND POLY(DIALLYLDIMETHYLAMMONIUM CHLORIDE) FUNCTIONALIZED MONTMORILLONITE

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The novel functionalized montmorillonites (Mts) with non-ionic poly(2-ethyl-2-oxazoline) (PEtOx) and cationic poly(diallyldimethylammonium) (PDDA) were created via an intercalation method with different loading ratio of both polymers. Their comprehensive physicochemical characteristics were analysed through carbon analysis, PXRD, FTIR, TGA/DSC and BET-N2 adsorption analysis. The influence of hydration on PEtOx-Mts and PDDA-Mts was investigated using gravimetric analysis and NIR spectroscopy. PXRD analysis showed a significant increase in 001 diffraction of PDDA-Mt corresponding to a PDDA interlayer with a d001 ranging from 1.47 to 1.49 nm. The increased of basal spacing exceeding 2 nm for PEtOx polymer was observed. After modification of Na-Mt with PEtOx polymer, FTIR spectroscopy revealed the presence of the carbonyl C=O group (3265 and 1641 cm^{-1}) and the stretching (2982, 2942 and 2883 cm^{-1}) and bending (1480 - 1200 cm^{-1}) vibrations of the CH_2 and CH_3 groups. The vibrations of the CH groups were also confirmed after PDDA modification. The results of BET-N_2 adsorption analysis showed a significant decrease in the specific surface (SSA) area after modification with a non-ionic PEtOx polymer. On the contrary, in the case of modification of Na-Mt with polycation PDDA, SSA increased slightly in two instances. TG analysis revealed greater mass loss for PEtOx-Mts compared to PDDA-Mts. DTG analysis confirmed the release of physisorbed bound water around 100 °C, decomposition of the organic phase within the 250 -550 °C range and dehydroxylation of OH groups around 550 - 800 °C in both cases. The results obtained from the gravimetry and NIR analysis indicated a greater hydrophobic nature for PEtOx-Mts compared to PDDA-Mts. These findings have considerable potential to improving the properties of novel organo-montmorillonites, thereby facilitating their application as adsorbents for pollutants, biodegradable materials, surface coatings, drug carriers, fillers in polymer nanocomposites, and various other important applications.

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REMOVAL OF Cd(II) IONS BY ADSORPTION ON INORGANICALLY MODIFIED MONTMORILLONITE COMPOSITE

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Heavy metals represent significant aquatic environment contaminants whose presence in the environment is predominantly the result of anthropogenic activities. These metals such exhibit high toxicity and non-biodegradability, leading to serious consequences for both ecosystems and human health. One of the important applications of sorption properties of clay minerals, especially montmorillonite and kaolinite, and/or composite clay materials is their use in removing heavy metals from aquatic systems. For the uptake of metal cations from wastewaters, synthetic oxides/oxyhydroxides of Mn, Fe, Al, etc., with negatively charged surfaces are also suitable. MnO_2 is a type of surface acidic oxide with a pH_{pzc} (point of zero charge) of about 2.0. However, most metal oxides are only available as fine powders, which leads to practical limitations, in particular the difficulty of solid-liquid separation. A possible solution is the preparation of alternative sorbents using montmorillonite as a carrier for manganese oxides. The aim of this work was to investigate the properties of manganese oxide coated montmorillonite (Mn-Mt) as adsorbent for removing Cd(II) ions from solutions in a batch laboratory system. The effective connection of manganese oxide with the montmorillonite was confirmed by the results of the X-ray diffraction analysis and X-ray photoelectron spectroscopy, the oxide coated on montmorillonite surface is presented mainly as cryptomelane (αMnO_2). XPS measurements in manganese-modified montmorillonite composites confirmed the manganese chemical status, the valence states of the precipitated manganese ions had state of Mn^{4+}. The sorption of Cd(II) ions by Mn-Mt composites was pH dependent and the adsorption isotherms revealed that the uptake of Cd(II) ions could be described by the Langmuir model.

Sorption experiments demonstrated that the synthesis of inorganically modified montmorillonite composites offers the possibility of obtaining materials that can potentially be used as sorbents for the removal of Cd(II) ions from aqueous solutions.

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COMPREHENSIVE APPROACH TO THE ANALYSIS OF THE LAYER CHARGE DISTRIBUTION IN SMECTITES: A CASE STUDY OF THE 10TH KHUTOR INDUSTRIAL DEPOSIT (REP. KHAKASSIA)

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The layer charge and its distribution are fundamental characteristics of smectite minerals, which determine their physicochemical properties, including adsorption and solvation (hydration) processes and also structural, mechanical, and other properties of bentonites and materials based on them. However, the formal approach commonly used to calculate structural formulas of smectites and derivation of the layer charge does not provide sufficient or accurate information about their structure. This approach may lead to inaccurate interpretations of structural features of smectite. This work presents the results of a study on the localization of the layer charge in smectite and its effect on the properties of bentonite clays. The approach involved a combination of several methods, including the Lagaly method, a method for derivation of structural formulas based on elemental and mineral compositions, and the Grenne-Kelly method for charge distribution analysis in tetrahedral and octahedral sheets. Detailed studies were conducted on the samples from the 10th Khutor deposit, which is the deposit with the largest bentonite production in the Russian Federation at present. It is located within the Minusinsk Depression (Republic of Khakassia) and consists of several productive bentonite layers of volcanogenic-sedimentary origin.

For the analysis several particle-size fractions were separated (<0.2, <0.6, <1, and <2 μm) from the commercial batch sample and additionally converted to monocationic forms. CEC values were determined using the Cu-trien method. LOI and chemical composition (using XRF method, PANalytical X-ray spectrometer, Axios MAX). To assess the composition and content of impurities, a quantitative XRD analysis was performed.

The structural formula method leads to a systematic overestimation of the layer charge density and CEC, which can be due to inaccurate assessment of impurity content and composition, as well as the complex state of K, which may or may not be exchangeable under different conditions, being part of not only smectite structure but more complex mineral phases. Finally, when evaluating the charge distribution in tetrahedral and octahedral sheets, it is important to rely on the results of adsorption measurements. These results should be considered along with the results of other methods, such as the method of structural formulas and the AA method. The Green-Kelly test must also be used to confirm or refute the experimental data that reflects the actual structure of smectites.

Application of clays in industry, medicine and environment

Poster presentation

MECHANISMS OF OXYANION REMOVAL BY CARBONATE-BASED LAYERED DOUBLE HYDROXIDES: A COMBINATION OF ADSORPTION MODELING AND SOLID-STATE ANALYSES

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The mobility of elements in the environment is significantly influenced by mineral/water interfaces, including various types of clays. Due to the ability to influence the mobility of both cations and anions, layered double hydroxides (LDHs), i.e. anionic clays, are particularly interesting for environmental applications. Although the adsorption behavior of LDHs has been extensively studied, the main shortcoming of the existing studies is the still prevalent use of empirical models to describe the adsorption data. However, such models cannot provide direct information on the removal mechanisms and/or individual binding arrangements. In contrast, surface complexation models (SCM), combined with detailed solid-state analyses, enable the specification of the binding arrangements to the mineral surface, including establishing stability constants of individual surface complexes. To fill this research gap, this study aimed to combine SCM with various solid-state analyses to describe the adsorption of As and P onto carbonate-based Mg-Fe LDHs in both single-ion and competitive systems. In general, Mg-Fe LDHs showed good removal efficiency for both As and P in single-ion adsorption systems. In contrast, a decrease in adsorption for both oxyanions was evident in competing systems. The results of the solid-state analyses showed that surface complexation is the predominant mechanism at lower As/P loadings. However, at higher loadings and/or lower pH values, the formation of Fe phosphates/arsenates was observed. In addition to the basic empirical models, the primary attention was then focused on the description of pH-dependent adsorption data at lower As/P loadings using two types of SCM, namely the diffusion layer model (DLM) and the charge-distribution multisite complexation model (CD-MUSIC). Although CD-MUSIC requires a larger number of input parameters, it allows, unlike DLM, to evaluate the formation of both inner-sphere and outer-sphere complexes. The best description of the adsorption data was achieved by combining these two types of surface complexes, namely inner-sphere complexes at lower pH values and outer-sphere complexes at higher pH values. Such a comprehensive approach combining solid-state analyses and advanced modeling approaches thus provides more detailed information on the surface properties of LDHs and, therefore, could be beneficial in predicting the oxyanion mobility in water or soil when LDHs are present as reactive phases.

ADSORPTION PROPERTIES OF ALUMINOSILICATE-FLY ASH COMPOSITES

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Preparation of composite adsorbents from recycled and/or waste products represents new discipline for possible obtaining broad-selective adsorbents thanks to the combination of properties of all participating components (Han et al., 2019).

The composite adsorbents were prepared as dry mixtures of three AL with FA from biomass combustion in the weight ratio of 1:1. The suspension of each mixture with distilled water was agitated in the batch manner at 20 and 60 °C for 24 hours. The identical suspension was aged in autoclave at 110 °C for 5 days. Each suspension was then filtered off, dried at 60 °C and homogenized mechanically in the mortar. The composites were tested for the separate adsorption of toxic cations (Pb^{2+}, Cd^{2+}) and anions (AsO_4^{3-}, CrO_4^{2-}), and for the cation and anion co-adsorption from model solution.

The FA from biomass combustion represented a promising aditive to AL composite adsorbents. AL-FA composites were more selective for cation adsorption, which mostly ran according to the Langmuir model, at a high adsorption capacity and low sorbent consumption. The adsorption of anions was less effective, although AsO_4^{3-} was effectively adsorbed (>80%) on some composites, but at an order of magnitude lower capacity and higher sorbent consumption compared to cation adsorption. The increased preparation temperature (65 °C) and even autoclave treatment (110 °C, 5 days) did not affect either the structural and surface or the adsorption properties of composites. The adsorption potential of composites can be assumed in co-adsorption of differently charged ions, where the variability of adsorption sites and mutual affinity of adsorbed ions can support effective adsorption In co-adsorption systems, up to 50% higher adsorption yield was generally achieved compared to the adsorption of a separate ion. In the case of anions, the presence of oppositely charged ion enhanced the adsorption yield up to five fold (Doušová et al, 2024a; Doušová et al, 2024b).

The composites were more effective adsorbents compared to the source AL. The other benefit of AL-FA composites was observed in increased homogeneity compared to the individual material.

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References

Hana H., Rafiq M.K., Zhoua T., Xua R., Mašek O., Lia X. (2019): A critical review of clay-based composites with enhanced adsorption performance for metal and organic pollutants. *Hazard. Mater.* **369**, 780–796.

Doušová B., Pilař L., Koloušek D., Bedrnová E., Lhotka M., Maxová K. (2024a): Adsorption properties of fly ash-clay composites from Central European sites: A case study. *App. Clay Sci.*, **255**, 107395. 7 p.

Doušová B., Bedrnová E., Maxová K., Koloušek D., Lhotka M., Pilař l., Angelis M. (2024b): Kaolin–Fly Ash Composite for Pb^{2+} and AsO_4^{3-} Adsorption from Aqueous Systém. *Applied Sciences,* **14**, 5358, 14 p.

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FROM RAW MATERIAL TO LOW-CO2 BINDER - META-CLAY PRODUCTION FOR BUILDING MATERIAL APPLICATIONS

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The Institut für Angewandte Bauforschung Weimar supports industrial companies in the development of pozzolanic cement or composite cement (LC3 cement). For this purpose, meta-clays are produced on a small industrial scale. The basis for this is the analysis of the raw materials (XRD, WD-XRF, DSC/TG) in the institute's own laboratory. From this, the potential pozzolanicity of the subsequent meta-clays can be estimated. The rotary kiln pilot plant (DRO) can produce between 0.5 and 2 tons for concrete testing. A small-scale flash calciner is also in operation. The application limits of the cements developed are being verified in mortar and concrete technology tests.

Analytical methods: The Raw material analyses including XRF, XRD, DSC/TG and BET surface are used to estimate the raw material quality. Thermal activation on a laboratory scale [600 - 1050°C] is used to determine pozzolanicity by means of the Chapelle test (CTb), R3 test (calorimeter), thermal analysis (DSC/TG) and mineral phase analysis (XRD temperature chamber). Thermal activation takes place in the DRO pilot plant (< 1200°C) or the flash calciner (since 2024). Subsequently, mortar tests are carried out to determine the strength index, spreading dimension, setting times and spatial stability.

The material transformation processes of clay raw materials are known from the ceramics industry. From this, characteristic temperature ranges for pozzolanic activation can be derived for various clay minerals. As a result of the raw material analyses, the respective clay mineral composition as well as types and contents of the accompanying minerals, in particular quartz, carbonates, feldspars and Fe minerals, can be determined. The expected pozzolanic activities can be empirically estimated from this. After thermal treatment of the respective raw materials on a laboratory scale, these activities are determined using modified Chapelle tests. The optimum calcination temperatures are determined from this. Batches of up to 10 kg can be calcined for mortar tests in the laboratory chamber furnace. The pilot rotary kiln system and the flash calciner allow the production of several hundred kg up to 2 tonnes of metatone. For the final evaluation of the products, standardised mortar tests are carried out in accordance with standards. The various clay minerals exhibit different levels of pozzolanicity after optimised thermal treatment.

THE ROLE OF ANTIMICROBIAL CLAY NANOFILLERS ON THE STRUCTURE AND DEGRADATION OF POLYCAPROLACTONE NANOCOMPOSITE FILMS: A COMPREHENSIVE STUDY

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Currently, the big challenges and topics in the medical fields is the increasing incidence of resistant microbial infections, which represent one of the most serious complications.

Among the dynamically growing areas of material research is the development of polymer nanocomposites, as they play an important role in the field of antimicrobial materials for medical applications, because the surfaces of medical equipment and supplies are required to have sufficient antimicrobial properties, to be free of biofilm and to prevent such infectious surface transmission.

Addition of *nanofiller* leads to a two-way increase in the polymer nanocomposite activity, firstly by reinforcing the overall polymer structure and secondly acting as an active element against microbial infections. On the other hand, there is a polymer matrix, which, in view of the ever-increasing concerns about current environmental pollution, should be chosen from among *biodegradable polymers*. Therefore, hybrid nanocomposites, which are the result of the interaction between *clay minerals* and *biodegradable polymers*, appear to be very promising for these purposes.

The aim of this study is to present a comprehensive view on role of used antimicrobial clay based nanofillers on structural and degradation properties of novel PCL/clay nanocomposites combined with the antimicrobial agents chlorhexidine diacetate and/or octenidine dihydrochloride and ZnO, which appear to be promising materials with extended antimicrobial properties. The results showed that clay nanofillers contained ZnO significantly decreases thermal and mechanical stability of prepared films. Further, nanofillers with the higher hydrophilic character are responsible for the faster degradation of PCL nanocomposite films.

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MINERALOGICAL COMPOSITION CONTROLS SOIL ORGANIC CARBON IN TROPICAL VERTISOLS

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Vertisols are a group of clay-rich soils with great agronomic relevance in many tropical regions. Their characteristic mineral constituents are smectites which display high sorption capacities for a wide range of organic compounds. Yet, Vertisols frequently possess low contents of soil organic carbon (SOC) and it remains unclear how variations in soil mineral composition relate to their SOC storage potential. We thus aimed to unravel the mineralogical diversity of tropical Vertisols in a confined geographical area displaying a high geological and climatological heterogeneity and relate mineral inventories to SOC contents. We sampled Vertisols in northern Cameroon covering a wide range of parent materials and hydrological regimes, and performed selective Fe extractions as well quantitative X-ray diffractometry (Rietveld method). Organic carbon contents were determined by dry combustion at 1060 °C. Mineral inventories showed a high variability among sites. Smectite contents ranged between 15 and 40 wt%, and illite contents were <4 wt%, suggesting minor illite-smectite interlayering. In heavily inundated soils receiving ultramafic alluvium, nontronite was the dominating smectite mineral. Extractable soil Fe was strongly controlled by the hydrological regime: While short-range ordered (SRO) Fe oxides were highly abundant in soils heavily inundated during rainy seasons, they were depleted in soils experiencing only shallow annual inundation or leaching due to close proximity to a major river. Besides the inundation regime, the abundance of SRO Fe oxides was further controlled by the supply of weatherable Fe-rich parent material. Soil smectite contents were positively correlated to total Fe content and to the relative abundance of SRO Fe oxides. Soil organic carbon contents (<2 wt%) and the C/N ratio (~10) were generally low, the latter indicating the preferential accumulation of N-rich organic compounds or inorganic N (NH_4^+). Soil organic carbon contents were positively correlated with the abundance of SRO Fe oxides but negatively with the content of crystalline Fe oxides (goethite, hematite). This suggests a minor role of crystalline Fe oxides in SOC stabilization in tropical Vertisols which is in stark contrast to other tropical soils. Despite the strong positive correlation between smectite content and relative SRO Fe oxide abundance and between SOC content and Fe in SRO Fe oxides, we found no relationship between smectite contents and SOC. Our results imply that tropical Vertisols display a considerable mineralogical variability that warrants detailed assessment. Furthermore, SOC contents appear to be controlled by sesquioxides rather than expandable phyllosilicate clays.

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MINERALOGICAL CHANGES IN SAZ-2 BENTONITE REACTED WITH POTASSIUM OXALATE AFTER CA SATURATION OF TWO 8-MONTH TEST SERIES AT 25 AND 200 °C.

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Bentonite clay can be used as an appropriate backfilling material between the canisters with high level radioactive waste and the host rock. Besides being recognized as a thermodynamic seal, concerns regarding their long-term stability remains. The illitization of smectite leads to a reduction of swelling and therefore to a loss of the self-sealing property of the bentonite. The bentonite that was used for this study is the SAz-2 Bentonite from Arizona which was provided from the Clay Minerals Society. For the experiments, the <1 µm size fraction was separated. The bentonite was saturated with 0.1 M K-oxalate solution, and then treated at temperatures of 200 °C and 25 °C, for periods ranging from one to eight months, with samples being collected monthly or bimontly. The dried reaction products were afterwards Ca exchanged with a 0.1 M $CaCl_2$ solution prior to XRD measurements to replace the exchangeable K^+ ions with Ca^{2+} ions, in order to prevent the overestimation of illite content due to the presence of K-smectite. The quantification of the illite-smectite mixed layered relative contents was done with Rietveld refinement and Sybilla modelling. Different relative amounts and ordering of mixed layered illite-smectite were formed at different temperatures. At 25 °C, R0 ordered illite-smectite was observed. The content of illite in this illite-smectite was 11 % after eight months. Beside the illite-smectite, whewellite was also present in all samples. At 200 °C, R1 ordered illite-smectite was formed, which changed into an R3 ordered illite-smectite after four months. Within the first month, an illite-smectite with 77 % illite was formed, which turned to an amount of 90 % after eight months. The reaction of the illitization occurs very fast within the first month. From the fourth month a stagnation in the illite formation can be observed. The amounts of illite are around 89 % from the fourth to the eighth month. Between the second and the third month a new mineral, sanidine, was formed. It can be assumed that the potassium from the K-oxalate solution is used for the formation of illite and sanidine. The results of this study have implications on the long-term stability of the SAz-2 Bentonite as backfilling material. The illitization of smectite occurs faster under higher temperatures. It is important to see that small amounts of illite were already formed at 25 °C. The reaction rate at 200 °C was more than eight times faster than at 25 °C.

IN SITU FORMATION OF LDH-BASED NANOCONTAINERS ON Zn ALLOY - A DETAILED INVESTIGATION OF THEIR MORPHOLOGY AND STRUCTURE

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Layered double hydroxides (LDHs) are materials of broad interest to researchers and industry. They are layered materials with a structure corresponding to minerals of the hydrotalcite group. The layers, composed of octahedra in which the central positions are occupied by two- and three-positive cations, respectively, generate a positive charge, balanced by interlayer anions. This is why they belong to the group of clay minerals called anionic clay minerals. Consequently, with this property and taking advantage of their ion-exchange and adsorption properties, LDHs can find application wherever the aim is to retain a particular ion in the structure. The high affinity of LDH for various types of anions has already been demonstrated and is becoming increasingly important in biomedical-related applications in particular in dealing with corrosion problems of alloys. Recently, much attention has been paid to magnesium and zinc alloys as temporary biodegradable implants due to their biocompatibility, nontoxicity, and positive effects on the growth of new bone tissue. The main obstacle to the application of Mg/Zn alloys as a temporary implant is their fast biodegradation rate. Therefore, protective coatings must be used to control the degradation profile and improve the functional properties. Implementation of coatings with layered double hydroxide structure will allow the creation of biodegradable materials with enhanced corrosion resistance, biocompatibility, and controllable degradation.

In this study, we focus on the development of LDH films by their in situ formation on the surface of Zn alloy using the substrate alloy as an internal source of Zn cations. To obtain the series of Zn Al- NO_3/CO_3/LDH naturally adherent coatings on the surface of Zn alloys the pH and temperature of mother liquor containing $Al(NO_3)_3$ 9 H_2O were under control. In this approach, the degree of alloy substrate polishing (with 1000 and 4000 grit), the time of growth (3 and 20 h), and the thickness of LDH structure coatings were comparatively investigated towards the formation of a dense LDH surface layer, which later on worked as the LDH-based nanocontainers for incorporation of corrosion inhibitors and chitosan film. The effects of the preparation methods, the structure, and the morphology of LDH coatings were gauged using SEM, XRD, and FTIR methods. EDS analysis showed the presence of Zn and Al in the micro-areas of the formed LDH layer. Consequently, the amount of Al increases with progressive synthesis time, which confirms the crystallization of the hydrotalcite-like layer on the Zn alloy surface. XRD and FTIR analysis revealed the changes in the LDH layer as a function of exposure time to the solution containing Al^{3+} ions. A comparison of the diffractograms of the ZnAl-LDH /Zn alloy samples revealed the presence of a highly amorphous ZnAl-LDH phase on the surface of the Zn alloy next to small intensity reflections of ZnO.

Computational methods in clay science

Poster presentation

Book of Abstracts, 11th Mid-European Clay Conference (MECC 24), Plzeň, September 15-20, Czech Republic, M. Šťastný and M. Pospíšil (eds.)

HALLOYSITE AS A SORBENT OF FOREVER CHEMICALS AND PESTICIDES FOR SOIL DECONTAMINATION

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Halloysite (HNT), is an aluminosilicate clay mineral of kaolin group, with spiral-shape nanotubular morphology. The tetrahedral sheet (SiO_2) composes the outer surface of the nanotube giving it a negative charge, while the octahedral sheet ($Al(OH)_3$) composes the inner surface of the tube giving an opposite positive charge. Its particularity is based in its structure and charges, while it is extensively investigated for its use in a variety of fields due to the creation of interactions with a wide range of molecules. Thus, HNT has the potential to be used in soil and water decontamination, i.e. as sorbent material for a variety of contaminants.

PFAS are more than 12000 anthropogenic chemical compounds [1], known also as forever chemicals as they are extremely persistent, lasting thousands of years. This behavior is owned to the strong carbon-fluorine bond which is present in PFAS. PFAS were extensively used in several applications, including the fabrication of resisted fluorinated plastic containers. When aqueous solutions were stored in such containers, PFAS as well as perfluoroalkyl carboxylic acids (PFCAs) can be also released (Whitehead, Peaslee, 2023). More specifically, U.S. EPA reported that when methanol or water directly interacted with such containers, parts-per-billion concentrations could be released after only one week of exposure, which increased over time (Nyguyen, 2021). Pesticides are substances that frequently stored in the form of aqueous solutions in fluorinated containers, potentially releasing PFCAs. When pesticides are used in agricultural areas, the soils may be contaminated in both PFCAs and pesticides.

In the present study, classical molecular simulation methods were used for the insight investigation of halloysite and the simplest form of PFCAs, the perfluorobutanoic acid (PFBA), which was used as a model of PFCAs for the investigation of soil decontamination by halloysite mineral. The simultaneous sorption of pesticides, i.e. atrazine (ATR) and diuron (DIU) which were used as model substances, and PFBA was investigated.

From theoretical point of view, halloysite found to be a sufficient sorbent of PFBA creating stable complexes comparable with the halloysite/herbicides models (Gianni et al., 2022). When both PFBA and herbicides (ATR or DIU) were loaded into HNT, the high energy stability of the complexes was proved giving comparable results with the initial models (i.e. HNT/PFBA, HNT/ATR, HNT/DIU). Electrostatic interactions between the organic pollutants and the HNT prevailed in the system. Further experimental data and computational calculations are needed for the application of HNT in real scale soil decontamination.

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References

Gianni E., Moreno-Rodríguez D., Jankovič L., Scholtzová E., Pospíšil M. (2022): How herbicides like atrazine and diuron interact with the spiral halloysite structure. *Journal of Environmental Chemical Engineering*, **10**(6), p. 108785.

Nyguyen T. (2021): Rinses from Selected Fluorinated and Non-Fluorinated HDPE Containers.

Whitehead H.D., Peaslee G.F. (2023): Directly Fluorinated Containers as a Source of Perfluoroalkyl Carboxylic Acids. *Environmental Science & Technology Letters*.

FOCUSED ION BEAM – SCANNING ELECTRON MICROSCOPY (FIB-SEM) TOMOGRAPHY AND COMPUTER VISION (CV) OF THE PORE STRUCTURE OF REPOSITORY RELEVANT CLAYSTONES: METHODOLOGY AND OUTLOOK

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FIB-SEM tomography in combination with computer vision is an excellent tool for analyzing the pore structure of claystones. Shape and size of the micropores can provide insights into the rock's diagenetic history and aid in the evaluation of the mechanical and hydrodynamic properties. One important aspect is the changes that occur relative to the burial history of these sedimentary rocks, where systematic changes in micropore structure occur during progressive diagenesis. In this study, a selection of repository-relevant claystones with varying degrees of thermal maturity were selected from Europe and North America to establish the patterns in pore space evolution.

One vital challenge is to obtain high-quality image sequences with FIB-SEM from these claystones for 3D microstructural characterization and quantification. This requires that several analytical problems be overcome. Heterogeneity in material properties can lead to curtain artifacts and/or poor milling quality. To avoid this, it is essential to precisely adjust the FIB milling current. Both qualitative and quantitative analyses have shown that a gallium ion source operated at 350 µA offers a good compromise between milling time and image quality, whereby a spatial resolution of 10 nm in sufficient analysis volumes (10 μm^3) for most studied clay rocks.

It is common to use the secondary electron detector (SE2) at low acceleration currents (< 1.5 kV) to better visualize the pores due to the enhanced contrast and reduced material charging. However this approach also does introduce increased signal gradients and noise. Traditional computer vision methods for denoising often remove noise at the expense of image detail and edge resolution by removing or averaging information. One solution to mitigate these effects is to use re-utilized ensembles of open-source latent diffusion models (LDMs), in combination with grayscale ControlNets, to upscale and denoise FIB-SEM images and preserve the intricate details. Another challenge is encountered in achieving effective segmentation of the micropore structure. Most traditional CV methods only rely on information from a single pixel and neglect spatial context. However, due to occasional unclear boundaries and 2.5D characteristics, a precise analysis of the relationship between neighboring pixels is required. Therefore, one intermediate goal is the development of a robust machine-learning model for micropore structure segmentation. This poster showcases examples of these improvements and provides an overview of the current advancements in enhancing and segmenting the micropore structure in FIB-SEM images of for nuclear waste repository-relevant claystones.

MOLECULAR SIMULATIONS STUDY OF ATORVASTATIN IN LDH

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Atorvastatin is a widely prescribed drug for treatment and prevention of cardiovascular diseases. It is typically used in the form of calcium salt which, however, has low bioavailability. Layered double hydroxides (LDH) are a class of layered materials used in many industries and pharmaceutics for their ability to intercalate (and subsequently release) various anions. Intercalation of atorvastatin into LDH is a potential new form of administering which could increase its bioavailability, allow more controlled release into the bloodstream and possibly mitigate some side effects of atorvastatin.

Mg-Al LDH structure intercalated with three different concentrations of atorvastatin was modelled using the force field method molecular modelling with the Condensed-phase Optimized Molecular Potentials for Atomistic Simulation Studies (COMPASS) force field. Various starting arrangements were used for each concentration.

Several suitable final arrangements were found through geometry optimization to reach the energy minimum and then studied with molecular dynamics methods. The formation of hydrogen bonds between the carboxyl groups of atorvastatin and LDH layers was observed. The resulting basal spacing values of LDH showed good agreement with values obtained from X-ray diffraction measurements. Our results show good promise for the possibility to administer atorvastatin in the LDH-intercalated form; despite of this further study and tests are needed.

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MOLECULAR SIMULATION OF PALYGORSKITE AND SEPIOLITE PORES FOR NO_3^--N AND NH_4^+-N SORPTION AND DESORPTION

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Molecular simulations methods were used to describe the mutual interactions between nitro (NO_3^-) or ammonium (NH_4^+) ions and fibrous clay minerals palygorskite and sepiolite as adsorbents. Specifically, the ribbon- like structures of palygorskite and sepiolite, as well as the molecular structure of the nitrogenous ions and water molecules, were built in Materials Studio software and analyzed via the geometry optimization to reach energy minimum by using molecular mechanics and dynamics methods. Molecular dynamics was used to describe and understand of adsorption behavior of ions.

It was shown that both nitrogenous ions were mainly interacted with the free zeolitic water molecules presented in the pores of palygorskite and sepiolite, yielding the mutual electrostatic interactions among them and clay as the dominant ones. It was shown that the dimensions of both clay pores were crucial parameter for the developed bonds strength, especially in NH_4^+ ion case. Based on molecular dynamic calculation results, the inner pore size determines the palygorskite and sepiolite removal capacity and subsequently desorption efficiency of NH_4^+ ions. Specifically, according to obtained binding energies the larger sepiolite pores facilitated the interactions with two NO_3^- molecules (-1098 kcal/mol) instead of one NO_3^- molecule (-42 kcal/mol) with palygorskite, while deeper NH_4^+ penetration and stronger bonding could be achieved only on sepiolite. This explains the low NH_4^+ release rate compared to palygorskite.

The calculated results were compared to previously publish experimental data of our research team and a good agreement was reached. This study presents the importance and usability of molecular simulations contribution in evaluation and characterization of inner adsorption processes which could not be prove experimentally in the fibrous clay minerals.

Reference

Lazaratou C.V., Papoulis D., Vayenas D.V., Pospíšil M. (2024): Molecular simulation approach for $NO3^-$ -N and $NH4^+$-N sorption and desorption in the pores of palygorskite and sepiolite clay minerals. *Applied Clay Science*, **254,** 107371. https://doi.org/10.1016/j.clay.2024.107371

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THEORETICAL AND EXPERIMENTAL STUDY OF CHROMATE POLLUTANTS ADSORPTION BY POLY-(N-BUTYL ETHYLENEIMINE)-MODIFIED MONTMORILLONITE

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Hexavalent chromium, Cr(VI), can be found in natural aquatic systems and is hazardous to the environment. The worldwide contamination of water by heavy metal compounds, such as Cr(VI), is considered a significant problem with severe consequences for human health. Also, it harms the stability of natural ecosystems (Fu, Wang, 2011). In general, Cr(VI) has been shown to be toxic to bacteria, plants and animals (Gładysz-Płaska et al., 2012). A feasible method for removing toxic hexavalent chromium is adsorption (Salgado-Gomez et al., 2014). It has become one of the preferred methods for removing toxic contaminants from water into a solid phase because it is effective, economical, versatile and simple (Fu, Wang, 2011).

This paper presents the combined theoretical and experimental study of the adsorption of hazardous Cr(VI) into the interlayer space of poly-(N-butyl ethyleneimine)-modified montmorillonite. This paper presents the combined theoretical and experimental study of the adsorption of hazardous Cr(VI) into the interlayer space of poly-(N-butyl ethyleneimine)-modified montmorillonite. The main goal of this research is to provide a comprehensive structural investigation that includes the calculation of the structural stability and determination of the strength and number of hydrogen interactions of individual systems. Finally, the measured FTIR spectra were explored using the calculated vibrational modes obtained from the projected vibrational density of states using the *ab initio* molecular dynamics (AIMD) approach.

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References

Fu F., Wang Q. (2011): Removal of heavy metal ions from wastewaters: A review. *J. Environ. Manage.* **92**, 407-418.

Gładysz-Płaska A., Majdan M., Pikus S., Sternik D. (2012): Simultaneous adsorption of chromium(VI) and phenol on natural red clay modified by HDTMA. *Chem. Eng. J.* **179**, 140.

Salgado-Gomez N., Macedo-Miranda M.G, Olguin M. T. (2014): Chromium VI adsorption from sodium chromate and potassium dichromate aqueous systems by hexadecyltrimethylammonium-modified zeolite-rich tuff. *Appl. Clay Sci.* **95**, 197.

General session
Poster presentation

Book of Abstracts, 11th Mid-European Clay Conference (MECC 24), Plzeň, September 15-20, Czech Republic, M. Šťastný and M. Pospíšil (eds.)

SYNTHESIS AND EVALUATION OF CERAMIC MEMBRANES FROM DD KAOLINS FOR TEXTILE WASTEWATER TREATMENT

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Keywords: Ceramic membranes, DD kaolins, Textile wastewater, anionic dye, Adsorption

The high cost of commercial membranes has prompted the search for alternative materials that facilitate the practical application of membrane technology. Among the most promising alternatives are ceramic clay-based materials. These materials, characterized by their low cost, natural abundance, and long-term functional robustness, offer a feasible solution for scaled-up systems. In this study, the local DD1 and DD3 kaolins extracted from the Djbal Dbagh mountains in Guelma province (Algeria) were valorized for the preparation of flat ceramic membranes with dimensions of 50 mm diameter and 3 mm thickness using a uniaxial pressing method. These membranes were specifically tested for the removal of anionic dye. The raw material underwent characterization using X-ray fluorescence (XRF), scanning electron microscopy (SEM), X-ray diffraction (XRD), and thermogravimetric analysis (TGA) techniques. In addition, several techniques were used to assess the characteristics of the prepared membranes. Various experimental parameters, including pH, contact time, temperature, initial concentration, and adsorbent mass, were investigated in a batch adsorption system. The results demonstrate that ceramic membranes based on DD3 kaolin exhibit high adsorption efficiencies. The physicochemical characterization of the prepared membranes presents encouraging results, opening up a wide range of development and application prospects.

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CHARACTERIZATION OF CLAY MINERALS USING ADSORPTION TECHNIQUE

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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 kaolinite, bentonite, montmorillonite and rehydroxylated kaolinites using the adsorption methods. The adsorption isotherms were measured on an ASAP 2020 and 3Flex surface analysers (Micromeritics, Norcross, GA, USA) using the gas sorption technique (N_2 at 77 K). These adsorption isotherms were fitted according the Brunauer-Emmett-Teller (S_{BET}) method and t-plot method ($S_{t\text{-}plot}$) for specific surface area, the micropore volume by the t-plot method and the pore-size distribution by the Barrett-Joyner-Halenda (BJH) method and Density Functional Theory (DFT) method. In addition, the scanning adsorption isotherms of all the mentioned samples were measured. Scanning isotherms provide important information about the pore network geometry, including its connectivity and pore size distribution, which cannot be revealed from the main adsorption and desorption isotherms.

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.

References

Brunauer S., Emmet P. H., Teller E. (1938): Adsorption of Gases in Multimolecular Layers**.** *J. Am. Chem. Soc.* **60**(2), 309.

Cimino R., Cychosz K. A., Thommes M., Neimark A. V. (2013): Experimental and theoretical studies of scanning adsorption-desorption isotherms. *Colloids and Surfaces A: Physicochem. Eng. Aspects,* **437**, 76-89.

CHARACTERIZATION AND CORRELATION OF SELECTED GLACIAL TILLS NEAR GLOWE (RÜGEN)

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This study uses the clay mineralogy of Pleistocene tills on the Jasmund peninsula (Rügen, SW Baltic Sea coast) to identify relationships between various tills which were deposited during the last glacial periods (Elsterian-, Saalian- and Weichselian glaciations) to improve their understanding in the context of age, provenance, and climate. For this purpose, a widespread sediment sampling was conducted, one near Glowe at a coastal cliff, the other one at a coastal cliff called "Glowe-West". The samples were size separated (< 2 µm and < 0,5 µm). Random powders, airdried-, glycolated- and heated oriented aggregates were prepared for X-ray diffraction (XRD) analyses. Grain size distribution of the tills were also conducted.

To determine possible correlations between the tills, a detailed visual comparison of the diffractograms and Rietveld refinement/quantification using Profex were done. The XRD analyses show that all samples from all horizons generally contain the same mineral phases. The main difference between them is the mineral contents. For example, the lithostratigraphic units M-02, M-1o and M-3 vary in chlorite content and degree of weathering from the rest. Even if the differences between the lithostratigraphic units are not great, they are noticeable.

Further investigation reveals that environmental conditions leading to an increase of chemical weathering might be the reason for the mineralogical differences. Indicators like chlorite content, ratios of different minerals and the CMAI (clay mineral alteration index) imply such changes (Warr 2022; Warr et al. 2024). This is supported by the lithostratigraphic order of the tills. Those with reduced chemical weathering were deposited at the end of a glacial period or before an interstadial. A rise of temperature implies greater influence of chemical weathering on those sediments due to the warmer climate that comes along with it.

References

Warr L. N. (2022). Earth's clay mineral inventory and its climate interaction: A quantitative assessment. *Earth-Science Reviews*.

Warr L. N., Grathoff G., Haberzettel T. (2024): The Clay Mineral Alteration Index (CMAI) as an improved indicator of climate change. *Applied Clay Science - Elsevier*.

MINERALOGICAL AND GEOCHEMICAL ANALYSIS OF TWO SOIL PROFILES IN THE LAKE VINDEREL AREA, MARAMUREȘ, ROMANIA

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The research area is located in the Inner Eastern Carpathians, which are part of the Dacia megaunit. Lake Vinderel is located in the Black flysch unit, which belongs to the Outer Dacids as the innermost cover of the flysch zone of the Eastern Carpathians. The study of soil samples from the vicinity of Lake Vinderel is carried out as accompanying research of the lake itself. Soil, lake samples and surrounding rocks were sampled in June 2023. Lake Vinderel is located at an altitude of 1680 m above sea level (ASL). The first soil profile (V2; 120 cm, 5 samples in depth: 0-3, 5-15, 15-25, 30-50, 100-115 cm) was sampled directly at the edge of the lake in a landslide on the border of a grassy meadow and a part with almost no vegetation. The soil was developed on a gray sandy clay similar to that sampled from the lake sediments. Fragments (up to 5 cm) of sandy phyllite were found in the area and within the profile. The second soil excavation was made on the grassy place of the Farcău peak (1957 m ASL). Stony soil with depth 40 cm (V4, 3 samples in depth: 0-3, 5-15, 20-40 cm) was located on partially weathered but solid basalt. In most studied samples, the fraction below 63 μm (47-71 wt.%) dominates. Except for sample V4B, where the main fraction is above 2 mm. The pH increases with the depth of sampling. A strongly acidic environment prevails. Chemical and mineral analysis of soil and surrounding rock samples did not show any significant differences. The main clay mineral phases are illite and chlorite throughout the studied profile V2.

The results show that these are typical mountain soils with the initial stage of pedogenesis, belonging to the group of Leptosols. The soil developed on the basalt (Farcău peak) can be classified as Skeletic Leptosol. Probably also the soil profile at Lake Vinderel, but there it is not possible to talk about the predominance of the skeleton because the soil is on sandy clay, which also formed a larger part of the profile.

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