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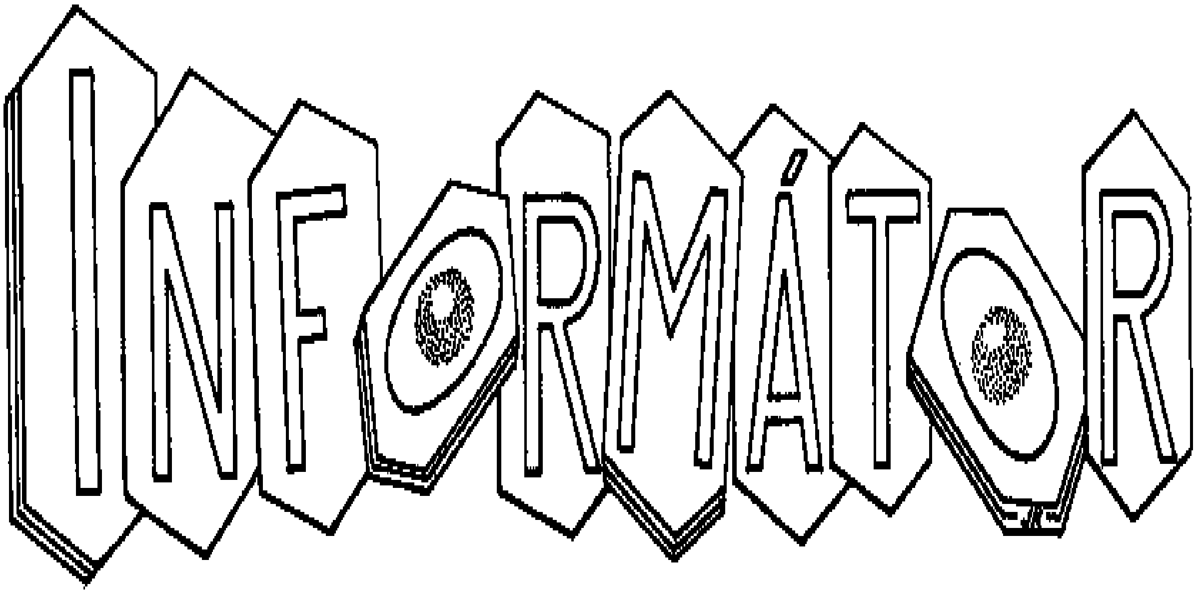

INFORMÁTOR

Book of Abstracts

Martin Šťastný and Anna Žigová (eds.)

6th Mid-European Clay Conference (MECC´12), September 4-9, 2012, Průhonice

Czech National Clay Group, Průhonice

6th Mid-European Clay Conference

Průhonice, Czech Republic
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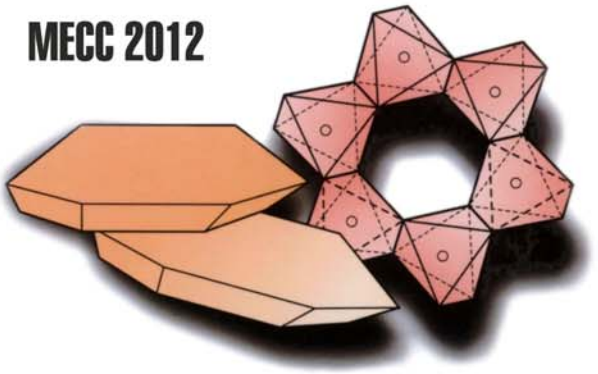

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matematicko-fyzikální fakulta

6th Mid-European Clay Conference (MECC'12)

Book of Abstracts

Martin Šťastný and Anna Žigová (eds.)

September 4–9, 2012, Průhonice

Content

Plenary lectures

STRUCTURAL AND MECHANICAL PROPERTIES OF METAKAOLIN AND RED MUD BASED GEOPOLYMERS

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Geopolymers, a class of largely amorphous aluminosilicate binder materials, have been studied extensively over the past several decades. New geopolymer formulations were elaborated by sodium silicate/NaOH activation of mixtures of metakaolin (MK-1200S, France), iron oxide and red mud. The effects of source materials on the microstructure and mechanical properties were studied by comparing three types of geopolymers.

The metakaolin MK-1200S (France) was used as a source of alumina-silicate. In water medium, alkaline activators NaOH (Chemicals analytical reagent grade) and $NaSiO_2$ (Merck, Germany; 8.5 wt% Na_2O, 28.5 wt% SiO_2, 63 wt% H_2O) were used for dissolution of aluminosilicate to insure that no residual sodium. The constituents were formulated according to the following molar oxide ratios: $SiO_2/Al_2O_3 = 1$, $Na_2O/Al_2O_3 = 1$. The water content for all the samples was kept the same with a molar ratio of $H_2O/Na_2O = 17$. Other geopolymers were prepared by substitution of metakaolin by 1/4, 1/6, 1/8, 1/10 and 1/12 of red mud (RM) and 1/12 of commercial Fe_2O_3.

The disparities in initial formulations, inducing different degrees of geopolymerization reactivity, were reflected in the phase composition and microstructure between the three tested compounds. Moreover, the variation in strength between the geopolymers is attributed to the same factors, with higher rates of voids and nonreactive phases located in red mud based geopolymer matrix.

Nevertheless, the initial formulations of the geopolymers (with MK or RM) did not influence so much their mechanical properties. The compressive strenght of the geopolymers gave maximum values around 8 MPa.

NANOCOMPOSITES CONDUCTING POLYANILINE/CLAY

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Phyllosilicates – thanks to their unique properties – represent very interesting component in composites with conducting polymers. It is well known that phyllosilicate layer charge of montmorillonites and vermiculites affect the electronic structure and spectral properties of intercalated organic dyes and leads to changes in position, profile and intensity of photoluminescence emission bands (Klika et al., 2009; Simha Martynková et al., 2008; Klika et al., 2007). In case of conducting polymers phyllosilicates play triplicate role in nanocomposites: (1) improve the mechanical and thermal stability; (2) facilitate the design of functional units and (3) tunning spectral properties. Three forms of polyaniline/clay (PANI/clay) nanocomposite samples have been prepared and characterized: (a) powder samples, (b) pressed pellets and (c) thin solid films. The properties and parameters studied in this project were: Structure, conductivity, optical properties – transmittance, reflectivity and optical homogeneity. Samples were characterized by a series of experimental methods: X-ray diffraction, IR, UV VIS and Raman spectroscopy, transmittance mapping (for thin films) and electrical conductivity measurements. Experimental methods have been supplemented by molecular modeling using empirical force field in *Materials studio* modeling environment. Results of this study can be briefly summarized as follows: Nanocomposites PANI/vermiculite exhibit lower conductivity than PANI/montmorillonite in all forms (powders, tablets, thin films) thanks to higher layer charge in vermiculite. Conductivity of pressed pellets depends on pressure and exhibits strong anisotropy. Two-dimensional conductivity of pressed tablets PANI/montmorillonite is nearly the same as for pure PANI tablets, however nanocomposite tablets are mechanically and thermally more stable than pure PANI tablets. Relationship technology – structure – properties (optical and electrical) has been revealed for various methods of sample preparation.

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GEOLOGY, MINERALOGY, GEOCHEMISTRY AND GENESIS OF HYDROTHERMAL KAOLINITE DEPOSITS WITHIN NEOGENE VOLCANITES OF THE SİMAV AREA, KÜTAHYA (WESTERN ANATOLIA), TURKEY

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The Simav area (Kütahya) kaolinite deposits formed by alteration of dacitic and andesitic tuffs related to Neogene volcanism that was associated with extensional tectonics. Altered units and related host rocks were examined using polarised-light microscopy, X-ray diffractometry, scanning electron microscopy, infrared spectroscopy, and chemical methods. Feldspar phenocrysts show degradation and argillisation, biotite and hornblende are opacitised and chloritised, sanidine is sericitised and argillised, volcanic glass is devitrified and quartz is fragmented and cemented by micronetworks of reddish-brown Fe oxides, which coexist with poorly crystalline silica phases and zeolite crystals. The kaolinite deposits locally coexist with alunite and contain silica and Fe- and Ti-bearing phases (pyrite, goethite and rutile) in vertical and subvertical veins that diminish and then disappear upward. Mineralogical zonation outward from the main kaolinite deposit is as follows: kaolinite ± smectite ± alunite + illite + opal-CT + feldspar; feldspar + kaolinite + quartz + smectite + illite; quartz + feldspar + volcanic glass. Illite and smectite increase downward. The veins and mineral distributions indicate that hydrothermal alteration was the main process in the development of the kaolinite deposits of the area. The very sharp, intense, diagnostic basal reflections at 7.2 and 3.57 Å, as well as non-basal reflections, well-defined pseudohexagonal crystallinity with regular outlines, ideal differential thermal analysis-thermal gravimetric curves, and ideal, sharp, infrared spectral bands indicate well-crystallised kaolinite. Micromorphologically, the development of kaolinite plates and smectite flakes at the edges of altered feldspar, devitrified volcanic glass, and acicular crystals of opal-CT are indicative of an authigenic origin. Lateral increase in $SiO_2+Fe_2O_3+MgO+Na_2O+CaO+K_2O/Al_2O_3+TiO_2$ from the centre of the kaolinite deposit outward also indicates hydrothermal zonation. Depletion of Sr, Rb, Ba, Ca and K in altered and partially altered rocks relative to fresh volcanic-rock samples demonstrates hydrothermal alteration of sanidine and plagioclase within the volcanic units. In addition, depletion of heavy rare-earth elements (*HREE*) relative to light rare-earth elements (*LREE*) in the kaolinised materials may be attributed to the alteration of hornblende. Negative Eu anomalies suggest the alteration of feldspar by hydrothermal fluids. Thus, the kaolinite deposits are understood to have formed by hydrothermal alteration of volcanic glass, feldspar and hornblende via a dissolution-precipitation mechanism which operated under acidic conditions within Neogene dacite, andesite and tuffs.

CLAYS IN RADIOACTIVE WASTE DISPOSAL - OVERVIEW AND A TYPICAL BENTONITE BUFFER APPLICATION IN ÄSPÖ, SWEDEN

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Bentonites are candidate materials for the encapsulation of radioactive waste. In the ABM project (Alternative Buffer Material test) thirty blocks of nine different bentonites and two different clay stones were packed on each other with a heater in the centre (iron). The buffer materials which were mainly from large deposits initially had different exchangeable cation compositions. The first 'ABM package' was heated for approximately 1 year and the bentonites have been exposed to the maximum temperature of 130° C (altogether 28 months in the crystalline rock).

The aim of the present study was to describe results of exchangeable cation (EC) and cation exchange capacity (CEC) analysis before and after the experiment. Obviously ECs were exchanged to a larger extent than expected. Different methods were applied to suppress carbonate dissolution, particularly for two selected blocks (No. 10 and 17). Horizontal variation of any EC was not detected for block No. 17 between 1 and 7 cm distance from contact. This trend was also found in the other examined blocks of the field experiment. On the other hand large total differences of the exchangeable cation population ($EC_{population}$) were measured for the blocks in comparison with the starting composition (n=21 blocks).

CEC decreased from initially 66 meq/100 g to 62 meq/100 g after the experiment (n=12 blocks). The neighbouring blocks had a minor influence on the cation redistribution during the ABM experiment. It is likely that the material composition of the adjacent blocks was not important for the adsorption behaviour, but the position within the test parcel. The peak temperatures at the contact didn't correlate with the extent of the redistribution of the $EC_{population}$. Although the largest changes were detected on the large scale of the whole test parcel significant changes were also recorded in the vertical direction over adjacent blocks. ECs didn't equilibrate to the same ratio at the direct contact between two blocks.

ADSORPTION PROPERTIES OF IRON RICHED CLAYS

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Clays and aluminosilicates are well known as selective sorbents for cationic particles thanks to a low pH_{ZPC}. Iron chemistry in clays can markedly affect their adsorption properties due to a possible change of the surface charge. The stability and forms of iron in natural and Fe-modified clays depended not only on pH/Eh conditions, type and purity of clay, but also on the oxidation state, content and crystallinity of iron particles (Manceau et al., 2000; Burleson, Penn, 2006). Four natural and two Fe-modified clays with a high content of iron (Table 1) were investigated in term of Fe stability under acid/alkali or balanced conditions, and consequently, in term of the changes in surface and sorption properties during the above mentioned treatment.

Table 1: Relative content and forms of Fe in natural and modified clays (*% wt.*)

	locality	characteristic	Fe (% wt)	Fe form
Kaolinite	Király Hill, Hungary	natural	3.0	hematite (91 %), Fe^{3+}oxides (9 %)
Illite clay	Illite pit in Tokai, Hungary	natural	1.7	Fe^{3+}oxides (36 %), hematite (64 %, nanocr.)
Smectite clay „Red clays“	Lignite pit, Visonta, Hungary	natural	to 6.9	hematite/maghemite (19 %), Fe^{3+}oxides (72 %), Fe^{2+} particles
Calcined kaolin	West Bohemia, CR (pit)	modified Fe^{2+}/Fe^{3+}	4.1/27.2	Fe^{3+}oxides (100 %)
Bentonite	West Bohemia, CR (pit)	natural modified Fe^{2+}/Fe^{3+}	15.2 17.8/28.6	hematite nanocr. (30 %), Fe^{3+}oxides (65 %), Fe^{2+} particles
Kaolinite clay	West Bohemia, CR (clay deposit)	natural	8.9	hematite (55 %), Fe^{3+}oxides (34 %), Fe^{2+} particles

Well crystalline Fe^{III} phases proved relatively high stability under acidic and alcaline conditions; poorly crystalline and amorphous phases were much more available forming new ion-exchangeable Fe^{III} ions. Fe-modified clays, which contained mostly Fe^{3+} surface particles accumulated in an active, ion-exchangable form, were less stable in most investigated environments, but they proved significantly higher adsorption capacity to anions compare to clays with naturally bound Fe (Doušová et al., 2009). The acid leaching of Fe-riched clays with naturally bound Fe mostly increased their sorption affinity to anions, on the other hand, the aqueous leaching inhibited their adsorption properties significantly.

Acknowledgments

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SEDIMENTARY ENVIRONMENTS AT THE LOMONOSOV RIDGE (ARCTIC OCEAN) DURING THE CRETACEOUS-PALEOGENE TIME

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Deposition of sediments in the Arctic Ocean is strongly influenced by the climate changes which can be reconstructed by the detailed study of clay fraction composition. This work is based on the materials obtained from the ACEX-IODP-302 drilling at the Lomonosov Ridge, Central Arctic Ocean. It is aimed to identify the influence of sedimentation and postsedimentary factors on the composition and structure of clay minerals. 427 meters of sediments have been drilled. During this work about 200 m of sediments, with the the age range from the Cretaceous (Campanian) to the Paleocene-Eocene, were investigated in details by the following methods: X-ray diffraction, scanning electron microscopy, infrared spectroscopy.

In contrast to recent time, the warm humid conditions prevailed in the Arctic Ocean region during Paleocene-Eocene time. Shift of weathering condition can be traced by changes in the clay minerals associations from kaolinite-smectite to illite predominated in Pleistocene. Two climatic optimums detected in Arctic sediments: Paleocene-Eocene Thermal Maximum (PETM) about 55 Ma and "Azolla" event about 29Ma. It is characterized by increasing of smectite component and correlated to a maximum degree of weathering intensity in the central Arctic.

Basin at that time was relatively shallow and the material was transported from the nearby land (during PETM) or synthesized in-situ (during Azolla-event). Similar changes were recorded in the region of Southern Caucasus, the Crimea and the Russian platform, when tropical and subtropical conditions prevailed in these areas. Between warm and humid periods the processes of desilication were evolved in the soils formation, producing a large amount of abiogenic amorphous silica. First seasonal ice appeared around 44.5 Ma. This event was recorded in the sediments by abrupt changes in the content of clay minerals.

It was detected based on experimental and analytical data, that Cretaceous sediments were formed from the redeposited material while the Paleocene-Eocene sediments were formed due to the alteration of volcaniclastic material. Ash material could be delivered to the sedimentation basin in the form of aerosols or transferred with a marine suspension water flows through the development of the meridional channels. Extensive development of transformational change of the ash material to smectite minerals suggest an enhanced volcanic activity on the planet, which appears to subsequently led to a gradual decrease in average annual temperatures during the Eocene and the emergence the first seasonal ice at about 45 Ma.

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ORDOVICIAN K-BENTONITES: ISSUES IN IDENTIFYING AND INTERPRETING ANCIENT TEPHRAS

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The Ordovician record of explosive volcanism consists of examples of both near-vent pyroclastic flows and ignimbrites and distal sequences of altered fallout tephras known as K-bentonites. Questions frequently arise as to whether a particular clay-rich bed might be an altered volcanic ash fall in the form of a bentonite or K-bentonite. These beds are often datable using fission track and U/Pb dating of zircons, K/Ar, and Ar/Ar of amphibole, biotite and sanidine. Due to their unique composition, they provide an indispensable tool when correlating sections. The criteria for recognizing such beds are varied, but fall into two broad categories, field criteria and laboratory criteria. Ideally, one would want both, but often that is not possible. However, there are key features to look for in each case that can aid in reliable identification.

Field Criteria: K-bentonites can be different colors when wet (blue, green, red, yellow) but are characteristically yellow when weathered. Due to their clay rich nature, they will feel slippery and waxy when wet. Some K-bentonites contain euhedral to anhedral volcanogenic biotite, quartz, feldspar, amphibole, zircon and apatite, and less commonly, clinopyroxene, magnetite and garnet. The typical appearance of a K-bentonite bed in outcrop is that of a fine-grained clay-rich band ranging between 1 mm – 2 m in thickness that has been deformed by static load from the enclosing siliciclastic or carbonate sequence. Accelerated weathering of K-bentonites causes them to be recessed into the outcrop face. For thicker K-bentonites there is often a zone of nodular or bedded chert in the adjacent strata at both the base and the top of the bed.

Laboratory Criteria: Most bentonites and K-bentonites are smectite- or illite/smectite-rich, although some may contain a considerable amount of kaolinite, and those that have undergone low-grade metamorphism may be dominated by R3 I/S and/or sericite plus chlorite/smectite (corrensite) and/or chlorite. So initial steps should begin with separation and XRD analysis of the clay fraction. Wet sieving the sample is important to separate the clay portion from the volcanic crystals that could possibly be present in the sample. Bentonites may contain volcanic phenocrysts and volcanic glass. Study of the non-clay fraction under a high quality optical microscope is satisfactory to determine what types of crystals are present in the sample. Thin section study may also be used. Isotopic ages can be extracted from K-rich phases, such as sanidine, amphibole or biotite, U-rich phases, such as zircon, or by fission track measurements on apatite or zircon crystals. Many phenocrystic phases are composite crystals, however, representing inherited cores with magmatic rims and thus must be measured with great care.

Applications of clays (ceramics, agriculture, building industry, pharmaceutical, polymer industry, ...)

Oral presentation

SYNTHETIC HALLOYSITE-TYPE NANOTUBES AS ADDITIVES FOR POLYMER COMPOSITES

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The preparation of kaolinite nanostructures is accompanied with morphological changes. The application of halloysite-type nanotubes (HNTs) as polymer additives prepared from kaolinite via multiple intercalation is in the focal point of worldwide interest. The HNTs can be dispersed rather uniformly in thermoplastic polymers like polyamide 6, polypropylene, or polybuthylene terephtalate (Du et al., 2008; Marney et al., 2008; Du et al., 2008). Although the significant difference in the polarity of polyolefins and the mineral additives can cause a significant difficulty in the preparation of the nanocomposites, the compatibility can be ensured via the functionalization of the nanotube surface with organic molecules (*connecting organic ligands through surface OH-groups or oxygen atoms)* and subsequnetly a significant improvement can be achieved in the mechanical properties. In addition, the connection between the nanotube and the organic ligand also can be made via hydrogen bonding or through a charge transfer mechanism (Lu et al., 2006).

In this work halloysite-type nanostructures were prepared via multiple intercalation starting from a kaolinite-potassium acetate precursor. It was stated that the resulting morphology is significantly influenced by (i) the way of precursor preparation, (ii) the energy transfer procedures used to reduce reaction time, (iii) the water content, and (iv) the structural order of kaolinite.

The surface characterization of the obtained nanotubes showed that the BET and BJH surface increased significantly, while the pore size distribution showed only a negligible change,. The specific surface area increased in parallel with the increase of the structural order. Inverse gas chromatographic (IGC) investigations showed a significant decrease in the dispersion coefficient of the surface energy, which is a favourable change in the light of polymer composite preparation.

Nanotubes obtained from three different types of kaolinites with varying structural order were embedded in PLA and PCL polymers without the use of reactive modifiers in an amount of 1% w/w. The mechanical properties: tensile strength (Rm) and the Young modulus (E) were measured. The in addition to the morphology of the additive – by the rate of dispersion in the matrix and the bonding forces at the interface.

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GEOCHEMICAL AND MINERALOGICAL „FINGERPRINTS“ OF HISTORICAL BRICKS FROM AUSTRIA

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Clays and sediments rich in clay are used as typical raw materials for the brick industry. Austria has an old tradition in the production and usage of bricks. The oldest known bricks in Austria were probably produced by Romans about 1800 years ago in order to have enough construction material to fortify military camps close to the Danube River. After the collapse of the Western Roman Empire the knowledge about brick production in Central Europe, as well as in Austria, was lost. Not until medieval times, when huge amounts of building materials were needed for the construction and preservation of the Vienna town walls, the fabrication of bricks was rediscovered. At last, the urban expansion of Vienna in the 19th century leads to the self-evident usage of bricks as we know today.

The present work aims to trace the origin and age of historical bricks in Austria. Therefore, the importance and significance of different parameters like chemistry, mineralogy and production technologies have to be proofed by archeometric methods. Mineralogical and petrographical parameters as well as technological properties were determined by analysing ~100 historical brick samples from different parts of Austria. Elemental analyses were performed on total digestions of the powdered materials using inductively coupled plasma mass spectrometry (ICP-MS) for the determination of the trace element composition of the samples.

The natural elemental distributions of bricks reflect the geochemical and also the geological environment of the used raw material, and therefore can be consulted as "fingerprint" to differ brick samples. Initial REE determinations showed significant patterns for brick samples of different provenances. Furthermore, element ratios like Sr/U, Ni/As, Ca/Sr and Ni/Ti gave individual scatter-plots for the particular origin of the brick sample.

Macroscopical and petrographical observations predominantly give information about technological processes during brick fabrication. Brick signs, the symbols of the producers, sometimes are available and can help identifying the brick origin. Additionally, fragment inclusions of the bricks like aggregations, rock-fragments or recycling-fragments, can be used for the detection of the production facility.

THE STRUCTURE/REACTIVITY RELATIONSHIP FOR NITRATE REDUCTION OF IRON-BASED LAYERED DOUBLE HYDROXIDES

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Layered Double Hydroxides (LDH), sometimes also called "anionic clays", exhibit interesting properties for the remediation of anionic pollutants such as adsorption, ionic exchange or reduction. The structural cohesion of LDH is governed by the nature of the cations and the anions present in the interlayer and their electrostatic interactions (de Roy et al., 2011; Ruby et al., 2010). Ordered crystallographical models are considered to understand the stability of different M^{II}-M^{III} LDH, where M^{II} and M^{III} represent metallic cations of the brucite-type sheets. Moreover, the lower limit of composition $x = M^{III} /(M^{II}+ M^{III})$ is correlated to the difference $\{P(M^{II}) - P(M^{III})\}$, where P is the cationic polarizing power. The domain of composition of iron-based LDH can therefore be predicted and a range of x values [~0.25-0.33] is obtained for Co^{II}-Fe^{III} and Fe^{II}-Fe^{III} LDH, in good agreement with experimental observations.

The LDH containing both Fe^{II} and Fe^{III} species, commonly called green rust (GR), is particularly relevant for nitrate remediation in aqueous medium because the Fe^{II} species act as reducing agent for nitrate and the Fe^{III} cation is an electron acceptor for dissimilatory iron reducing bacteria (DIRB). Therefore, DIRB may regenerate the reactive Fe^{II} species of GR in anoxic conditions. The reactivity of GR toward nitrate anions is studied in abiotic conditions as a function of the ratios $x = Fe^{III} / Fe_{tot}$ and NO_3^- / Fe_{Tot}, pH and phosphate concentration. High value of x ($x > 0.5$) and high concentration of phosphate inhibit completely the reduction of nitrate. In alkaline condition and for $x = 0.33$, NO_3^- species are fully transformed into more toxic ammonium NH_4^+ species. Interestingly, in the presence of low phosphate concentration ($PO_4^{3-} / Fe_{tot} \sim 0.5$ %), about 70 % of NO_3^- are transformed into gaseous N species. It is strongly suspected that the partial phosphate saturation of reactive Fe^{II}-Fe^{III} sites situated on the lateral faces of the hexagonal crystal of GR (Bocher et al., 2004) is responsible of both the decrease of reactivity and the concomitant increase of selectivity, i.e. transformation of NO_3^- into gaseous N species.

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SWELLING CLAYS AND SWELLING INHIBITORS IN CONSERVATION OF BUILT CULTURAL HERITAGE

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Sedimentary stones used in buildings and monuments of significant cultural and historical value may contain swelling clays, which during wetting and drying cycles generate differential strains and stresses on the order of the strength of the stone. Damage in the field is observed to be primarily surface delamination and buckling, consistent with damage during wetting (Jiménez-González, Scherer, 2011; Wangler et al., 2011). Additionally, porous stones in restoration projects are commonly treated with ethylsilicate consolidants to increase mechanical rigidity. The presence of swelling clays in these stones, however, has rendered consolidation treatments ineffective after only a few wetting cycles (Félix, 2000). The use of α,ω diaminoalkanes as swelling inhibitors has been proposed as a potential solution to this problem, and while these have successfully reduced swelling, they have not eliminated it (Wangler et al., 2011).

Clays swell over two distinct ranges: short-range, discrete intracrystalline swelling, and longer-range, continuous osmotic swelling. Identification of the swelling mechanism is important in the diagnosis of this problem and in the development and improvement of mitigation strategies. In Portland Brownstone, an important historical building stone in the northeast United States, dilatometric measurements of swelling with polar organic solvents can be interpreted such that the swelling in this stone is almost completely intracrystalline in randomly dispersed swelling clay layers in the clay fraction, and begins from a completely dehydrated interlayer (Wangler, Scherer, 2008). Building on this result and combining it with intercalation experiments with Na-montmorillonite as a model swelling clay system, the mechanism of swelling inhibition in the stone can be interpreted as intercalation followed by subsequently reduced rehydration (Wangler, Scherer, 2009). Additionally, bis copper (II) ethylenediamine is shown to be a more effective swelling inhibitor. Finally, the latest results of current research on the molasse of Switzerland are presented.

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HISTORICAL CLAY AND CERAMIC SAMPLES FROM THE COLLECTION OF THE VIENNA TECHNICAL MUSEUM

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The Vienna Technical Museum has a large collection of merchandise, including clays and ceramic products, from the 19th and early 20th century. The origin and composition of the material is not well known. Different raw materials, mixtures for the production of porcelain, stone ware and glaze, and ceramic products (clay pipes and Seger cones) were analysed. The mineral content of the samples determines the material properties and can give information about provenance, processing and firing temperature.

The bulk and clay mineral content of the raw materials was determined by X-ray diffraction and Simultaneous Thermoanalysis (STA). Grain size analyses were made by a combination of wet sieving and sedimentation. The clay fraction of all samples consists mainly of both well and poorly ordered kaolinite, in some samples traces of illite and vermiculite were found. The clay content of the raw materials ranges from 45 mass% to 85 mass%.

Mixtures for hard-paste porcelain contain usually 50 % kaolinite, 25 % quartz and 25 % plagioclase and potassium feldspar. Traces of mica are found in all samples. The presence of mullite in the mixtures for stone ware verifies the use of fired material as grog.

Different clay pipes from England, France and Austria were probably exhibited 1873 at the World´s Fair in Vienna. Pipes were made from high-quality clay to get a fine pored product. The mineral composition was determined nondestructive by X-ray diffraction. Main component of all pipes is quartz, only in the English pipes mullite was found, which indicates a higher firing temperature or an admixture of that mineral. Small amounts of mica were present in most of the specimens. Two black pipes from Austria, made by the same manufacturer, showed remarkable differences in the composition of the glaze.

Seger cones are small ceramic bodies which deform at specified temperatures. They have been used since 1886 to check the "heat work", i.e. the combined effect of temperature and time, in a kiln. They are made of mixtures of clay and alkali- or earth-alkali oxides.

Computational methods in clay science

Oral presentation

ETHYLENE GLYCOL INTERCALATION IN SMECTITES

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Intercalation of ethylene glycol in smectites is widely used to discriminate smectites and vermiculites from other clays. During this process, ethylene glycol molecules enter into the interlayer spaces of the swelling clays, leading to the formation of two-layer structure (~17 Å) in the case of smectites, or one-layer structure (~14 Å) in the case of vermiculites. In spite of the relatively broad literature on the understanding/characterization of ethylene glycol/water-clays complexes, only the simplified structure of this complex is known. This study was therefore undertaken to investigate this structure in more detail using molecular dynamics simulation.

The structural models of smectites were built on the basis of pyrophyllite crystal structure, with substitution of particular atoms. Atoms of the smectites were described with CLAYFF force field, while atoms of water and ethylene glycol with flexible SPC and OPLS force fields, respectively.

Results of the simulations show that in the two-layer glycolate the content of water is relatively small: up to 0.8 H_2O per half of the smectite unit cell (thereafter phuc). Clear thermodynamic preference of mono- or two-layer structure of the complex is observed for typical smectite. Based on the calculated radial distribution functions, it was confirmed that water and ethylene glycol molecules compete for the coordination sites of the calcium ions in the clay interlayers. It was also found that the differences in the smectite layer charge, charge location, and the type of the interlayer cation affect the ethylene glycol and water packing in the interlayer space and as result have strong influence on the basal spacing and on the structure of complex. Varying amounts and ratio of both ethylene glycol and water are, however, the most important factor influencing the extent of the smectite expansion. Comparison of two-layer structure obtained from molecular dynamics simulations with previous models leads to the conclusion that the arrangement of ethylene glycol molecules in the interlayers, used in simulations of X-ray diffractograms of clays, should be modified. The main difference is that, for different location of the clay charge, interlayer ions tend to change their positions. Water in these structures does not form distinct layers but is distributed rather broadly with a tendency to be concentrated close to the smectite surface. One-layer structure of ethylene glycol/water-smectite complex, characteristic of vermiculite was also proposed.

Geology and mineralogy of clays

ORGANO-CLAY COMPLEXES OF HOLOCENE PALAEOSOLS AND PALEOENVIROMENT RECONSTRUCTIONS

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The present study was related to the soil biogeochemical processes in connection with climate variation and duration of weathering. Palaeosols can act as integrative records of past climatic, lithological, geochemical, biological, and hydrological conditions. Properties of palaeosols, as natural environmental recorders in the steppe belt of southern Russia, were compared with the sequence of environmental events. Archaeological monuments, known in Russian scientific literature as khourgans, are typical attributes of the southern Russian steppe landscape; they preserve a range of palaeosols recording past environmental changes through last 5000years. Stable isotope ratios (reported as δ13C) of organic carbon preserved in paleosols has potential utility as a valuable paleoecological indicator. The soil carbon isotopic composition of the paleosols has been studied to reflect the variation of the quaternary paleovegetation and corresponding paleoclimate and paleoenvironment in in the steppe belt of southern Russia. Organic matter is likely to be associated with clay fraction as clay-organic complexes in soil and sediments, the organic carbon content in clay fraction of paleosols is two time higher than in whole soils. Interactions of clay minerals with OM have the large-scale effect on the physical, chemical and biological properties of soils. Solid state NMR spectroscopy (^{13} C) and Fourier transformed infrared spectroscopy techniques were employed to determine the fractionation behavior of organic matter (HA) for bulk samples and clay fractions of palaeosols. Clay fractions generally show higher content alkyl-C groups than whole soils. Existing relationships between clay mineralogy and the chemical nature of the associated humic substances indicates that either soil clay mineralogy strongly influences the humification process or that humic substances with different properties are selectively adsorbed on clay minerals**.** Carbon isotope compositions of organic mater in paleosols shows an increase in δ13C with decreasing mean annual precipitation (MAP). Isotope date for clay fraction or clay-organic complexes in paleosols demonstrate higher intensity of this shift than in bulk soil samples. Isotopic shifts suggest changes of the paleovegetation and climatic conditions over time.

PALUSTRINE BEDS IN LATE MISSISSIPPIAN EPEIRIC-SEA CARBONATE SUCCESSION (SOUTHERN MOSCOW BASIN, RUSSIA) AS CALCIMAGNESIAN PEDOSEDIMENTARY SYSTEMS

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The upper Mississippian (Lower Carboniferous) of the Moscow Basin is one of the brightest examples of epeiric – sea carbonate sedimentary systems with numerous subaerial exposure horizons marked by paleokarsts and paleosols (Kabanov et al., 2012). The Late Visean subaerial profiles have long been known in local geology as "rhizoidal limestones" (Shvetsov, 1948), but the pedogenic environments of their formation have not been studied. Here we present the results of detailed study of three Late Mississippian unconformities at Mikhailovian - Venevian (2 profiles) and Venevian-Tarusian boundaries. The 80-130 cm thick "black limestone" at the Michailovian – Venevian boundary is a transgressive non-marine bed is onlapping the distinct paleokarst profile with residual yellow montmorillonitic clay blanket filling up karstic voids. The "black limestone" in two studied localities is massive to weathered, contains numerous internal sedimentary discontinuities, penetrated by multiphase Stigmaria rhizophores and their appendixes (rooting systems of arborescent lycopsids) which has been referred to as the "rhizoidal character" of the bed. In top the "black limestone" grades almost conformably to Venevian shallow-marine limestone via thin (2-3 cm) dark brown fissile marl. Another unconformity at the Venevian-Tarusian boundary is 55 cm thick "black" rooted limestone, its upper 2-3 cm is weathered, more clayish and brown in color. All three profiles are calcimagnesian systems containing micritic calcite and are characterized by the following common properties. Carbonate (35-78 %) – is fresh water calcite with $\delta\,^{13}$C (- 2.3 ‰)- (-7.1 ‰) of bulk samples and $\delta\,^{13}$C (- 5.9 ‰)- (-10.7 ‰) of micrite. The main clay mineral is authigenic Mg – rich trioctahedral smectite – saponite. The beds are almost free from terrigenous material, coarse (>2 μm) fraction besides fresh water calcite nodules contains traces of quartz and dolomite. Authigenic saponite is developed in alkaline media with large MgO (min. 6 %) and small Si and Al concentrations.Such conditions correspond to shallow marine or salted continental basins of arid/semi-arid climates with prevailing of evaporate conditions. We interpret the studied beds as extremely shallow-water lacustrine deposits transformed by repeated subaerial emersion episodes into palustrine pedosediments. In all studied beds saponite from the top laminated layer demonstrates the degradation of crystal structure. Both beds from the Malinovka quarry contain visibly less micrite in their top layers. At Novogurovskiy, the "black limestone" has the greatest concentration of micrite and also contains gypsum. Both these features testify for the prevailing evaporate conditions connected with drier climate or longer subaerial exposure of the territory. In Malinovka, the top of the "black limestone" contains lepidocrocite (г FeOOH) suggesting periodical changes in redox and wetting-drying conditions.

RECENT GLAUCONITE FORMATION IN A DEEP SEA ENVIRONMENT AT ODP SITE 959, IVORY COAST-GHANA MARGINAL RIDGE

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Authigenic, green, Fe-rich clay minerals formed in a deep sea environment of the ODP Site 959, Ivory Coast-Ghana Marginal Ridge, suggest that a complete mineral series from the Fe-smectite to the glauconite group exists. Although the formation conditions, mineralogy, and chemistry of glauconite genesis are generally well understood, the precise process and timing of the Fe-smectite-to-glauconite reaction at low temperature are still under debate. Cores from the ODP Site 959 provide a condensed and undisturbed sedimentary record of foraminifera and nannofossil oozes mixed with detrital silicates and authigenic, green clays without large hiatuses since at least the Miocene. Hence, sediments from Hole 959C have potential to study *in-situ* glauconitization at high resolution, besides providing a powerful archive to determine the role of special micro-environments, pore water geochemistry, and sediment composition on the glauconitization process.

Petrographic (e.g. thin sections), mineralogical (XRD) and geochemical analyses (XRF, ICP-OES, SEM, FIB-SEM, and TEM including EDX and SAED) were performed on the bulk sediment as well as on the separated light, medium, and dark green glauconitic grains in order to study the glauconitization process in a deep sea, low temperature environment.

Glauconitization at Hole 959C has occurred predominantly in tests of calcareous, planktonic and benthic foraminifera. Incomplete glauconitic infillings were also found in radiolarians and fecal pellets, but are rare. XRD and TEM-EDX data of the light green grains from 0.16 mbsf reveal the predominance of Fe-smectites, which are the glauconite precursor phases at this site. TEM-EDX-SAED observations and 3-D reconstructions based on FIB-SEM indicate that these Fe-smectites were formed soon after deposition (< 10 ky) *via* direct precipitation from an amorphous precursor gel generated by microbial activity in an organic-rich, semi-confined micromilieu. With increased stage of early diagenesis related to burial, the initial veil-like Fe-smectites (8-24% illite layers - 92-76% smectite layers) change steadily into intermediate, Fe-rich mixed-layered illite-smectite (62-64% illite layers - 38-36% smectite layers) and finally into lath-like glauconite (91-93% illite layers - 9-7% smectite layers) without a compositional gap between the Fe-smectite and the glauconite. Accompanying the mineralogical evolution of the green grains, a reduction of the light green grains with increased depth was observed, while the relative percentage of the medium and dark green grains increases continuously. This suggests that the glauconitization process does not stop near the seafloor. Furthermore, the pore water data display increased contents of K^+, Si^{4+}, Ca^{2+}, Mg^{2+}, and Fe^{2+} up to 25% relative to the ambient seawater as well as a reduced pH (7.7-7.2), but a higher alkalinity within the upper 25 m of sediment pile. These findings are indicative of i) dissolutions of detrital silicate minerals and Fe-oxyhydroxides, ii) microbially enhanced oxidation of organic matter, and iii) decompositions of skeletal calcite and opal-A within the special micromilieu of glauconitization.

Based on these observations, glauconitization at the ODP Site 959 has occurred as follow: **1)** Fe-smectites precipitated rapidly after deposition in an organic-rich micro-environment such as foraminifera tests supported by microbial activity and cation supply from seawater and pore water by chemical diffusion. The formation of Fe-smectite, hence, is the first step of an overall glauconitization process. **2)** The Fe-smectite-to-glauconite conversion reaction is then triggered by early diagenetic micromilieu-pore water interactions depending on geochemical (cation supply) and thermal (low temperature) conditions, but also on the reaction kinetics. The absence of a compositional gap between the Fe-smectite-glauconite group suggests that a complete solid solution exists *via* the formation of glauconite-smectite mixed-layered clays.

LABORATORY EXPERIMENTS SHOW PATHWAYS OF VOLCANIC GLASS ALTERATION THROUGH INORGANIC AND MICROBIALLY-MEDIATED PROCESSES

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Obsidian of rhyolitic composition has been reacted at ambient temperature with water of several representative compositions and added organic nutrients (peptone and glucose) to boost biological activity, in order to study the effect of water chemistry and biological activity on the composition and formation mechanisms of clay minerals. Experiments of up to 18 months used freshwater from a lake and a spring, seawater and hypersaline water from a lake (Mg-Na-SO4-Cl-rich), and ground obsidian (150-250 µm). Six-year experiments used obsidian chips (mm-size), freshwater from a spring, bottled water, seawater and brine water (NaCl-rich). Both sets of experiments had control tests in which no nutrients were added to avoid biological activity. The solids were studied using cryo-SEM-EDX to investigate modes of glass alteration and interaction between the glass and microorganisms and their secretions. The composition of the newly formed clay particles was investigated using TEM-AEM. The 6-year experiments produced the complete in situ transformation of the volcanic glass into quartz, with minor alunite and calcite. Such transformation is surprising because quartz is not reported as a product of volcanic glass alteration and because the quartz growth rate was more than ten orders of magnitude faster than expected. The transformation apparently took place by in situ recrystallization. In the 18-month experiments, the glass altered only superficially. In all experiments clay formation took place mainly by the direct alteration of glass into dioctahedral clay (montmorillonite to kaolinite composition) and the larger chemical control was from the glass (where $Al > Mg$). This transformation was observed as changes in the morphology and chemistry of areas of the glass surface, as small glass grains (<10 µm) with compositions indicating partial alteration, and clay particles with glass morphology, interpreted as completely altered glass grains. The trend toward dioctahedral clay formation was altered by (1) pH and chemical conditions that favoured the formation of Mg-rich clay and (2) the entrapment of glass grains within biofilms where Mg concentration became higher than in the bulk solutions, which also generated Mg-rich clays. Mg-rich clays appeared to have formed frequently in dissolution-precipitation processes. The entrapment of the altering glass grains within the biofilm was the main route of biological effect on the clay composition.

BIOGENIC WEATHERING OF BASALTIC GLASS AND AUTHIGENIC MINERAL FORMATION

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Basaltic glass, formed by rapid cooling of magma, is of widespread occurrence at the ocean floor and different volcanic terrains. Due to its relatively high dissolution rate, being ~10x higher than for crystalline basalt, basaltic glass has a significant effect on the release of metals and nutrients on local scale as well as for global element budgets. The alteration product from the interaction of water with volcanic glass is palagonite, where, depending on the specific environment, different authigenic minerals can form. Precipitation of secondary phases may lead to a sealing of the fresh glass from the surrounding water, which can suppress alteration. Besides abiotic hydration and exchange reactions also microbial congruent dissolution is observed in submarine lavas (McLoughlin et al., 2010). Weathering by bacteria gets increasing attention in geochemical processes as they can act both, as catalyst and inhibitor of mineral precipitation and dissolution reactions (Ganor et al., 2009).

In this paper basaltic glass pieces exposed to sea water at the Mid Atlantic Ridge were studied. The vicinity of the site to hydrothermal vents is thought to accelerate biological processes. In polished sections tubular microcavities were observed by electron microscopy. Tubules are filled with authigenic minerals, whereby these are located more in the central part of the tubule and not at the walls on the fresh glass. The chemical composition of the phases in the tubules determined with an electron microprobe is strongly different in comparison with the surrounding glass. Both FeO and P_2O_5 are strongly enriched in the secondary phases compared to the base glass (40 vs. 10.17 wt% FeO; 2.5 vs. 0.11 w.% P_2O_5). Broad IR-absorption bands indicate the amorphous property of secondary phases. In fissures, dense brownish palagonite platelets are observed. After cleaning external surfaces of the glass pieces by ultrasonic treatment, bacterial imprints were identified. A C-content of 1.7 wt.% and a C/N ratio of 10 indicate the presence of microbes in the mud on the glass surface. Whereas commonly chemical alteration round off sharp edges of the glass to decrease the total surface area, the openings of tubules at the surface are not rounded indicating a rigid mechanism for tubule formation. Most of the alteration features observed can be assigned to bioalteration. To determine the driving forces of biochemical weathering, effects of different electrolytes including organic anions on element release and zeta potential of basaltic glasses were traced with time. The zeta potential is used to determine surface layer formation of a basaltic glass in inital stages, which is important due to microbial congruent dissolution of basaltic glass. Microtomography for analysis of morphological issues of tubule formation is in progress.

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CHARACTERIZATION OF SOIL CLAY MINERALS OF THE RIVER NILE SEDIMENTS, SOHAG REGION, EGYPT: DECOMPOSITION OF X-RAY DIFFRACTION PATTERNS

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The dynamics of soil mineral change will determine farming practice in the future if one wishes some approach to sustainable agriculture. These are the challenges of the 21^{5t} century. Yet more methods with higher precision are needed to correctly follow the very rapid mineral change observed in some agricultural systems (illite loss in as little as 15 years).

Although the importance of the method of numerical analysis of X-ray diffraction recordings (curve decomposition) as a new, powerful tool for mineral identification and the numerous applications done allover the world along the last decades, no attempts have been made to identify and trace the changes in clay minerals of soil profiles of Egypt. Structural characterization of this soil clay minerals often remains limited despite their key influence on soil properties. In this soils, complex clay parageneses result from the coexistence of clay species with contrasting particle sizes and crystal-chemistry and from the profusion of mixed layers with variable compositions. So, the present study aimed at characterizing the mineralogy and crystal chemistry of the < 2 µm fraction along a profile typical of soils from the River Nile flood plain, Sohag regionUpper Egypt. X-ray diffraction (XRD) patterns were interpreted using the combination of XRD pattern decomposition and NEWMOD PROGRAM method. This approach implies direct XRD profile fitting and has recently led to significant improvements in the structural characterization of clay minerals in diagenetic and hydrothermal environments.

The X-ray X-ray patterns of the studied soil clay fraction reveals that 2:1 clay minerals are much more abundant than kaolinite and that this clay fraction contains fair amounts of K-feldspar and quartz. Decomposition of XRD patterns indicate 5 or 6 different clay phases including smectite, illit-smectite mixed layers (I/S), Poorly crystalline illite, kaolinite and chlorite.

Structural characteristics of the different clay minerals, including the composition of mixed layers, did not vary significantly with depth and are thus indicative of the parent material. The relative proportion of the < 2 µm fraction increased with increasing depth simultaneously with smectite relative proportion.

MINERALOGY, GEOCHEMISTRY AND GENESIS OF THE HYDROTHERMAL HALLAÇLAR KAOLINITE DEPOSIT WITHIN NEOGENE VOLCANITES, UŞAK PROVINCE, WESTERN TURKEY

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The Hallaçlar kaolinite deposit formed by alteration of dacite and andesite of the Miocene Karaboldere volcanites. These units were examined using polarised-light microscopy, X-ray diffractometry, scanning electron microscopy, transmission electron microscopy, differential thermal analysis-thermal gravimetry, infrared spectroscopy, and chemical and isotopic methods. Mineralogical zonation outward from the main kaolinite deposit is as follows: kaolinite ± smectite + illite + opal-CT + feldspar; feldspar + kaolinite + quartz + smectite + illite; quartz + feldspar + volcanic glass; S-phases (goethite, lepidocrocite, hematite, pyrite, jarosite, gypsum/anhydrite) suggest that hydrothermal-alteration processes resulted in kaolinisation. Very sharp, diagnostic basal reflections at 7.2 and 3.57 A°, as well as non-basal reflections, well-defined pseudohexagonal to hexagonal blocky and vermiform crystallinity, ideal differential thermal analysis-thermal gravimetric curves, and ideal, sharp, infrared spectral bands indicate well-crystallised kaolinite. Subparallel correlation of Ba+Rb with K, enrichment of Sr, and depletion of Rb+Ba, Ti, and HREE relative to LREE, with a distinct negative Eu anomaly (average Eu/Eu* = 0.66-0.86), are responses to the fractionation of feldspar and hornblende by the hydrothermal fluid. The Hallaçlar kaolinite fractions are characterised by low SiO_2 (39.53-49.7 %), high Al_2O_3 (34.24-37.75 %), Fe_2O_3 (0.04-1.23 %) and LOI (13.5-17.4 %), with SiO_2/Al_2O_3 ratios between 1.04 and 1.45, and an average structural formula of $(Si_{3.98}Al_{0.02})(Al_{3.83}Fe_{0.03}Mg_{0.01}Mn_{0.0005}Ti_{0.03})(Ca_{0.01}Na_{0.001}K_{0.009}P_{0.05})O_{10}(OH)_8$. The $\delta^{18}O$ ve δD values from kaolinite and smectite indicate that hydrothermal-alteration processes developed at 134.1-183.4° C and 65.6° C, respectively. The negative $\delta^{34}S$ (-20.7 ‰) value from gypsum/anhydrite indicates formation from geothermal-water-derived sulphur. Under the influence of a tectonically controlled hydrothermal process, feldspar, hornblende and volcanic glass were altered resulting in the conservation of Al and depletion of Si, Na, Ca, K, Mg and Fe in an open hydrological system such that formation of kaolinite under acidic conditions in the central part of the deposit, and development of smectite and illite under basic conditions upward and outward, were favoured.

DIAGENETIC PATHWAYS OF CLAY-RICH CHALK: A CASE STUDY FROM THE OUTER CARPATHIAN MARLS

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The Outer Carpathian marls correspond to dirty chalk facies that have been deposited by gravity flow or slumping. Three major periods of their deposition in the Outer Carpathian basin were recognized: (1) Upper Jurassic (Goleszów Marls); (2) Upper Cretaceous (Siliceous-Fucoid, Węgierka, Węglówka, Frydek, Żegocina and Jasienica Marls); (3) Eocene-Oligocene (Łącko, Zembrzyce, Budzów, Leluchów, Niwa, Grybów, Jawornik and Dynów Marls).

Based on their optical and FESEM/SE/BS microscopic images and XRD analyses, the Outer Carpathian marls appear to have been consisted of diagenetically altered calcareous nanofossils (8-73 %) with variable content of clay (3-58 %) and siliceous material (8-64 %).

The primary components and diagenetic pathway in all marls studied were basically the same. However, diagenetic processes involving carbonate and silicate components progress differently in different marls. Resulting marls: (1) carbonate-clay-silica bearing; (2) carbonate-clay supported; (3) clay dominated; (4) carbonate-silica supported; (5) clay-silica supported, are interpreted to represent varying diagenetic pathways driven by initial mineral inputs.

The diagenetic pathways taken particularly by unconsolidated mud enriched in reactive carbonate (nannoplankton) and silica (siliceous bioclasts) spaces as well as labile volcanic ash, varying spatially and temporally, were a key factor in controlling mineralogy of resulting marls. The diagenetic history of carbonate in the marls studied appears to progress basically along the pathway taken by pure chalk and include diagenetic transformation from the time of deposition through reactions in the zone of unconsolidated mud sediment-water interface to early burial, and down to depths corresponding to intermediate and deep diagenetic reaction. Carbonate diagenesis included dissolution, combination of mechanical compaction and chemical recrystallization, pore-stiffening cementation, pressure-solution and pore-filling cementation. This pathway was locally modified, enhanced and inhibited due to alteration of volcanic ash disseminated within the host sediments. Current models demonstrate pore stiffening of chalk at a relatively shallow depth (1100 m). Early pore stiffening of marls was a factor probably heavily influences the burial diagenesis of clay and silica, which appear to be derived originally from the alteration of volcanic ash. Because the strengthening of marl was rapid, the progress of deep burial diagenesis has been inhibited. Therefore, the noncarbonate mineralogy of the marls studied is typically dominated by high smectite illite-smectite and also includes nano-quartz microspheras. The abundance of smectite layers in the I-S, in spite of deep burial, suggests that the availability of K during clay diagenesis in marls was limited.

Acknowledgments

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CLAY MINERALOGY OF FOSSIL AND ACTIVE HYDROTHERMAL SYSTEMS AROUND HİSARALAN GEOTHERMAL FIELD, SINDIRGI, BALIKESİR, TURKEY

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Study of clay minerals in geothermal systems can be used for determination of past and present hydrothermal conditions. Within this respect, Hisaralan geothermal field hosted by Miocene volcanics was studied.

A geothermal drill hole (HS-2) material and surface samples were examined by X-ray diffraction (XRD) and scanning electron microscopy (SEM). While smectite and mixed layer clay minerals are dominant at the surface and shallow levels, illite and chlorite are the main clay minerals in deeper parts of the system. The clay mineral assemblages indicate at least two successive alteration stages. The first assemblage consists of chlorite and illite and belongs to the fossil hydrothermal system (propylitic alteration). This stage is widespread around the geothermal field. The second stage consists of smectite and mixed layer illite/smectite and belongs to the active hydrothermal system.

The mineral saturation values indicate that the geothermal fluids are oversaturated with respect to clay minerals. On the other hand, calculated aquifer temperatures are not higher than 150° C These data are well compatible with the occurrence temperature of smectite and mixed layered clay minerals in hydrothermal environments. The δD vs. $\delta^{18}O$ values of clays show that the clay minerals in the geothermal field under study are hypogene in origin.

AUTHIGENIC DOLOMITE IN BAVARIAN BENTONITE DEPOSITS

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The Bavarian bentonite deposits near Landshut formed from distal, resedimented Mg-poor rhyolitic volcanic ash within the Upper Freshwater Molasse (UFM, Middle Miocene) of the North Alpine Foreland Basin. These important industrial clays are processed in part by acid-activation but locally contain varying amounts of carbonates that have a negative impact on resource quality. The presence of authigenic dolomite and Mg-bearing montmorillonite in the bentonites requires that Mg has been introduced, possibly indicating a genetic link between dolomite and smectite formation. The soft to partly indurated calcareous, dolomitic and mixed carbonates are present predominately within the smectite-rich zones, while the weakly altered rhyolitic glassy tephra ("Platte") is generally devoid of carbonates, except rare calcite in the Gabelsberg deposit. Dolomite is the only carbonate present in some deposits (Rehbach), while in others (Zweikirchen), a change from a calcareous to a dolomitic facies is observed. The largely micritic, microsparitic or peloidal carbonates document times of brecciation, reworking, bio- and pedoturbation, as well as, repeated wetting and drying. Rootlets, circumgranular shrinkage cracks in nodules, and deeply incised gravel channels underpin paleo-surface vicinity. The $\delta^{13}C_{VPDB}$ and $\delta^{18}O_{VPDB}$ values of dolomite in bentonite show a mean of -6.8±0.4 ‰ (1σ, n=18) and -4.9±0.7 ‰ (1σ, n=18) respectively. In contrast, calcite in bentonite and glassy tephra reveal a larger range from -11.9 to -8.3 ‰ (n= 27) for carbon and from -9.1 to -6.2 ‰ (n=27) for oxygen. Carbon and oxygen isotope fractionation between dolomite and calcite is close to but does not match recently established equilibrium oxygen fractionation values. Carbon isotope compositions of dolomite imply a well homogenized C3-plant-dominated carbon source in relatively dry ecosystems - with a small addition of atmospheric carbon - consistent with recent estimates based on regional fossil wood fauna and herpetological assemblages. The temperatures of dolomite formation based on oxygen isotope data and previous determinations of isotope compositions of paleo-meteoric waters yield an average of 22.6±3.4°C. The microfabrics and isotope data suggest microbially mediated dolomite formation with a strong pedogenic component close to or within an oscillating groundwater body, possibly with palustrine influences in some deposits. Bentonitization of rhyolitic tephra in the UFM occurred in a near-surface, non-marine and non-arid environment shortly after deposition, probably during times of enhanced groundwater flow. Dedolomitization of Alpine dolomite clasts in the fluviatile sediments is considered as the principal Mg source for dolomite and montmorillonite formation.

ALTERATION OF OPHIOLITIC UNITS AND RELATED ARGILLACEOUS SEDIMENTS IN THE SOUTHEASTERN PART OF THE CAPPADOCIAN VOLCANIC PROVINCE (ARAPLI – AKKÖY, KAYSERİ), CENTRAL ANATOLIA, TURKEY

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The study area is situated between the villages of Araplı and Akköy (Kayseri) in the southeastern part of the Cappadocian Volcanic Province (CVP) in central Anatolia. An ophiolite complex tectonically overlies the Kırşehir crystalline massif and rocks of the Tauride orogenic belt and developed as a result of collision between the Afro-Arabian and Eurasian plates, representing a basic rock unit within the CVP. This progressive tectonic regime resulted in a context appropriate both for ophiolite formation and, since the Early Miocene, development of the main depression (basin) in the CVP. The Yeşilhisar conglomerate of Oligo-Miocene age was the first terrestrial sedimentary unit in this basin, with components derived from ophiolitic and metamorphic rocks. The Mustafapaşa Formation (Late Miocene) overlies the ophiolitic basement and the Yeşilhisar basal conglomerate in the villages of Akköy and Araplı, respectively, and is overlain in turn by altered white Cemilköy ignimbrite. Fresh and partially altered rocks were examined using polarized-light microscopy, X-ray diffractometry and chemical methods. The ophiolitic units are made up mainly of pyroxene, hornblende and accessory olivine. Texturally, the presence of oriented iron-oxide-bearing fractures in amphibole, pyroxene, and hornblende crystals - coexisting with serpentine, talc and chlorite- suggest that the alteration developed authigenically with tectonic control. Micromorphologically, the presence of spongy smectite in mudstone of the Mustafapaşa Formation as coatings on detrital materials suggests *in situ* precipitation driven by dissolution and precipitation mechanisms. Mineralogical distribution from south to north is as follows: chlorite ± analcime ± amphibole + quartz + calcite + dolomite + feldspar; amphibole + chlorite + calcite + smectite + illite + feldspar; talc + serpentine + quartz + smectite + feldspar + calcite. Relative increases in Al+Fe+Mg/Si ratio, LOI, and heterogenic Ni, Co and Cr contents northward from and upward in the basin, in addition to local increases in Rb, Ba and Sr upward in proximity to the Cemilköy ignimbrite, suggest basinward palaeoflow and supply of ophiolitic detrital, chloritic clayey and local volcaniclastic materials. Thus, physical, chemical and biological weathering of olivine, pyroxene, amphibolite, chlorite and feldspar favourably contributed to the development of smectite deposits under alkaline fluvial and lacustrine conditions within the Mustafapaşa Formation.

CLAY MINERALOGY OF A STRONGLY WEATHERED PODZOL IN DENMARK

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In Mid Jutland, Denmark close to the average extension to the west of the Weichsel ice, moraines from the Saale glaciation were left as islands in the sandy outwash materials from Weichsel. These "Hill Islands" which represent the top materials from Emian were exposed to strongly weathering during Weichsel and in the site discussed here (Bording, "Hill Island") no trace was left of the interglacial soil which developed during the Eemian period. Remnants of the Eemian soil can be found in places buried in other sediments. All basic soil data will be presented here along with XRD of the mineralogy of sand, silt and clay fractions of the podzolic soil horizons. The sand fractions contain only quartz (0.426 and 0.234 nm) and potassium feldspar (0.324 and 0.319 nm) in horizons from A1 to BC. The silt fractions contain except from quartz and feldspar a little mica (1.0 nm) and kaolinite (0.72 nm) Preliminary results from clay minerals analyses of the horizons from A1 to BC indicate that there is very little content of clay minerals in the < 2µm fraction. Quartz and feldspar dominate the < 2 µm fraction with traces of mica (1.0 and 0.5 nm) and kaolinite (0.72 and 0.357nm) and indication of 1.4 nm mineral in the E horizon. The Saale morain material has went through very strong weathering proceses and this can be the explanation why this soil is much poorer in clay minerals than podzols developed in Weichsel morain materials which it will in this presentation be compared to.

ORIGINS AND THERMOCHEMICAL CONDITIONS FOR THE FORMATION OF THE SEPIOLITE FROM CENTRAL ANATOLIA AND PALYGORSKITE FROM EASTERN ANATOLIA IN THE NEOGENE LACUSTRINE BASINS

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The Upper Miocene-Pliocene lacustrine sediments of the Central Anatolia contain numerous economic lenticular sepiolite deposits. Two individual sepiolite beds with dolomite deposited in playa lakes and its swamps are located near İlyaspaşa and Yenidoğan villages (Eskişehir-Central Anatolia). The underlying clayey-calcerous units comprise trioctahedral smectite, dolomite, calcite, magnesite, chlorite, illite, quartz and opal-CT. On the contrary, the Middle Miocene-Pliocene lacustrine sediments of Kangal basin (Eastern Anatolia) contain remarkable amounts of palygorskite and dioctahedral Mg-smectites. Also, calcite, dolomite, opal-CT, quartz, chlorite, serpentine and feldspar are other encountered minerals in calcareous claystones intercalated with clayey limestone.

The intensive meshwork structure of the sepiolite fibers parallel to the lamination covering the dolomite and organic materials in İlyaspaşa and interwoven fibers and fiber bundles of palygorskite between carbonate rhombs in Kangal indicate the chemical precipitation from the alkaline lake environment as the main mechanism of the formation. However, mineral assemblages in the both basins reveal that they were precipitated from solutions having diverse chemical conditions. The aim of this study is to define the chemical conditions of solutions by means of thermodynamic concentrations of aqueous ions (Mg, Ca, Al, Si, H) and to identify the diagenetic trends and new possible precipitations caused by present day ground water in the study areas. For these purposes, activity diagrams generated by thermodynamic calculations with considering all the possible phases in the system of MgO-Al_2O_3-SiO_2-CaO-H_2O-CO_2-HCl were used and groundwaters data were plotted on them.

Sepiolite and dolomite or magnesite in İlyaspaşa and Yenidoğan precipitate from the solution with high Mg activity and pH with the presence of Si (quartz saturation limit). Ca activity determines the type of carbonate minerals. When low amount Al is present in that solution, trioctahedral smectite (Mg-saponite) accompany to sepiolite and dolomite. Groundwaters precipitate quartz and dolomite at low Al activities, Mg-montmorillonite at high Al activities and dissolves magnesite and partly dolomite. In the Kangal basin however, increasing Al activity (kaolinite+pyrophyllite saturation) causes the precipitation of dioctahedral smectite (Mg-montmorillonite) and palygorskite from the solutions. Higher pH, Mg and Si activities are more favourable for the formation of palygorskite than Mg-montmorillonite. Increasing Al activity provides Mg-saponite formation prior to sepiolite and Mg-montmorillonite prior to palygorskite from solution. Groundwaters precipitate quartz and dolomite at low Al activities, Mg-montmorillonite and palygorskite at high Al activities and dissolves magnesite. Some of the waters are in equilibrium with sepiolite. Sources of cations in both lacustrine environments are ophiolitic rocks at the basement. Additionally, more Al is provided from volcanic rocks in the Kangal basin.

NEW OCCURRENCES OF WHITE KAOLINE DEPOSITS IN THE NORTHERN PART OF SINAI, EGYPT

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In this paper, white kaoline deposits were recorded for the first time in North Sinai and found either as alternating beds within thick glass sand successions, or as a matrix for sand grains and recorded. Remte sensing data and field studies indicate that The Lower Cretaceous white kaoline deposits interbedded with the sand stones of the Malha Formation. They are recorded at the cores of Gabal Manzour, Gabal Falig, Gabal El Halal and Gabal Yelleq.

In the present work, 20 samples of white kaoline-bearing glass sands were processed with the purpose of separation of high grade kaolin and sand, which satisfy the industrial requirements. Crushing, attrition and sieving processes as well as separation by hydrocyclone were applied. Minerallogically, most of these deposits are formed of kaolinite, in addition to quartz as a non-clay mineral. They are characterized by high alumina content (22 – 27 %), low content Fe_2O_3 (0.3 – 0.5 Fe_2O_3) and titanium (1.3 –1.9 %). Also, they are generally characterized by very low alkalies and alkaline contents

White kaoline is the purest, whitest, most expensive clay and chracterized by moderate plasticity and possess good industrial potentialities. It can be used in fine–coated printing papers, medical industries, pottery, rubber, white cement and ceramics.

MINERALOGICAL AND GEOCHEMICAL STUDIES ON THE CLAY DEPOSITS, NORTH SINAI, EGYPT: USING REOMTE SENSING DATA

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Practical and economical constraints prompt the need of obtaining lithological and structural information with reduced field effort In the present work, the clay deposits are recorded in several localities (e.g. east Gabal Libni, east Wadi El Hema and southwest Gabal Risan Eniza in north Sinai). Twenty samples from these deposits (Kafr El Sheik Fm) east Gabal Libni were analyzed using X-Ray Diffraction (XRD) analysis. These analyses revealed the samples are composed of the following minerals in a decreasing order of their abundance: quartz, montmorillonite, kaolinite and calcite. The chemical analyses for fiftten sample from these samples using XRF analysis indicate that SiO2 ranging from 54.06 to 55.75 %, Al2O3 ranging from 15.84 to 20.82 % in samples T1, T2 and T3.

In this study, band ratioing, principal component analysis (PCA), false-color composition (FCC), and of ASTER (VINIR and SWIR bands) and ETM+ data have substantially improved visual interpretation for detailed mapping of the studied areas in North Sinai of Egypt. By compiling field, geochamical and spectral characterstic analysis data, controls on claymineralization have been assessed in terms of association of clay deposites with particular lithological units and structure features. Spectral characteristic analysis (SCA) followed by both principal component analysis (PCA) and band ratio analysis of the nine ASTER bands enabled selection of appropriate band combination, principal components and band ratio for discriminating the exposed rock units associated with clay deposites throughout the study area. Comparing the resultant of both PC and band ratio color images with the available geological maps followed by field check as well as the chemical analyses indicates that ASTER data provides new information about the reflectance of the rocks that can be used for precise lithological mapping in unmapped areas and verify and update the existing geological maps.

EVOLUTION OF DIOCTAHEDRAL VERMICULITE IN GEOLOGICAL ENVIRONMENTS: AN EXPERIMENTAL APPROACH.

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Dioctahedral vermiculite (hereafter divermiculite) is a dioctahedral 2:1 phyllosilicate with layer charge 0.6 - 0.9 per half unit cell and the interlayer space occupied by hydrated cations. It forms in soils by weathering of dioctahedral mica mainly. In most of the studies describing divermiculite the behaviour of only the strongest (001) XRD reflection (at about 14 Å in Mg – saturated form) is presented, thus using the available data it is not possible to distinguish between mixed layered minerals rich in divermiculite and a discrete mineral. Divermiculite commonly occurs in soils and fresh water sediments, but has not been reported from marine sediments and sedimentary rocks. The evolution of the mineral between weathering and diagenesis remains obscure. According to the available literature divermiculite is likely to exhibit strong potential for selective sorption and fixation of potassium. The fixation is expected to involve interlayer dehydration and collapse leading to the formation of 10 Å mica-like structure. The objective of the present study was to answer the question if divermiulite is likely to transform into 10 Å mica-like phase by fixation of K^+ in soils and/or selective sorption (and fixation) of K^+ from sea water?

Because of the fact that no divermiculite standard reference material was available, two natural soil clays rich in dioctahedral vermiculite were used in the study. The clays were saturated with potassium using different protocols simulating natural processes taking place in soil and marine environment. The solid products obtained in the experiments were analysed for potassium content using flame photometry. The influence of the treatments used on the structure of dioctahedral vermiculite was studied using X-ray diffractometry.

In general all the treatments involving potassium saturation caused K- fixation and irreversible collapse (i.e. contraction to 10 Å) of at least a portion of the vermiculite layers Air-drying of the K-saturated samples greatly enhanced the degree of the collapse and the amount of K fixed. It is not clear whether the time had a significant effect on the degree of the irreversible collapse or not. Selective sorption of K^+ from artificial sea water was observed for both the samples.

The results of the experiments conducted indicate that transformation of dioctahedral vermiculite into 10 Å mica-like phase is likely to occur in soils during weathering and in sediments during early diagenesis. Both the processes have to be taken into consideration in evaluation of detrital input into sedimentary basins.

BASIN HISTORY RECONSTRUCTION USING CLAY AND AFT DATA: LOWER PALEOZOIC OF THE DNIESTER SLOPE, UKRAINE

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Dniester slope is a SE part of the large shale gas field on the Peri-Tornquist margin of the East European Craton. The Silurian shale facies are presently buried, but to NE the carbonate facies containing thin shales and bentonites are cropping out in the Dniester gorge. Clay mineral composition of the carbonates, shales, and bentonites was investigated by XRD. Overlying Devonian shales from the Dniester gorge and the Silurian shales from two boreholes to NW from the gorge were also studied by XRD. K-Ar dates of fine clay fractions of the Silurian bentonites and accompanying shales and carbonates were measured, and AFT ages were measured for the apatites separated from these bentonites.

The clay fraction of bentonites is composed exclusively of mixed-layer illite-smectite with 1-15 % S. The end-member clay is not true illite but aluminoceladonite. The clay fraction of accompanying shales and carbonates contains almost non-expandable illite with KI=0.55-0.98°, indicating the maximum palotemperatures close to 200° C. In the overlying Devonian shales the diagenesis is slightly less advanced: KI=0.71-1.15°, confirming burial origin of the diagenetic alteration. Both sections correspond to the conodont diagenetic zone CAI=2-3. In NE zone of CAI=1-1.5 the Silurian shales from a borehole contain illite-smectite up to 29 % S, at the top of the profile. In SW zone of CAI=4-5 anchimetamorphic non-expandable illite with KI=0.29° was found.

In shales and carbonates the clay fraction contains also chlorite, most abundant in the anchimetamorphic sample. In the borehole samples the chlorite is strictly non-expandable, while in the outcrop samples both non-expandable and expandable chlorites were found. In consequence, the expansion of chlorites, which in extreme cases produces clays resembling smectite, is interpreted as recent weathering phenomenon. For this reason, chlorite from the outcrop samples should not be used as the indicator of diagenetic grade.

The K-Ar dates for the Silurian bentonites and shales range from the Middle Devonian to the Carboniferous/Permian boundary (390-310 Ma). They document former extension of a thick cover of the Upper Devonian_and Carboniferous sediments of the Lublin-Lviv basin far to SE, eroded entirely during Mesozoic and not accounted for by current paleogeographic reconstructions. This cover may have been either sedimentary or partially tectonic (Variscan intracratonic duplexes) and the thickness, necessary for the observed level of diagenesis may have been reduced by an elevated heat flow along the major tectonic zone at the edge of the craton (TESZ). The presence of such cover is confirmed by totaly reset Cretaceous AFT ages of the Silurian bentonites. The AFT dates imply also a Tertiary heating event in the area.

CLAY MINERALS AS A TOOL FOR TRACING LOW SULFIDATION SYSTEMS – EXAMPLE FROM THE KREMNICA ORE AND INDUSTRIAL MINERALS FIELDS (SLOVAKIA)

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Clay minerals are important product of alteration associated with low sulfidation epithermal systems, present in close vicinity of veins (wall rock alteration) as well as in regional-scale hydrothermal alteration sometimes reaching several kilometers from vein mineralisation. Study of clay minerals combining xrd and stable isotope analyses can provide important information about geological processes, such as temperature, fluid sources, fluid flow paths and history of mineralisation-alteration. Kremnica hydrothermal system in the Central Slovakia Neogene Volcanic Field is a typical low-sulfidation Au-Ag deposit, accompanied by several localities of economic and non-economic accumulations of industrial minerals (K-bentonite, bentonite, zeolite, limnosilicite, kaolinite). The Au-Ag epithermal deposit is hosted by andesitic rocks, situated on marginal faults of a resurgent horst in central part of a volcanotectonic graben. Less mineralised S section of the vein system and industrial mineral accumulations are hosted by rhyolite domes and volcanoclastic rocks, filling the graben.

Illite and illite-smectite occur in vein wall rock alteration and in K-bentonite deposit located close to the southern end of the vein system. I/S is mostly of R1 and R3 type with 1M polytype and expandability mostly between 6 and 45 %. Equilibibrium $\delta^{18}O$ and δD fluid compositions are similar to that of vein quartz, indicating origin of K-bentonite by lateral outflow of hydrothermal fluids from veins into permeable pumiceous/glassy volcanoclastic rocks. Paleotemperatures (135-180°C) were obtained by concordance of oxygen isotope and I-S expandability geothermometers and vein fluid inclusion data. $\delta^{18}O$ values and expandability show a clear positive correlation. Smectite (bentonite) accumulations occur predominantly in distal S and SE part of the system, often interlayered with limnic/lacustrine silicites. $\delta^{18}O$ and δD analyses indicate heated groundwaters as the source fluid. $\delta^{18}O$ values of both smectite and silicites increase from N to S-SE due to decrease in temperature (70 to 15°C), which results from paleoflow of the fluids and/or recrystallisation during shallow burial. Smectite mean thickness decreases in this direction and correlates with $\delta^{18}O$ values. Kaolinite often accompanies wall rock and regional alteration. Isotopic composition of wall rock kaolinite indicates origin from steam-heated fluids, overprinting mineralised structures. Minor accumulation of kaolinite in southernmost part of the regional alteration area have isotopic signature typical of supergene origin.

THE UEFFELN PYROPHYLLITE DEPOSIT, WESTERN LOWER SAXONY BASIN, GERMANY

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Pyrophyllite deposits are generally hosted either by high-temperature acid hydrothermal alteration zones of felsic volcanic systems or by Al-rich regionally metamorphosed rocks. We present new mineralogical, geochemical, fluid inclusion and geochronological data on the unusual Ueffeln pyrophyllite deposit near Bramsche, Lower Saxony Basin (LSB), Germany. Upper Oxfordian to Kimmeridgian deltaic sands and clays in the western LSB were transformed within the local "Bramsche" thermal anomaly into quartzites and metapelites. The quartzites are mined for construction aggregates, while the pyrophyllite-rich pelitic rocks are used in brick industries. The brownish fine-grained massive metapelitic rocks reveal no obvious slaty cleavage. They consist of 2M pyrophyllite, R3 illite(>0.9)/smectite, 2M1 illite and quartz with minor amounts of K-feldspar, plagioclase, goethite, pyrite, anatase, berthierine, chlorite, and kaolinite. Minerals that are indicative of high-temperature acid hydrothermal alteration, such as alunite, dickite, diaspore, corundum, andalusite or dumortierite, are notably absent. The pelitic rocks are characterized by 17 to 25 wt.% Al_2O_3, 5 to 10 wt.% Fe_2O_3 and 2.2 to 3.2 wt.% K_2O.

Early closed quartz veins in the underlying quartzite host aqueous two-phase inclusions with homogenisation temperatures of 210 to 220° C and low salinities of less than 5 wt.% NaCl-equiv. Co-existing high-density CO_2-CH_4 inclusions indicate trapping pressures of about 800 bar and thus significant burial of at least 5 km. Much lower homogenization temperatures of aqueous fluid inclusions (150 to 170° C) are recorded in quartz crystals of the open fractures in the quartzite indicating cooling of the hydrothermal system. The <0.2 μm fraction of an I/S- and illite-bearing sample yields a K-Ar age of 117 ± 2 Ma, while the <2 μm fraction gives 159 ± 4 Ma. Thus, the illitic clay minerals were mostly generated by illitization of smectite during a thermal event and contained only minor detrital components.

The Ueffeln pyrophyllite deposit formed from kaolinite- and smectite-rich precursor clays during an Early Cretaceous high-temperature (>240° C) hydrothermal event probably related to a short extensional phase at the SW margin of the Lower Saxony Basin.

Rb-Sr AND Sm-Nd SYSTEMATICS OF CLAYEY SIZE FRACTIONS: VENDIAN SHALES OF SOUTH URALS

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The <2-µm fraction of shale sample from the Bakeevo Formation was separated into 1-2, 0.6-1, 0.3-0.6, 0.2-0.3, 0.1-0.2 µm and <0.1 µm subfractions (SF). They were studied by the XRD, Rb-Sr and Sm-Nd methods. The finer SFs (0.2-0.3, 0.1-0.2 и <0.1 µm) include low-temperature $1M_d$ illite and admixtures of 1M illite. They have high CIS (Kubler Index) values 1.08-1.12° complying with the zone of diagenesis. The coarser SFs (1-2, 0.6-1, 0.3-0.6 µm) include 1M illite and admixtures of detrital $2M_1$ illite. The SFs were leached with 1N HCl and leachates and residues after leaching were studied by the Rb-Sr and Sm-Nd methods.

Character of distribution of the Rb, Sr, Sm and Nd and their isotopes in the silicate residues of the SFs allows us to suggest two groups of the SFs: 1) 0.2-0.3, 0.1-0.2, <0.1 µm, and 2) 1-2, 0.6-1, 0.3-0.6 µm (Table). The Sr, Sm and Nd concentrations and isotope ratios in both groups smoothly vary with clay particle size. The Rb, Sr concentrations and the ^{87}Rb/^{86}Sr and ^{87}Sr/^{86}Sr ratios in the leachates of this group vary in the same manner. The linear arrangement of points in the coordinates ^{87}Rb/^{86}Sr – ^{87}Sr/^{86}Sr indicates two-component mixing systematics in both groups.

Group	SF, µm	CIS	Residuals							
			Rb, ppm	Sr, ppm	^{87}Sr/^{86}Sr	^{87}Rb/^{86}Sr	Sm, ppm	Nd, ppm	^{147}Sm/ ^{144}Nd	^{143}Nd/ ^{144}Nd
1	<0.1	0.82	187	25	0.85938	21.900	1.671	13.4	0.0752	0.511691
	0.1-0.2	0.82	190	26	0.86388	21.694	1.858	16.8	0.0670	0.511859
	0.2-0.3	0.80	184	36	0.82678	15.046	2.787	27.0	0.0624	0.511456
2	0.3-0.6	0.72	175	37	0.82968	13.709	3.152	29.7	0.0642	0.511482
	0.6-1	0.72	167	40	0.82978	12.353	3.494	33.1	0.0638	0.511641
	1-2	0.70	164	67	0.78306	7.214	6.162	59.2	0.0629	0.511462

One of the end-members from coarser group (0.3-0.6 µm) is diagenetic 1M illite with slight admixture of detrital illite 2M1. It is not possible to consider Rb-Sr model age (622 Ma, ^{87}Sr/^{86}Sr$_{initial}$ - 0.708) as an age of diagenesis, however, makes it possible to estimate its upper limit. The model age of end-member from finer group (0.2-0.3 µm), which is dominated by postdiagenetic $1M_d$ illite, is 554 million years and allows us to estimate the lower limit of the age of diagenesis. Thus, the age of diagenesis of bakeev sediments appears to be in the range of 554-622 Ma and correlate with Rb-Sr isochron age of Tolparovo Formation - 593±15 Ma.

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Clays in environment and in radioactive waste applications

Oral presentation

THE TESTING OF LOADED BENTONITES IN CONNECTION WITH DEEP REPOSITORY ENGINEERED BARRIER

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It is planned that spent nuclear fuel will be disposed of in deep geological repositories concerning the design of which a number of different concepts exist depending on the geological formation chosen. For the future Czech repository (as with those of Sweden and Canada) granite rock has been chosen as the host rock formation. The repository will require several so-called engineered barriers one of which is referred to as the buffer. The purpose of the buffer will be to protect the canister from water infiltration in the disposal well as well as to reduce the risk of the migration of radionuclides into the biosphere. Bentonite is considered the most suitable material for the buffer.

The Centre of Experimental Geotechnics (CEG) is performing a series of tests which involve subjecting bentonites to a number of procedures which simulate the loading of the buffer under deep repository conditions. Two important factors are being considered: temperature (produced by the still active spent nuclear fuel) and the chemical impact of the infiltration of local water both of which are being tested in the CEG's laboratory as well as in-situ at the Josef Underground Laboratory (http://www.uef-josef.eu/stola-josef). All the relevant geotechnical parameters (hydraulic conductivity, swelling pressure, liquid and plasticity limits, uniaxial compressive strength and thermal conductivity) are evaluated following the loading of the samples and subsequently compared with values obtained from tests on non-loaded samples. Several different types of bentonites have been tested in previous projects, i.e. the material from MOCK-UP-CZ experiment, Spanish bentonite from the FEBEX experiment and raw Czech bentonite from the Rokle deposit. Currently the CEG team is testing a further two Czech bentonites: industrially prepared (dried and sieved) Ca-Mg bentonite B75 and the Na-activated form thereof (Sab65).

Previous project revealed that the material changes to a limited extent after loading the most apparent of which from the geotechnical point of view concerned the evaluation of liquid limits. However, all the changes identified were relatively minor and the bentonite continued to meet the tough requirements for use as a deep repository barrier material. For a better understanding of the changes which take place in the material it is important to take into account a previous project which studied geochemical and mineralogical changes the results of which correspond to the geotechnical changes discovered by the CEG team.

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THE DEVELOPMENT OF SPRAYED CLAY TECHNOLOGY WITH RESPECT TO DEEP REPOSITORIES FOR RADIOACTIVE WASTE

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The investigation of sprayed clay technology has been underway at the Josef Underground Laboratory for a number of years. This technology was developed principally with respect to the backfilling of shafts and galleries in deep repositories providing access to disposal wells containing high-level long-lived radioactive waste. At present research is being focused on the use of this technology to fill the space between the spent fuel container and the wall of the disposal well.

It is currently envisaged that the spent fuel canister will be surrounded by prefabricates made of highly-compacted bentonite; however a barrier consisting of such blocks has the disadvantage of featuring a large number of discontinuities, i.e. joints. Research suggests that the discontinuities will become sealed due to the self-healing ability of bentonite. However the possibility cannot be discounted that even following self-sealing, preferential paths will remain which might allow radionuclide migration. As part of the current research programme advanced shot clay technology is being developed which should allow for the mitigation of the number of discontinuities and thus enhance the safety of the disposal concept.

In order to prevent radionuclide migration the sealing material must have a very low level of water permeability. Since it has been established that permeability is strongly dependent on the density of a material, the dry density and water content of the material make up the most important parameters monitored during the testing procedure. All the most important material parameters in terms of the prevention of potential radionuclide migration depend on these two key values. An assessment was carried out of selected materials prior to technological testing; the relationship between permeability and dry density was examined and subsequently established within this phase of the research which then allowed the rapid verification of the suitability of both the sprayed material and the technology employed for use in deep repositories by means of the simple checking of the dry density value of the material.

This paper describes the various stages of the research including the results of several shot clay mixture tests.

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THERMO-HYDRO-MECHANICAL BEHAVIOR OF ARGILLITE

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Argillite is a very low permeability geomaterial widely encountered: that is the reason why it is an excellent candidate for the storage of long-term nuclear waste depositories. This study focuses on argillites from Meuse-Haute-Marne (East of France). The multiscale definition of this material suggests the derivation of micromechanics reasonings in order to better account for the mechanisms occuring at the local (nano- and micro-) scale and controlling the macroscopic mechanical behavior. In this work, upscaling technics are used in the context of thermo-hydro-mechanical couplings. The first step consists in clarifying the morphology of the microstructure at the relevant scales (particles arrangement, pore size distribution) and identifying the mechanisms that take place at those scales. These local informations provide the input data of micromechanics based models (Dormieux[a]). Schematic picture of the microstructure where the argillite material behaves as a dual-porosity, with liquid in both micro-pores and interlayer space in between clay solid platelets, seems a reasonable starting point for this micromechanical modelling of clay (Dormieux[b]). This allows us to link the physical phenomena (swelling) and the mechanical properties (elastic moduli, Poisson's ratio). At the pressure applied by the fluid on the solid platelets appears as the sum of the uniform pressure in the micro-pores and of a swelling overpressure depending on the distance between platelets and on the ion concentration in the micro-pores. The latter is proved to be responsible for a local eslastic modulus of physical origin (Dormieux[b]). This additional elastic component may strongly be influenced by both relative humidity and temperature. A first contribution of this study is to analysing this local elastic component by different approaches depending on the water content in the interlayer space. For large water content, the liquid in between the platelets may be considered as a continuous phase and the double layer theory is relevant. For decreasing water content value, the liquid domain becomes a discrete phase. The theory of disjoining pressure of wetting films and molecular dynamics method are then more adapted.

Within this context, we propose a constitutive law for argillite accounting for temperature and relative humidity effects. The homogenization process starts with the thermoelastic behavior definition of the particle in the shale matrix of clay, which takes into account the lamellar structure of clay particles. Then we provide a model description of the morphology of the shale matrix where the shale matrix appears as a polycrystal composed of elementary particles distributed in a disordered pore space. This description suggests to implement the self-consistent scheme that allows us to estimate the mesoscopic behavior of the shale matrix of argillite. The estimated Young modulus, depending on both temperature and relative humidity, is in a good agreement with the results obtained experimentally by mechanical tests of Micro-indentation on its evolution and its magnitude. In the final step, we propose an elastic constitutive law for argillite integrating inclusions in the shale matrix. The equation obtained for agillite is then compared with mechanical compression tests on partially saturated argillite at different temperatures. This allows to consider that the effects of temperature and relative humidity on argillite poroelastic behavior are well integrated in our multi-scale modelling.

Properties of clays (catalysis, pore systems, transport properties in organic rich shales, ...)

Oral presentation

TREATMENT OF ILLITIC CLAYS FROM LATVIA WITH ORGANIC ACIDS

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Clays and clay minerals are widely used as excipients and active ingredients in cosmetic products and pharmaceutical preparations. The use of clay minerals are based on many properties, one of them being particle size. Another important factor is the purity of clay samples [1,2]. Naturally occurring clays typically are mixtures of clay minerals and non-clay minerals, such as quartz, feldspar, carbonates, metal oxides and hydroxides. The distribution of clay particle size in raw clay samples are influenced by these impurities, mostly by carbonates and iron containing compounds. They behave as cementing agents, thereby inducing the aggregation of clay particles. Because of these aggregates the stability of clay suspensions decreases and the purification of raw clay samples from non-clay minerals is hindered. The removal of carbonates and iron compounds can be performed by dissolution with organic and inorganic acids [3].

In the present study the use of organic acids for carbonate and iron compound dissolution treatment and the effects on mineralogy and grain size distribution is investigated. The clay samples were taken from deposits in Latvia, containing 13-15% carbonates and illite as the main clay mineral. Clay – aleirite fraction < 63 μm was used. The samples were treated with various concentrations of citric, oxalic and malic acids for 4-6 h. Changes in mineralogical composition were identified by using X-ray diffractometer. Particle size distribution was measured for fractionated and non-fractionated clay samples with laser particle size analyzer. In the dissolution process of the carbonates soluble and insoluble calcium and magnesium salts are formed as by-products.

The influence on the aggregation and size distribution of clay particles depends on the type and concentration of the acids. Both calcite and dolomite is completely dissolved only in 0.2 M acids. Dissolution of iron compounds increases with increasing the concentration of acids.

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REHYDROXYLATION OF SMECTITES IN USED FOUNDRY SANDS – MECHANISTIC STUDIES

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Bentonites in foundry sands are exposed to high temperatures for different time periods during the metal casting process and partial dehydroxylation of the included smectites occurs. Dehydroxylation is partially reversible in dependence of smectite structure and process parameters (T, t). Bentonites and smectites, respectively, that are used as binders in molding sands are often alkaline activated initially Ca-rich materials. Alkaline activation improves the mechanical properties like green compression strength and partial exchange of interlayer Ca^{2+} by Na^{+} occurs.

Thermal stability of smectites is primarily related to the kind of octahedral cations and distribution of octahedral cations in dioctahedral 2:1 layer silicates (Drits et al., 1995; Wolters, Emmerich, 2007), but interlayer cations also influence dehydroxylation temperature (e.g., Emmerich et al., 1999).

The objective of the present study was to elucidate the influence of layer structure and interlayer cation on spontaneous rehydroxylation of Ca-rich and Na-exchanged montmorillonites under ambient conditions.

Simultaneous thermal analysis (STA) device (Netzsch, 449C Jupiter) was used for dehydroxylation at 540 and 700 °C and analysis of the rehydroxylated samples after storing at 53 % relative humidity (r.h.). Both dehydroxylation and rehydroxylation duration were varied. Evolved water during dehydroxylation and during STA of rehydroxylated samples was recorded with a quadrupole mass spectrometer (Netzsch, Aeolos) linked to the STA device.

Three montmorillonites (< 2μm) that differ in layer charge, cation exchange capacity and ratio of *trans*-vacant (tv) to *cis*-vacant (cv) 2:1 layers were used.

We showed that even pure cv montmorillonites lost about 50 % of their hydroxyl groups when kept at 540 C for 12 h. Montmorillonites with 34 to 45 % of tv layers lost about 80 to 90 % of their hydroxyl groups when kept at 540 C for 12 h. Heating at 700° C even for short periods produced nearly anhydrous montmorillonites from all starting materials.

All dehydroxylated samples spontaneously rehydroxylated under ambient conditions (53 % r.h.) and a high amount of cv layers in the starting material resulted in a higher extend of rehydroxylation after partial dehydroxylation but not after full dehydroxylation.

We also found that Na^{+} at interlayer positions increased mass loss during dehydroxylation and decreased mass gain due to rehydroxylation for low charged montmorillonites but hardly influenced de- and rehydroxylation of medium charged montmorillonite.

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DISSOLUTION OF KOPERNICA BENTONITE IN HCl AND RECENTLY PUBLISHED PERTINENT DATA

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Changes occurring upon acid dissolution of a <2 micron fraction of Kopernica bentonite in 6 mol.dm^{-3} HCl at 95° C for up to 36 hours with occasional stirring are discussed. The Kopernica deposit is situated on the south-western margin of the Kremnické vrchy Mts. in the Western Carpathians, Slovakia, just next to the better known but mostly already spent Jelšový Potok bentonite. Kopernica is considered a perspective material to substitute for Jelšový Potok in many applications. Both these clays originated by alteration of rhyolitic materials, are relatively low in iron content, and have Al-Mg montmorillonites as the dominant minerals. Quartz, cristobalite, K-feldspar, kaolinite and biotite were the accessory minerals present in the fraction used for the reaction. Afterwards, the solid reaction products were filtered and washed with water, the liquids were combined and analysed for Al^{3+}, Fe^{3+}, and Mg^{2+} and the dissolved fractions of these metals were calculated to obtain the dissolution curves. The solids were dried and ground to pass through a 0.2 mm sieve and investigated by XRD, IR and NMR spectroscopies. Gradual shift of the complex Si–O stretching band from 1041 cm^{-1}, typical for Si bound in the layers, up to 1102 cm^{-1} in the spectra of the most extensively dissolved materials proved substantial modification of the nearest environment of Si atoms upon the reaction. This position is characteristic for Si–O bonds in three-dimensional framework, occurring in amorphous silica, the final reaction product. Further changes in the IR spectra include gradual decrease in the intensities of the OH bending vibrations, appearing between 820 and 920 cm^{-1}, and Al–O–Si vibrations near 525 cm^{-1}. The near-IR spectra showed a gradual decrease in the intensities of the structural OH overtone and combination bands reflecting less octahedral atoms. Isolated SiOH groups were found in all acid treated materials while two OH groups bound to a Si atom (HOSiOH) only in extensively treated samples. ^{29}Si MAS NMR spectra show the presence of Si bound in quartz, in the smectite layers, and in the reaction product containing also SiOH and HOSiOH groups. Octahedral and tetrahedral Al is detected in the ^{27}Al and ^{29}Si MAS NMR spectra. Data on dissolution of octahedral cations from the solutions correlate well with those obtained from the analyses of the solids and with the decrease in the cation exchange capacity. Total specific surface area of the samples decreased with the extent of dissolution.

ADSORPTION OF WATER ON ACID-TREATED BENTONITE KOPERNICA: NEAR-IR STUDY

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Bentonites are abundant clay with wide utilization in industry and environment protection. Although bentonites are effective adsorbents even in their natural form, the significant improvement of their sorption and/or catalytic properties can be achieved by acid activation, i.e. partial dissolution in inorganic acids. The aim of this study was to investigate the effect of montmorillonite structure degradation on its hydration properties. Na-saturated <2 μm fraction of bentonite from Kopernica deposit (Na-Kop) containing montmorillonite as the dominant component was dissolved in 6 mol.dm^{-3} HCl at 95° C from 1 to 36 hours. The infrared (IR) spectra confirmed that montmorillonite structure was considerably disturbed upon treatment for 8 hours and only fragments of the layers were present in the solid reaction product. Presence of the bands related to SiO vibrations of amorphous silica at 1101, 800 and 469 cm^{-1} in the IR spectra of samples dissolving in HCl longer than 12 hours indicated complete destruction of the montmorillonite structure. The IR spectra in the near-IR (NIR) region showed the increasing intensity of the band at 7314 cm^{-1}, assigned to the first overtone of the free SiOH groups, proving the rising content of the protonated amorphous silica with time of treatment. A NIR UpDRIFT accessory enabling the measurement of spectra directly in closed glass vials was used to study the effect of acid treatment and hydration on the strength of H-bonding between water molecules and to determine the amount of water adsorbed on the samples at 52 % relative humidity. With increasing content of water the combination $(\nu+\delta)_{H2O}$ band near 5250 cm^{-1} was shifted to lower wavenumbers indicating stronger H-bonds. In contrast, the upward shift of the band in the spectra of acid treatment samples indicated only weak H-bonds between water molecules and amorphous silica phase. The presence of H-bonded SiOH groups in hydrated samples was confirmed by the OH combination region. Gravimetric analysis and NIR spectra in the $(\nu+\delta)_{H2O}$ region allowed determination of the amount of water adsorbed on the samples. The hydration increased from Na-Kop to Na-Kop dissolved 5 hours for which the maximum value (12.5 mass %) and the highest $(\nu+\delta)_{H2O}$ band area were detected. Longer dissolution of montmorillonite in HCl produced samples with high portion of amorphous silica with gradually decreasing ability to adsorb water molecules. A good correlation of the results obtained by gravimetry and NIR spectroscopy indicates that $(\nu+\delta)_{H2O}$ band area reasonably reflects the hydration of the samples and can be used for the estimation of water content within the set of similar samples.

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CHANGES OF SWELLING CLAY MINERALS PHYSICO-CHEMICAL PROPERTIES DUE TO CYCLIC WETTING AND DRYING

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Swelling clay minerals are the most important inorganic components in soils and in clay liners due to their sorption capacity and low permeability. Mineralogical and chemical characteristics (i.e. interlayer composition, layer charge, crystallite size) of clay minerals may vary with environmental changes, involving the changes of their physico-chemical properties, such as adsorption, ion exchange and swelling capacity. These changes may influence the chemical and physical properties of the soil or clay liner itself. Such a process is subsequent wetting and drying (WD), effects of which was studied in this work on different swelling clay minerals (smectites, vermiculites in metal and K adsorbed forms) by means of X-ray powder diffraction (XRD), transmission electron microscopy (TEM), thermal analysis (DTA-TG) and by sorption experiments.

The most important change during WD cycles in the case of metal-adsorbed swelling clays revealed by XRD and TEM is the decrease of crystallite size (both lateral dimension and thickness of clay platelets). After 120-140 WD cycles clay particles can be fully decomposed, even their chemical composition changes, being richer in Si and the adsorbed metal. Smectites do not loss their expansion capacity during WD cycles. Moreover, vermiculites originally with low expansion capacity become more swelling after several WD cycles. Pb-adsorbed soil smectite behaves similarly to K-saturated smectite. Extraction of lead by ammonium acetate decreases gradually with the number of WD cycles, and about 10% of the adsorbed lead can not be desorbed after 120 WD cycles. This indicates that Pb^{2+} initially adsorbed in the interlayer space becomes fixed in the clay silicate structure. Cyclic WD has significant effect on the lead adsorption capacity of potassium-saturated smectitic soil. Without WD K-smectite adsorbs 0.11 mol/kg Pb, after 60 WD cycles it adsorbs 0.087 mol/kg and after 120 WD cycles Pb uptake is only 0.07 mol/kg. This loss of 35 % of Pb sorption capacity is the consequence of potassium fixation ("illitization") due to WD cycles. Similarly, water sorption capacity of K-smectitic soils also decreases during WD cycles.

Results of the above laboratory experiments suggest that clay minerals alter and their properties change due to cyclic WD. One of the most important effect of WD may be the particle size decrease of clay minerals, suggesting that low crystallinity of clay minerals in soils is due to this process.

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CHARACTERIZATION OF SURFACE ACIDITY OF NATURAL CLAY MINERALS BY MEANS OF TEST CATALYTIC REACTION

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Clay minerals are prevalent on the Earth and widely applied in various industrial fields as sorbents and catalysts. Regulating of surface activity of natural alumosilicates is necessary to produce tailor-made materials and is realized through their chemical, physical, mechanical modification/activation. Surface acidity of clay minerals described in terms of Broensted and Lewis sites is usually determined by titration and spectroscopic techniques (FTIR, XPS, NMR) along with temperature programmed desorption (TPD) of NH3 and CO2 or catalytic test reactions. The present study is aimed to characterize surface acidity of various natural clay minerals using the test reaction of methylbutynol (MBOH) conversion previously applied to distinguishing between basic, acid and amphoteric sites. Samples of raw alumosilicates containing hydromica, kaolinite and palygorskite from Russian (R); bentonite, red and white kaolinite, diatomite, zeolite from Jordanian (J) deposits and ZSM-5 were tested in catalytic reaction of MBOH conversion in a fixed-bed reactor at 120° C being activated at 500° C for 4h. It was found that conversion of MBOH over studied samples decreases in the order: palygorskite-R (97 %) > kaolinite-R (61 %) > zeolite-J (56 %) > bentonite-J (48 %) > hydromica-R (36 %) > red kaolinite-J (32 %) > ZSM-5 (27 %) > white kaolinite-J (22 %) >diatomite-J (11 %) after 120 min. reaction time. This order corresponds to their Si/Al ratio and natural acidity earlier confirmed by TPD-NH3, as well as specific surface area and porosity of minerals. Fast deactivation was observed for kaolinite-R, hydromica-R and ZSM-5 probably due to strong adsorption of secondary products and irreversible surfaře modification by polyaromatic compounds and coke as proved by FTIR-spectra as a result of acid catalyzed polymerization of MBOH. High catalytic activity of palygorskite-R is explained by high content of the mineral in the sample and its unique needle-like structure providing high surface area of catalyst and accessibility of active sites for substrate molecules. The typical products correspond to mainly acidic and basic pathways of MBOH conversion. Higher yields of acid products over zeolite-J, palygorskite-R, bentonite-J and kaolinite-R are related to their higher acidity. For H-ZSM-5 only acidic products are formed whereas for hydromica-R yields of acid and basic products are practically identical. The lowest conversion and product yields in case of diatomite-J are caused probably by its low acidity as a result of partial condensation of surface silanols to siloxane groups by the thermal treatment. Increase of catalyst activation temperature from 500 to 700° C results in higher MBOH conversion over basic pathway of reaction by additional basic sites formed due to mineral dehydroxylation at temperatures T≥ 700°. Increase in content of montmorillonite-R in samples (10-80 %) provides high MBOH conversion.

NEW MANIPULATION METHODS TO DECREASE THE CLOGGING OF CLAYS DURING MECHANICAL TUNNEL DRIVING

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The decision on which kind of tunnelling method is to be used for traversing loose rocks depends on the lithological characteristics. Earth Pressure Balanced (EPB) shields are now the most widely used technology because they can operate in a much broader spectrum of lithological conditions and do not require expensive additional equipment. The soil permeability for EPB drives can reach values of up to $k = 10^{-3}$ m/s for the most porous soils (BPNL Lyon-Turin) and comes down to practically impermeable clay (Heathrow T5). Since this technique is used in homogeneous as well as in heterogeneous ground conditions, the TBM cannot be designed for the optimum of a specific geology, but for the overall optimum. When excavating with a TBM, an adhesion of clay to parts of the machine or the transportation equipment can occur in different steps of the construction process: cutting, conveying and deposition. Unfortunately, there have not been many case studies on clogging so far, especially not when compared with the large number of tunneling projects worldwide where EPB machines are employed. In earthwork operations clogging can occur even when the clay content is low. Unfortunately no precise information is given among the technical literature. Cohesive ground generally contains high amounts of highly plastic clays, which are characterized by a high liquid limit and a high plasticity index. These types of soil tend to become very sticky on contact with water, due to the swelling of the clay particles. Although the negative effects of stickiness in tunneling are quite high and countermeasures on an empirical base are for some situations available, a systematic investigation of the processes is missing to this day. For the following research both standard pure clays and very well-known sticky clay formations have been used. Kaolinite, smectite, illite, Ypresian and Boom clays were extensively studied. Several geotechnical, chemical and adhesive tests were performed by using different ethanol amount in the pore fluid, salt solutions or applying an electric field to observe the change in their physical properties.

VERMICULITE-BASED CATALYTS FOR OXIDATION OF ORGANIC POLLUTANTS IN WATER AND WASTEWATER

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Phenols are frequently encountered organic molecules in contaminated surface water and groundwater. They are characterized by low biodegradability, high COD and high toxicity. Industrial wastewater (coke plant sewage, petrochemical industry, paints factories) and municipal wastewater are main sources of phenols. The effective removal of refractory organic pollutants can be achieved using catalytic oxidation of organic pollutants in aqueous solution – one of so called advanced oxidation processes (AOP) (Rokhina, Virkutyte, 2011). To avoid secondary pollution efficient, "ecological" oxidants are used: ozone, hydrogen peroxide or oxygen. Catalysts studied in the oxidation of phenol are hydrotalcites, transition metal oxides and precious metals. Also silicates (natural and synthetic clays) can be used as catalysts in their pristine form or after modifications (Garrido-Ramírez et al., 2010).

In presented work natural expanded vermiculite was used as a starting material for synthesis of Fe-doped catalysts. Material was doped with increasing amount of Fe by ion-exchange and precipitation of iron oxide. Part of obtained materials was calcined at 600° C for 5 h. Composite materials (as prepared and calcined) were characterized with respect to their structure (XRD, FT-IR), agglomeration state of Fe (DRS-UV-Vis), chemical composition and surface area (N_2 sorption). Activity in H_2O_2 decomposition as well as in phenol oxidation was studied in liquid phase at atmospheric pressure and temperature up to 70° C. It was shown that doping with Fe increases catalytic activity. However, excess of iron resulted in formation of undesired side-products.

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THE INFLUENCE OF INDIVIDUAL CLAY MINERALS ON FORMATION DAMAGE OF RESERVOIR SANDSTONES: A REVIEW WITH SOME NEW PERSPECTIVES

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The influence of individual clay minerals on formation damage of reservoir sandstones is reviewed, mainly through the mechanism of fine particle dispersion and migration leading to the accumulation and blockage of pore throats and significant reduction of permeability. The minerals discussed belong to the smectite, kaolinite, illite and chlorite groups respectively. These minerals usually occur in an aggregate form in reservoir sandstones and the physicochemical properties of these aggregates are reviewed in order to reach a better understanding of the factors that lead to their dispersion in aqueous pore fluids. Particularly significant properties include the surface charge on both basal and edge faces of the clay minerals and how this varies with pH, external surface area of both swelling and non-swelling clays, porosity and pore size distribution in the micro- and meso-pore size range and overall aggregate morphology. For non-swelling clays, and perhaps even for swelling clays, dispersion is thought to be initiated at the micro- or meso-pore level, where the interaction between the pore solution and the charged clay surfaces exposed on adjacent sides of slit- or wedge-shaped pores brings about expansion of the diffuse double electric layer (DDL) and an increase in hydration pressure. Such expansion occurs only in dilute electrolyte solutions, in contrast to the effect of concentrated solutions which would shrink the thickness of the DDL and so inhibit dispersion. Stable dispersions are formed, particularly where the solution pH exceeds the isoelectric pH of the mineral, which is often at alkali pH values, so that both basal face and edge surfaces are negatively charged and the particles repel each other. The osmotic swelling of smectitic clays to a gel-like form, so effectively blocking pores *in situ*, is often invoked as an explanation of formation damage in reservoir sandstones. Such swelling certainly occurs in dilute aqueous solutions under earth surface conditions but it is uncertain that stable smectitic gels could form at the temperatures and pressures associated with deeply buried reservoir sandstones.

THE EFFECT OF ALUMINATION PROCESS ON SURFACE ACIDITY OF PCH STRUCTURES DERIVED FROM LAPONITE

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In contrast to purely siliceous mesoporous supports, which have to be functionalized in order to develop desired properties, PCHs represent intrinsically acidic materials. This is due to the existence of layer charge in the clay component and the need for its compensation. Replacement of inorganic interlayer cations by organic cations in the first stage of synthesis, followed by calcination and thus by destruction of organic surfactant, leaves protons as the only species available for neutralization of the clay layer charge.

Our work was focused on the possibility of further enhancement of PCH acidity via doping of Si-network with Al. In particular, the effect of the Si:Al ratio and the type of Al source were investigated. Al-containing PCH (Si/Al=40 and 10) were synthesised from Laponite via post-synthesis alumination using aluminium isopropoxide or nitrate as Al sources. Textural analysis revealed that alumination had a significant impact on the final porous characteristics, and led to the decrease of both the specific surface area and the total pore volume.

All applied methods of PCH alumination resulted in Al incorporation into the mesoporous silica framework. In samples with Si/Al=40, 27Al MAS NMR analysis showed the presence of tetrahedrally coordinated Al species, which confirmed the occurrence of Al for Si substitution. In materials with Si/Al=10, both tetrahedrally and octahedrally coordinated Al sites were observed, indicating that a certain amount of Al remained in the extra-lattice positions. Substitution of Al for Si in the tetrahedral positions represents potential source of Brønsted acidity. On other hand, Lewis acid sites could be developed due the presence of unsaturated Al-sites on the surface.

The in situ FTIR study using pyridine as a probe molecule as well as the TPD of ammonia were engaged to estimate the acidity of the synthesized PCH materials. The content and the strength of acid sites increased with increasing amount of aluminium used for preparation of the samples. The use of aluminium nitrate as Al source resulted in a higher overall acidity and higher amount of Brønsted sites than in the case of aluminium isopropoxide. Lewis acid sites most likely associated with the presence of unsaturated extra-lattice Al-sites were detected on the surface of all samples.

Acid/base properties of the samples were also assessed by the catalytic dehydration of ethanol. On all aluminated samples catalytic decomposition of ethanol proceeded via two reaction pathways: dehydration to ethylene catalyzed by acid sites (major) and dehydrogenation to acetaldehyde, occurring on basic centres (minor).

Teaching of clay science

Oral presentation

WHY DO WE NEED ELECTRON CRYSTALLOGRAPHY IN CLAY MINERALOGY? CASE STUDIES.

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Structure determination of a clay particle is challenging due to their size, disordered character, varying water content etc.. Recent electron crystallographic methods provide promising approaches to characterize crystal structures.

One of a pioneer method in structure determination is the so called Patterson-method, (Patterson, 1934; Patterson, 1935). In spite of its simplicity and effectiveness, it went out of interest, but has reborn today. Comparing to other methods, its great advantage is that there is no need for phase values in structure reconstructions. However, resulted Patterson-maps for unit cells with large numbers of atoms still remain unresolved.

We measured [001] projected synthetic illite crystals comparing their experimental electron-diffraction based Patterson-maps to the corresponding simulated ones. A Patterson-map provides solid evidence for identification of a given polytype.

High resolution transmission electron microscopy (HRTEM) is another effective way of structural study of clays. In reconstruction of density map of a single clay particle based on its HRTEM images using Crystallographic Image Processing (CRISP, Hovmöller,1992) proved to be efficient. We can retrieve phase value of reflections applying the CRISP.

The recently developed precession electron diffraction technique (PED, Vincent and Midgley, 1994; Own, 2005; Avilov *et al.*, 2007) and the electron-diffraction tomography (Kolb *et al.*, 2007, 2008) gave opportunity for structure determination of nano single crystals based on experimental "quasi-kinematical" diffraction intensity data sets. We determined crystal structures of single crystal kaolinite (Mád, NE Hungary), celadonite/glauconite (Úrkút, Bakony Mts., Hungary), as well as the same illite that was studied by Patterson method using PED+DT techniques in SHELX97 (Sheldrick, 2008) and SIR2008 (Burla *et al.*, 2007) and SIR 2011 (Burla *et al.*, 2012) software packages.

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CLAY MINERALOGY IN SOIL SCIENCE

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In soils clay minerals have been studied over some decades that have been summarized in the set of monographs (J.B. Dixon and S.B. Weed (Ed.), 1989; B. Dixon and, D.G. Schulze (Ed.), 2002; B. Velde and A. Meunier, 2008; et al.). Location of clay minerals in the texture fractions that are the most sensitive to pedogenesis due to their size makes importance of mineral composition knowledge for the set of questions: (i) mineralogical provinces and source areas of parent material and their influence to soil diversity coupled with bioclimatic conditions and geomorphology; (ii) "rock control" of soil morphology and soil formation; (iii) affect of allochthonous or inherited material the soil properties such as chemical composition, pH value, cation exchange capacity; (iv) weathering rates and transformation of inherited minerals in a soil profile, and recognition of composition of transformation phases, the latter is especially important for the differentiated profile such as Podzols where mineral composition of the upper horizons differ from the bottom ones by the appearance of swelling mineral(s); (v) estimation the source and availability of nutrients released from primary minerals to ecosystem due to weathering; (vi) prognosis of landscape evolution and soil features related to the changes of mineral association resulted from soil development; (vii) the susceptibility of the fresh rock (parent substrate and gravel fragments in profile) to weathering, especially in the case of permafrost affected soils, where physical breakdown and producing fresh mineral surfaces are highly susceptible for chemical weathering. The mentioned items of fundamental soil science are not a full list that could be investigated based on the data of the clay mineralogy. Nevertheless the identification of clay minerals in soil profile is complicated by their poor crystallinity, presence of some clay minerals that are characterized by similar identification characteristics, and occurrence of mixed layered and individual minerals in the same samples. Sometimes it is impossible to use the standards approaches for phyllosilicates recognition such as (i) di- and trioctahedral nature of minerals on the base of 060 reflex by X-ray diffraction data in the presence of quarts, or (ii) mixed layered illite-smectite with different content of smectite layers and individual smectite. Those topics and examples are planning to illustrate in the

Clays in absorption and intercalation processes

Oral presentation

ADSORPTIVE REMOVAL OF AROMATIC COMPOUND BY MONTMORILLONITE: APPLICATION OF FACTORIAL DESIGN ANALYSIS

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Phenolic compounds are common pollutants found particularly in the effluents from petroleum and petrochemical, coal conversion, and phenol producing industries. Due to their toxicity and carcinogenity, water and wastewater containing phenolic compounds must be treated before being used and discharged to receiving water bodies. There is a growing interest in using low-cost and commercially available materials for the adsorption of organic compounds. Clay minerals have great potential as inexpensive and efficient sorbents which can be used as alternative adsorbents to replace the costly activated carbon. They are widely applied in many fields of adsorption technology including the removal of amines, metals, ketones, phosphates, chlorophyll, non-ionic contaminants, and organic pigments/dyes. Montmorillonitic smectites, $\{(Na,Ca)_{0.33}(Al,Mg)_2(Si_4O_{10})\text{-}(OH)_2.nH_2O\}$ are one of the natural clay minerals that has specific surface chemical properties. In this study, a factorial experimental design technique was used to investigate the adsorption of phenol from water solution on montmorillonite. Factorial design of experiments is employed to study the effect of three factors pH (2 and 8), montmorillonite dosage (0.1 and 1.0 g/L) and initial concentration (10 and 100 mg/L) at the levels low and high. The efficiency of phenol adsorption was determined after 60 min of treatment. Main effects and interaction effects of three factors were analyzed using statistical techniques. A regression model suggested and it was found to fit the experimental data very well. The results were analyzed statistically using the Student's *t*-test, analysis of variance, *F*-test and lack of fit to define most important process variables affecting the percentage phenol adsorption.

ADSORPTION OF REACTIVE YELLOW 18 DYE FROM WASTEWATER USING FOUNDRY SAND WITH BENTONITE

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Textile industry includes high dirtiness, wastewater amount, and dyestuff dissolved. Because textile industry consists of very different processes. Textile wastewater can be diminished the level wanted with the physical, biological and chemical methods. One of the methods used for removal of clour from wastewater of textile industry is adsorption process. Adsorbent substance which is used the most because of high fertility in the adsorption is active carbon. Although the fertility of active carbon is high, being high of its cost causes to research cheaper adsorbents. Recently, using more economical substances in adsorption of dyestuff is common. Materials such as volatile ash, natural clay, apricot seed, walnut cover, sepiolit and zeolit were used as adsorbent in the experimental studies. Being cheapand gainful of these made attractive using in dyestuff removal in the economical way.

In this study, it is aimed that removal of reactive yellow 18 dyestuffs will be provided with adsorption method by using foundry sand with bentonite. The effects of contact time, adsorbent amount, pH, temperature and initial dye concentration were investigated. The adsorption isotherm and kinetics of the activated almond shell were studied.

INTERCALATION AND RETENTION OF CARBON DIOXIDE IN SYNTHETIC FLUOROHECTORITE CLAY AT NEAR-AMBIENT CONDITIONS

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We show using synchrotron as well as in-house X-ray diffraction methods that gaseous CO_2 intercalates into the interlayer space of the synthetic smectite clay fluorohectorite at conditions close to ambient. The rate of intercalation is found to be dependent on the interlayer cation (Li^+ or Na^+ in this case), with about one order of magnitude increased rate in Li-fluorohectorite compared to Na-fluorohectorite. We further show that Li fluorohectorite is able to retain CO_2 in the interlayer space at room temperature, which could have applications related to CO_2 capture, transport and storage. The CO_2 release starts occurring at temperatures exceeding 30 °C.

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MODIFIED KAOLINITES AND HALLOYSITE WITH ANION SORPTION PROPERTIES

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Kaolinite and halloysite are classified as 1:1 layered, dioctahedral polytypes which belong to the kaolin group minerals. The anion sorption on natural kaolin minerals takes place to a very small extent due to lack of centers which could attract anionic species. Thus their use for remediation purposes requires modification. In this research a procedure used for a highly ordered kaolinite by Letaief et al. (2008) was tested for kaolin minerals differing in degree of structural order. The main objective was to examine how the type of the mineral affects the amount of generated positively charged centers (PCC) in the interlayer space.

Three types of minerals from Polish deposits, described in Matusik et al. (2011), were chosen with different Hickley index values (HI): M - Maria III kaolinite (HI = 1.31), J - Jaroszów kaolinite (HI = 0.22), and H - Dunino halloysite (HI = 0.33). First, the M, J, and H were reacted with dimethyl sulphoxide (DMSO) to form pre-intercalates (MDS, JDS, and HDS). In the second step the MDS, JDS, and HDS were grafted using triethanolamine (TEA) (MT, JT, and HT) and finally a methylation of the water washed grafted complexes was carried out using iodomethane (CH_3I) (MTM, JTM, and HTM).

The XRD patterns of the MDS, JDS, and HDS revealed a 11.2 Å peak which confirmed the formation of the DMSO precursors. The d_{001} values of the grafted complexes MT, JT, and HT, washed with isopropanol after the reaction, were equal to ~11.3 Å. Further washing with water removed the remnants of the intercalated TEA and DMSO leaving only grafted TEA in the interlayer space. This led to a decrease of the d_{001} value to ~10.7 Å. Simultaneously a decrease of an intensity of the C-H stretching bands assigned to TEA as well as the disappearance of the bands attributed to DMSO in the IR spectra was observed. The decomposition of the complexes took place above boiling point of the TEA (190° C) in the temperature range of 260-370°C indicating successful grafting. After methylation the d_{001} values of the MTM, JTM, and HTM materials increased to 11.2 Å, 10.9 Å, and 10.8 Å, respectively. The attachment of CH_3 group to TEA nitrogen which induced the PCC generation was confirmed by FTIR and ^{13}C CP-MAS NMR. The amount of the PCC, estimated using CHNS analysis, increased with the increase of the minerals structural order. Preliminary sorption tests showed that the access of anions to the PCC is sterically possible. The future research will focus on the nanomaterials sorption properties towards selected anionic species of toxic elements e.g. chromates and arsenates.

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OXIDATION MODES OF GREEN RUSTS: THE KEY FOR PHOSPHATE REMOVAL?

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Phosphorus, which is an essential nutrient in nature for plants and living organisms, can cause eutrophication when significant quantities are present in water. The example of the bluish-green algae proliferation in Brittany (France) shows that phosphate (often combined with nitrate) removal methods have to be improved. The use of iron oxides, removing phosphate by an adsorption mechanism, is known to be a promising process.

The oxidation modes of Fe^{II-III} hydroxycarbonate green rust $GR(CO_3^{2-})$, $Fe^{II}_4Fe^{III}_2(OH)_{12}CO_3{\bullet}3H_2O$, are investigated to obtain a more stable phase. Indeed, due to its relative instability in anoxic condition, $GR(CO_3^{2-})$ may not be the most suitable material for water treatment applications. With low flow of oxygen bubbled in aqueous solution, goethite α-FeOOH forms by dissolution-precipitation mechanism whereas a mixture of non-stoichiometric magnetite $Fe_{(3-x)}O_4$ and goethite is observed for the slowest oxidation rates. On the other hand, rapid oxidation, with either H_2O_2 or dissolved oxygen under neutral and alkaline conditions, leads to the formation of ferric oxyhydroxycarbonate $GR(CO_3^{2-})^*$, $Fe^{III}_6O_{12}H_8CO_3{\bullet}3H_2O$, via a solid-state reaction. Its structure is strongly similar to that of $GR(CO_3^{2-})$ which belongs to the layered double hydroxide (LDH) family. The violent oxydation causes an *in situ* deprotonation of some OH^- ions without destroying the hexagonal crystals shape and by keeping CO_3^{2-} ions in the interlayers. Furthermore, by varying two different synthesis parameters, *i.e.* i) the aging period after the coprecipitation step to obtain $GR(CO_3^{2-})$ and ii) the H_2O_2 addition time, it is possible to control physico-chemical parameters such as the size, the morphology and the cristallinity of ferric green rust.

$GR(CO_3^{2-})^*$ adsorption efficiency for phosphate removal from aqueous solution is then studied. In all phosphate adsorption experiments, the removal effectiveness is enhanced for compounds displaying low cristallinity and high specific surface area. Analysis of kinetic data shows that the uptake of phosphate by ferric green rust followed a pseudo-second order model. Equilibrium adsorption data obey Freundlich isotherm. The phosphate removal by ferric green rust is moreover highly pH dependent and the maximal uptake is 64.8 mg g^{-1} at pH = 4, but still shows interesting values at higher pH. In summary, it is demonstrated that poorly crystallized ferric green rust should be a cost-effective adsorbent for phosphate removal from wastewater.

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METHYLENE BLUE AND ORANGE II REMOVAL BY KAOLIN AND METAKAOLIN: ABSORPTION AND PHOTOCATALYTIC ACTIVITY

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The environmental impact of dyes on natural soils is considered as a serious hazard when released by several painting and coloring industries and recent trials are conducted to minimize or neutralize them. This study investigated the removal of Methylene Blue and Orange II dyes from synthetic wastewater by the adsorption and photocatalysis by natural and commercial kaolin based materials.

As adsorbents we used a natural Kaolin (collected at Barracão region, Portugal), from Pliocene age, labeled K1, and a commercial one (VWR Prolabo, Belgium), labeled K2. As photocatalyst, we used TiO_2 (commercial, Degussa P25). Methylene blue MB (commercial, USA) was our cationic dye, whereas Orange II OII (commercial, China) was the anionic one.

For adsortion experiments, we used 0.5 g of both kaolins, 100 ml dye solutions with concentrations ranging from 50 to 200 ppm, time of adsorption ranging up to 120 min, and a UV-VIS spectrophotometer. For photocatalysis experiments, we used 0.25 mg of TiO_2+K1 or K2 (100/0; 50/50; 20/80), 500 ml of dye solution (c 10 ppm), time of photocatalysis ranging up to 300 min, and a UV-VIS spectrophotometer.

Kaolinitic clays show more efficiency to adsorb cationic dye (MB) than anionic dye (OII). In MB degradation under UV irradiation, the combined action of adsorption and photocatalysis give high efficiency in both kaolins. For OII performance of dyes, degradation differs with the used ratio of TiO_2, however even with just 20 %f TiO_2, degradation is up to 60 % (for K1). Kaolinitic clay from Barracão region gives optimal results comparable to the commercial kaolin.

In conclusion, the adsorption process was efficient with retention of practically 100 % of both dyes when untreated kaolin clays are used. On the other hand, when combined with P25 TiO_2 or just pillared ($TiCl_4$ suspension), the kaolin and metakaolin substrate showed a dye photodegradation superior to 20 %.

On-going research is focused on: 1) preparation of pillared TiO_2-clays using Ti sol-gel, 2) titration to clay suspension for photocatalysis purposes, 3) improve photocatalytic activity of some dyes.

EFFECT OF ACID TREATMENT ON THE ORGANO-MONTMORILLONITE STRUCTURE

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Modification of the clay mineral surface with quaternary alkylammonium cations results in a hybrid inorganic/organic material with properties considerably different from unmodified sample. The stability of organo-montmorillonites in 6 M HCl was examined and the effect of organic cation size on clay mineral decomposition was evaluated. The samples were prepared from Ca-SAz montmorillonite and tetrabutylammonium (4C4N+) or tetrapentylammonium (4C5N+) salts. Ca-SAz and organo-modified montmorillonites were treated with HCl for various time and the changes in the solid reaction products were evaluated by different methods. The 27Al MAS NMR spectra revealed gradual decrease of the intensity of the resonance peak ~ 4 ppm assigned to aluminium in octahedral coordination. After 8 h of treatment this peak almost completely disappeared from the spectrum of Ca-SAz-1. In contrast, spectra of both organo-montmorillonites unambiguously confirmed the presence of un-leached octahedral aluminium. Quantitative evaluation of the Al content based on NMR measurement showed that more than one half of Al remained in the solid reaction products of 4C4N-SAz and 4C5N-SAz after 8 h treatment, while Al content dropped below 5 % for Ca-SAz. Presence of *d*(001) diffraction in the XRD pattern of 4C4N-SAz and 4C5N-SAz confirmed that long-range ordering is still preserved in 8 h treated samples. These results prove that bulky alkylammonium cations covering the inner and outer surfaces of montmorillonite prevent effectively the access of protons to the layers protecting the mineral from degradation in the acid. Formation of acid sites during HCl treatment was investigated via pyridine adsorption. The IR bands of pyridine adsorbed on acid-treated samples confirmed the presence of both, Brőnsted and Lewis acid sites. These sites resist even heating of the samples at 200° C. For Ca-SAz the strength of acid sites decreased with increasing time of acid treatment, most probably due to significant destruction of the layers. On contrary, clearly visible absorption bands of pyridine of higher intensities compare to Ca-SAz were observed in the spectrum of 4C4N-SAz after same time of treatment. The results revealed that prepared organo-montmorillonites belong to materials with combined functionalities, hydrophobicity imparted by organic cations on one side and acidic properties evoked due to acid treatment providing formation of possible active sites.

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INTERACTION MECHANISM OF DISPERSING SOIL CONDITIONERS AND NEW ANTI-STICKING CHEMICALS FOR TUNNELLING APPLICATION IN SOFT SOILS

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Earth Pressure Balance Machine (EPBM) tunnelling is often a preferred excavation metod for tunnels in difficult ground conditions, e.g. in soft soils below the ground water table. This method uses the excavated soil to support the tunnel face. In clay soils it requires the injection of water and chemical additives for creation of a homogenous soil paste and prevention of clogging problems. The efficiency of the used chemicals can, however, vary to a large extent. The detailed interaction mechanisms between clays and chemicals are not understood in detail, creating a source of uncertainty for their application.

Presented here detailed analysis of the mechanical behaviour of different conditioned clay mixtures is based on newly developed methods for shear strength, adhesion and stickiness measurements. This laboratory analysis reveals important information about the working predominant mechanisms and confirms the strong dependency of their efficiency on the type of clay minerals. In the case of kaolin the mixture behaviour changes drastically into a viscoelastic paste with solid and fluid properties adding dispersing polymers. In contrast, for illite and bentonite, the influence is limited to a strength reduction only. The detected effect results from the reduced attraction forces between the clay particles and depends on the polymer concentration, but not on the chain length of the polymer. Adsorption measurements show a very low amount of adsorbed polymer. The reduced forces are mainly based on ion exchanges between clay particles and chemicals and edge charge neutralization. This in turn provokes reduced electrostatic attraction forces directly between the particles but also between the charged surfaces and the hydrated ions, leading to the enhanced particle lubrication.

This mechanism is also responsible for a reduced tangential adhesion between the soft clay pastes and steel surfaces. The clogging or stickiness potential however can only be lowered to a limited extent. To overcome this, a group of newly patented chemicals was proposed leading to a much more efficient reduction of the clogging potential. This dramatic antisticking effect is rooted in a different interaction mechanism based on chemical adsorption and sealing of the clay aggregates, protecting them from the entering water. The water is hold in thick films at the surface around the aggregates. The introduced chemicals show a drastic stickiness reduction over a large range of water content especially for the problematic illite and bentonite clays.

DIPOLAR ORDERING OF CLAY PARTICLES IN VARIOUS CARRIER FLUIDS

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We report here examples of complexity in composite materials. The objective of this work is to show that clay particles can be aligned in different hosting media, such as: silicone oil, paraffin-wax, polystyrene and ambient air. Clay particles are ideal for this purpose due to their inherent large anisotropy and correspondingly high degree of polarizability. When placed in an apolar medium and subjected to an electric field, the particles will orient and organize within a time frame that depends principally on factors such as *E*-field strength and viscosity of the surrounding medium. The particles may form chains that span the entire sample length, thus changing the macroscopic properties of the material. Most notably, there will generally be a large change in the overall rheological behavior, and materials of this kind are therefore highly interesting for applications where the mechanical and structural properties should be manipulated via an electric field. Some of the studies may have an application-oriented character. However, the focus of our research is aimed at better understanding of basic physics of such complex systems. Apart from the already mentioned fluid hosting media, we also here report for the first time structuring from clays in atmospheric air. The common denominator, for all studied systems, is the clay particle alignment in the presence of an *E*-field.

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ADSORPTION OF POLYACRYLAMIDE ON BENTONITE

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The interactions of bentonite with polyacrylamide underlie~~s~~ a wide variety of applications including drilling fluids, water treatment. Modification of bentonites with polyacrylamide provides a material suitable for use as backfill and waterproofing materials.

The study of interactions of polymer with bentonite was carried out by IR spectroscopy, X-ray diffraction. Bentonite from Cherkassy deposit was used for experiments. Bentonite is composed of Ca-montmorillonite (80%) and admixtures of quartz, calcite, feldspar and accessory minerals (rutile, anatase, etc.). Cationic, anionic and nonionic polyacrylamides with molecular weight of $10 – 23\cdot10^6$ and hydrolysis degree of 30 – 39 were used for the study.

X-ray diffraction showed that for the polymer concentration lower than 5% the penetration of polyacrylamide chains in the interlayer space of montmorillonite did not occur. Adsorption of the polymer occurred only on the external surface of montmorillonite crystals.

The results suggest that bentonite in aqueous solution of cationic polyacrylamide formed surface organic-mineral compounds due to the interactions of negatively charged sites of montmorillonite with positively charged sites of polyacrylamide chains. In addition, the interactions of polymer with montmorillonite may be caused by hydrogen bonding between the carbonyl groups of the polymer and corresponding sites on the surface of montmorillonite crystal.

Adsorption of anionic polyacrylamide on montmorillonite surface occurs mainly due to formation of hydrogen bonds between carbonyl and hydroxyl groups of the polymer and the corresponding active sites of the surface of montmorillonite crystals: Si-O-Si, Si-OH, and Al-OH. Probably, there are also interactions between the amino groups of the polymer and O-sites of montmorillonite with formation of electrovalent bonds. However, such interactions are of minor importance.

Adsorption of nonionic polyacrylamide on montmorillonite is mainly caused by formation of hydrogen bonds between carbonyl and hydroxyl groups of the polymer and corresponding sites of the montmorillonite surface.

The adsorption of polymer on the clay is significantly affected by the content of electrolytes in the solution. The adsorption significantly increases with increase of ionic strength of the solution. With a higher molecular weight of polyacrylamide the amount of adsorbed polymer decreased. It should be noted that the interactions of montmorillonite with cationic polyacrylamide were stronger than in case of anionic and nonionic polymer.

Key words: bentonite, polyacrylamide, adsorption.

ADSORPTION CHARACTERISTICS OF MONTMORILLONITE-PALYGORSKITE CLAYS FROM DASHKOSKOYE DEPOSIT (MOSCOW REGION)

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This work is based on the study of clays, formed in the Steshevskoe chron (Serpukhovian stage of the late Mississippian). These clays are used in industry as the main component of drilling mud, some building materials and as sorbents in pharmacological and chemical industries.

The aim of this work is to study particularities of composition and structure of montmorillonite-palygorskite clays and their influence on different adsorption characteristics.

Clay samples were obtained from lithological sections near the Serpukhov (Moscow region) and Kaluga. Studied horizons are represented by interbedded bentonites, palygorskite clays and thin layers of dolomite.

The composition of samples have been investigated by x-ray diffraction, x-ray fluorescence, middle- and near infrared spectroscopy. Texture and structure features have been investigated by grain size analysis and scanning electron microscopy. Adsorption properties were characterized by 1) cation exchange capacity determination by several methods, 2) kinetics of water vapor adsorption, 3) Cs^+ adsorption from solution in static conditions, 4) kinetics of methylene blue (MB) adsorption

XRD quantitative analysis showed that all the obtained samples consist of dioctahedral palygorskite and montmorillonite, calcite, dolomite and quartz at various ratios. Thus three samples which contain less impurities and contain montmorillonite in different ratios were selected for further detail study.

Experiments showed different activity of palygorskite and montmorillonite in presence of different adsorbates. It was figured out that palygorskite-rich samples demonstrate bigger specific surface, carried out by N_2 and H_2O adsorption, while adsorption characteristics in cases of different cations (MB, $[Cu(Trien)]^{2+}$, Cs^+) are lower and vice versa for montmorillonite-rich samples. In the process of study of water vapor adsorption kinetics 3 processes of a different duration and intensity were identified and distinguished..

Identification of clay minerals

Oral presentation

SELECTIVE AND SENSITIVE DETECTION OF SMECTITES IN AQUEOUS COLLOIDS BELOW PPM CONCENTRATION

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Analysis of the specimens with low smectite fractions using conventional methods is often very problematic. Until now, there has been no simple method for the detection of smectites at extremely low concentrations in aqueous colloids.

The method for a sensitive detection of smectites presented in this work is based on using organic dyes (methylene blue and rhodamine 6G) as molecular sensors. The dye molecules adsorbed on colloid particles of smectites form molecular assemblies, which exhibit spectral properties significantly different from those present in dye solutions (phenomenon called metachromasy). The sensitivity is limited by absorptivity of used dyes in a visible region, and, in some cases, can further be increased using the signals from a second derivative spectroscopy. Our method is able to detect smectites in the colloids at around ppm concentrations.

Spectrophotometric titrations provide the most sensitive way to estimate quantitatively the amount of smectite. The endpoint of the spectrophotometric titrations relates to the cation exchange capacity (CEC) of an analyzed sample. If CEC is known or could be estimated with a sufficient accuracy, the method can be used for a rough quantitative analysis. Metachromasy is selective only to expandable clays, which was proven by the experiments with various clay minerals. Spectra of dye molecular assemblies may provide information about the properties (layer charge) of smectites.

Spectrophotometric titrations using dye molecular sensors are cheap and efficient analytical method having a promising future in the analysis of industrial specimens, soils, clays and aquatic systems, etc. They are applicable in various scientific and industrial fields. The application of the spectrophotometric titrations using dye sensors may also expand to the analysis of other nanomaterials which are able to induce dye metachromasy.

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ROLE OF CLAY MINERALS IN FORMATION DAMAGE

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Clay minerals are of great importance for reservoir geology. The interaction of clay minerals, especially of swelling clays, with aqueous solutions and the fines migration are the primary culprit for the damage of petroleum-bearing formations. Usually sandstones have large quantities of authigenic pore filling clays sensitive to aqueous solutions, such as smectite, kaolinite, illite, chlorite and mixed-layer clay minerals. X-ray powder diffraction is an essential and widely used tool for the analysis of clays and for the mineralogical composition of rocks. Many aspects of clay mineral identification, such as interstratification of two or more types are not readily accessible by any other technique. The study of clay minerals from the point of view of formation damage is always more fruitful when complementary techniques are used. Scanning electron microscopy is applied for identification of textural relationships and the morphology of clay minerals present in the rocks. The detrital clays are of interest from the point of view of mechanical formation damage because they usually form the skeleton of the porous matrix. The authigenic clays are loosely attached to the pore surface and they are mostly important from the point of view of chemical and physico-chemical formation damage.

During core flow studies (using representative core plugs) changes appear in the rock structure. We analyzed these rock plugs before and after acidation and after the treatment of plugs with water and potassium salt saturated water. The paper gives an overview of clay identification and presents the changes which have been appeared after wettability and acidation tests.

SYNTHESIS OF WELL CRYSTALLIZED A-TYPE ZEOLITE FROM MIXED SAMPLE OF FLY ASH AND KAOLINITE

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Zeolites are hydrated aluminosilicate minerals that can be synthesized using several source materials such as fly ash and kaolinite. Fly ash has been used in zeolite synthesis through a variety of methods, including hydrothermal reaction with fusion pretreatment. The use of kaolinite required calcination at high temperature (600-1000° C) before the conventional hydrothermal process in an alkaline solution. Only more recently a hydrothermal method based on the pre-fusion treatment with alkali has been considered. At low incubation temperature, zeolite X represents the stable zeolite synthesized from fly ash whereas A-type zeolite is the most common zeolite formed from kaolinite.

In this study samples of: i) fly ash, ii) poorly crystalline kaolinite and iii) mixture of both materials (1:1 weight ratio) were used to synthesize zeolite by hydrothermal activation with pre-fusion treatment at low incubation temperature (45 and 60° C) in distilled water. The fly ash used (F1) comes from an Italian thermoelectric powder plant whereas the kaolinite is from the Source Clay Repository of The Clay Minerals Society (KGa-2). The products of the synthesis were characterized by X-ray powder diffraction (XRD) and scanning electron microscopy (SEM).

XRD patterns of F1 and KGa-2 showed the presence of X-type and A-type zeolite, respectively whereas the XRD profile of F1+KGa-2 mixture indicated the main presence of A-type zeolite. SEM images showed the typical octahedral crystals of zeolite X (as the result of F1 incubation) and the cubic morphology of A-type zeolite (as the product of synthesis of KGa-2 and F1 + KGa-2 mixture). The data obtained clearly indicate that Si/Al ratio is a critical parameter in the zeolite crystallization from fly ash. Adding variable amount of pure kaolinite, the Si/Al ratio of the new source material changes thus controlling the type and the amount of zeolite formed. These results are particularly attractive because they show an advantageous method to improve the application field of a waste material (fly ash) and to reduce the exploitation of a mineral (kaolinite).

QUANTIFICATION OF KAOLINITE IN IRON ORES BY X-RAY POWDER DIFFRACTION AND THE RIETVELD METHOD

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The knowledge of mineral composition of ores, processing products and tailings is essential for the optimization of technologies and the optimum use of the value of deposits. In the case of iron ores, the presence of different iron oxides/-hydroxides together with fine-grained components like clays prohibits the application of traditional microscopy as well as any electron microscopy for mineral quantification. Thus, X-ray powder diffraction may be the method of choice. On the other hand, methodic problems like microabsorption, extreme peak overlap, and disorder of clay minerals must be overcome for establishing a user-independently working method.

The presentation shows (i) the influence and optimization of sample preparation and measurement, (ii) the treatment of disorder features of kaolinite, and (iii) the optimization of profile models for iron ore minerals. Mineralogical analysis of size fractions of special ore types was performed for estimating the compositional range for routine quantification and for structural characterization of the dominating minerals. Especially, several models for disorder in layer stacking have been tested to be able to describe correctly the diffraction patterns of kaolinite present in iron ores. About 10-12 min milling of 3-4 g material with 10 ml ethanol in a McCrone micronising mill was found to give a reliable particle size distribution with acceptable peak broadening for iron oxides. Artificial mixtures representing extreme compositions of different ore types and products were prepared from pure minerals. Measurements were performed with Co-radiation and different instrumental settings (fixed and theta-compensating slits, secondary beam monochromator with proportional counter and Si-strip detector with Fe filter). The most reliable and stable structure model for kaolinite consists in a summation of a b-axis disordered and an ideal structure. Disorder in kaolinite was described by the recursive method (Treacy et al., 1991) integrated in the structure description language of the BGMN Rietveld software (Ufer et al., 2008). Hematite, magnetite and goethite tend to anisotropic or sometimes bimodal line broadening what may be described successfully by the standard tools of the BGMN software. Mineral abundances in the reference mixtures could be reproduced within ± 1wt% (absolute) for two instruments by automatic Rietveld refinement. More precise and accurate results may be obtained by constraining of profile parameters but such constraints will limit the approach to a certain type of samples. However, adequate profile description and sample preparation are the key issues for accurate Rietveld phase quantification of iron ores.

^{7}Li, ^{27}Al AND ^{29}Si SOLID-STATE NUCLEAR MAGNETIC RESONANCE (NMR) SPECTROSCOPY OF DIOCTAHEDRAL SMECTITES

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Migration of interlayer cations into 2:1 layers upon heating has been studied by clay mineralogists since many years but structural changes are still controversially discussed (Heller-Kallai, 1995; Mosser et al., 1997; Theng et al., 1997; Madejova, 2006). Therefore we studied five dioctahedral smectites that differed mainly in layer charge, tetrahedral charge and iron content. Smectites were enriched from bentonites by separation of the < 2 µm fraction. After that the smectites were homoionically exchanged with Li^+ and then annealed at several temperatures (110° C, 150° C, 200° C and 300° C).

The structural formula of the five smectites were calculated according to Köster (1977) using chemical data from X-ray fluorescence analysis and layer charge.

Solid state nuclear magnetic resonance spectroscopy (NMR) of ^{7}Li, ^{27}Al, and ^{29}Si was used to characterize the chemical environment within the smectite structure. NMR in combination with Mössbauer spectroscopy, that was used to investigate the chemical environment of iron in more detail, were used to improve the structural formula with respect to portion of Al and Fe in the 2:1 layers.

In all five smectites ^{7}Li-NMR measurements indicate changes in the chemical environment of Li with heat treatment. The environment of the Li atoms is more paramagnetic with increasing temperature, which means, that Fe atoms were closely connected to Li after heat treatment. ^{29}Si-NMR measurements showed either one or two environments for Si ($Si(Si_3)$; $Si_3(Al)$), while ^{27}Al-NMR measurements showed two environments for Al (octahedral Al and tetrahedral Al). Tetrahedral Al decreased partially with increasing heating temperature. Furthermore the NMR measurements indicate changes in the ordering after heating.

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RIETVELD REFINEMENT OF DISORDERED ILLITE-SMECTITE MIXED LAYERED STRUCTURES ON SIMULATED ONEDIMENSIONAL PATTERNS

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The identification and the structural characterization of clay minerals is an important tool for the interpretation of diagenetic or hydrothermal processes for example. Most analytical techniques are based on X-ray diffraction measurements. Layer silicates show similar patrice constants in a and b direction, but clearly distinguishable differences in c direction. The preparation technique of the clay minerals as oriented mounts is widely used due to this. It pronounces the diagnostic basal reflections and suppresses the non-basal reflections. One way to extract structural information from these patterns is the comparison with calculated patterns using software codes like for example Newmod (Reynolds, 1985). It was shown recently that the Rietveld method in combination with a recursive calculation of structure factors is capable to refine structural parameters of stacking disordered structures (Ufer et al., 2008). The Rietveld method normally uses data from powder diffraction measurements of non- or weakly oriented mounts. It can also be adapted as well to measurements of oriented mounts. The applicability of the Rietveld method to fit basal patterns of disordered stackings is demonstrated by the refinement of simulated data. The DIFFaX code (Treacy et al., 1991) was used to simulate patterns of I-S with different ratios of illitic and smectitic layers and with different degree of long range ordering. Data of monomineralic samples and mixtures were refined with different structural models and different starting situations. The results of these refinements were evaluated in order to demonstrate the possibilities and the limitations of this approach.

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Applications of clays (ceramics, agriculture, building industry, pharmaceutical, polymer industry, …)

Poster presentation

CORDIERITE CERAMICS WITH FUNCTIONAL ADDITIVES

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Cordierite, with formula $2MgO.2Al_2O_3.5SiO_2$, is one of the phases of the MgO-SiO_2-Al_2O_3 system. The conventional methods for the synthesis of the cordierite based ceramic include the solid-state sintering of individual oxides of magnesium, aluminium and silicon of the corresponding chemical composition of cordierite. Cordierite ceramics were prepared also from the mixtures of natural clay minerals, fly ash, technical silica and feldspar. Sintering of cordierite processed under thermal treatments between 1250 and 1350 °C. Technological and mechanical properties of cordierite ceramics are direct function of their structure despite the fact that a very narrow interval of cordierite ceramics sintering practically disables to obtain dense structure. Nevertheless, cordierite compound is a ceramic material technologically applied in many fields due to its extraordinary properties, such as its low thermal expansion coefficient, low dielectric constant and high chemical resistivity.

The composition of mixtures as precursor of cordierite and functional additives modification can remarkably influence reactivity of the solid powders and final cordierite microstructure. Particularly, the mechanical treatment of solid powders is important since it can help to introduce changes in the texture and structure of the cordierite ceramics.

The aim of this work is to study the key role of carbon nanotube additives on the structural alteration of cordierite ceramics. Cordierite ceramic will be produced employing high temperature reaction in solid state of mixture consisting of kaolinite, vermiculite, talc, and alumina. The influence of different concentration of carbon nanotube additives on the ceramics grain size, microstructure and porosity will be studied.

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ANTIBACTERIAL PROPERTIES OF CU- AND ZN-EXCHANGED LAPONITES®

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The antibacterial properties of heavy metals are well documented (Lansdown, 2006; Hassen et al., 1998). The use of zinc, copper, and silver as antimicrobial agents in pharmaceutical applications has been somewhat limited. This is due to the large concentrations needed for there to be sufficient contact with the bacterial cell, as well as their reactivity with anions (most importantly chloride ions) in aqueous environments resulting in reduced antimicrobial effects. However, the absorptive properties (including bacterial cells and cell toxins) of clay minerals have been reported (Williams et al., 2008) and it is proposed that metal ion-exchanged clays enable direct contact between the metal ion and the bacterial cell. The combination of a hydrating gel-forming materials able to provide sustained control of bacterial ingression would be of great benefit in not only the pharmaceutical area but in a variety of other applications.

The aim of the present study was to prepare metal ion containing Laponites® and assess their antimicrobial activity.

The synthetic clay Laponite® FP, manufactured by Rockwood Additives Ltd. (Widnes, UK), was modified by ion-exchanging with $ZnSO_4$ and $CuSO_4$. Antimicrobial activity of the non-exchanged and both exchanged clays was assessed on two gram-negative strains (*Esherichia coli* and *Pseudomonas aeruginosa*), two gram-positive strains (*Staphylococcus aureus* and *Bacillus cereus*), as well as a methicillin-resistant *S. aureus* (MRSA) strain.

Growth of all strains was observed in the nutrient broth containing the non-exchanged Laponite® FP. Nonetheless, there was a concentration dependent reduction of growth noted. Introduction of metal ion-exchanged Laponite® FP to the culture broth in increasing concentrations had a markedly different effect on the growth of the tested strains compared to the non-modified clay material. The Cu-exchanged Laponite® FP had an improved antimicrobial activity compared to the Zn-exchanged equivalent for the gram-positive strains tested. On the contrary, the gram-negative strains tested seemed to be more susceptible to the presence of the Zn-exchanged Laponite® FP, with a significant reduction in growth observed at 2.5g/L for *E.coli* and 5g/L for *P.aeruginosa*. When the materials were tested on an MRSA strain it was observed that growth was affected by the presence of both the metal-exchanged clays tested.

There is growing interest in the application of clays in healthcare (Williams, et al., 2008; Carretero, 2007) and the potential of cost effective antimicrobial Laponites® should not be neglected. These results give promising indications that such materials may have applications in combating the multidrug-resistant strains, and further studies are planned to explore this.

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MONTMORILLONITE K-10 AND LAPONITE® COMPOSITES CONTAINING TETRACYCLINE AND CIPROFLOXACIN FOR DRUG DELIVERY

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Clays have negatively charged surfaces allowing the adsorption of cations. While other research teams have adsorbed drugs onto clays, few have investigated drug release or applied this to clinical problems (Parolo et al., 2010). This work examines the adsorption of two antibiotics onto different clays followed by the subsequent drug-release and antibacterial activity. The overarching view is to develop new ways of treating skin and soft-tissue infections.

Kaolin (KN), montmorillonite K-10 (MMTK10), and Laponite® RD (LRD) were dispersed in deionised water for two hours before solutions of ciprofloxacin (CIP) and tetracycline (TC) were added and mixed further. Drug adsorption and release was determined through UV-Vis spectrophotometry. Adsorption mechanism was determined through FT-IR spectroscopy and X-ray diffraction (XRD). Antimicrobial activity was measured on cultures of *Propionibacterium acnes* and *Staphylococcus epidermidis* utilising well-diffusion assays.

CIP and TC bound in their zwitterionic states (Wang et al., 2011; P-H. Chang et al., 2009) via positively charged amine groups as confirmed by FT-IR. Drug molecules were present within the interlayer spaces of the clays, indicated by an increase in $d_{\mathbf{001}}$ value on XRD spectra. KN adsorbed the least drug available due to its non-swelling nature; thus smaller surface area. Release of CIP and TC was retarded from the clay-drug composites. The strength of drug adsorption was shown through the low amount of drug released over time. LRD released the most TC but performed worse than MMTK10 in CIP release studies. Clay-CIP and clay-TC composites showed antimicrobial affects on *P. acnes* (Fig. 1) and *S. epidermidis*. The LRD-TC composite was the most potent against *P. acnes*. However, clay-TC composites were not very active against *S. epidermidis* due to bacterial resistance against tetracyclines.

Clay-antibiotic composites may therefore be candidates for new methods of topical drug delivery and the treatment of skin and soft tissue infections.

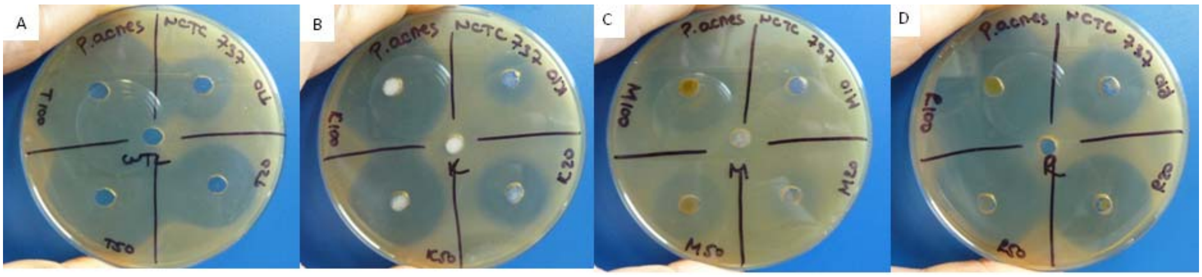

Fig 1. *P. acnes* cultures exposed to varying concentrations of (A) pure TC, (B) KN-TC composites, (C) MMTK10-TC composites, and (D) LRD-TC composites.

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SYNTHESIS OF SELECTED ORGANOCLAYS

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Montmorillonite, a natural mineral, is becoming widely used as an alternative material in areas where sorptive, catalytic and rheological applications are required. High ion exchange capacity and surface area and more importantly its relatively cheap price make it an attractive adsorbent. With a chemical modification, the inorganic exchangeable cations of clay can be replaced by organic alkylammonium cation (de Paiva et al., 2008) or associated by organic molecules containing alkyl groups and polyethylene oxide units (Guegan, 2010). By this way, the surface properties of the clay are changed from hydrophilic to increasingly hydrophobic. As a result, the modified organoclay becomes a powerful adsorbent for toxic organics.

Eight carefully selected organoclays from monoalkyl- to tetraalkylammonium type were prepared from a sodium-saturated fine fraction of Jelšový Potok bentonite (Slovakia). Four samples contained 1–4 octylammonium chains, from monooctylammonium (1C8) to tetraoctylammonium (4C8). Two cations had chains with 16 carbons each, hexadecylammonium(1C16) and dihexadecyldimethylammonium (2C16). Two cations contained a benzene ring, either without reactive bonds (benzyltrimethylammonium, C10) or with a double bond in 4-vinylbenzyl-trimethylammonium (C12). The d001 values depended on the size and structure of the organocation. The height of the interlayer space in the 1C8–4C8-Mt series increased from 0.45 to 1.68 nm. 2C8 cation opened the interlayer space more than 1C16; 2C16 was more effective than 4C8. Expansion of only 0.55 nm was obtained with C10 and C12. Mass losses between 150 and 800 °C in nitrogen flow were 13–38 % for 1C8–4C8-Mt and 40 % for 2C16-Mt. Infrared (IR) spectra were similar for 1C8–4C8-Mt but different for the samples with 16 C and 32 C atoms due to altered ratios of CH3 and CH2 groups. Downward shift of the CH2 stretching bands with increasing size of the alkylammonium cation suggest that alkyl chains adopt more ordered structure. The suitability of the prepared materials to be used as fillers for polymer nanocomposites will be tested.

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STRENGTH CHARACTERISTICS IMPROVEMENT OF BULGARIAN KAOLIN THROUGH BLENDING WITH BALL CLAY FOR USE IN THE MANUFACTURE OF PORCELAIN TABLEWARE

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It has been studied the possibility for improving the dry strength characteristics of a Bulgarian ceramic kaolin, manufactured by Kaolin AD, for use in the manufacture of porcelain tableware. For the purpose, the same is blended in 9:1 ratio with a local ball clay comprising smectite. The resulting product indicates a 3-fold growth in mechanical bending strength (3.1 MNm^{-2}), good chemical composition (SiO_2 - 50.50 %, Al_2O_3 - 34.81 %, Fe_2O_3 - 0.77 %, TiO_2 - 0.36 %, CaO - 0.19 %, MgO - 0.27 %, K_2O - 0.78 %, Na_2O - 0.15 %, L.o.i. - 12.05 %), a relatively good fired whiteness and rheological properties. The product's parameters are comparable with those of kaolins used in the production of porcelain tableware. Combining the kaolin and ball clay qualities, the novel product of Kaolin AD could find use in recipes for porcelain tableware reducing the necessity of ball clay in them.

INFRARED AND RAMAN SPECTROSCOPY OF ACID TREATED VERMICULITES

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Three natural vermiculites from different localities: Bulgaria, Brazil and South Africa were studied using Fourier Transform Infrared spectroscopy and dispersive Raman spectroscopy. The particle size fraction less than 40 μm were prepared using milling in vibratory mill and sieving through a sieve.

Selective leaching of clay minerals with acid is a simple technique for preparation of porous silica. The preparation of porous materials from clay minerals by selective leaching yields residues with large specific surface areas that can be used as adsorbents of contaminants or as catalysts. As protons penetrate into the clay layers and attack the OH groups, the resulting dehydroxylation occurs together with the removal of part of the cations from octahedra. Comparative IR studies of acid-treated smectites, saponites, sepiolite and palygorskite have been already published. Vermiculite has also been used to prepare porous silica. Comparative study of IR and Raman spectroscopy of vermiculites after acid treatment has not yet been presented.

The focus of this study was to prepare materials by acid attack which retain the layered morphology but develop a high specific surface area and still have the ability to intercalate organic molecules. These materials may preferentially be used as precursor for vermiculite-polymer nanocomposites.

Vermiculite samples were leached in HCl at concentrations of 2.0 M at 80 °C for several hours. Alteration of the vermiculites structures when acid attack dissolve the octahedral sheets by interlayer and edge attack is monitored using Fourier Transform Infrared spectroscopy and dispersive Raman spectroscopy and X-ray powder diffraction.

Acknowledgments

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PALEVYE (PALE) SOILS OF CENTRAL YAKUTIA (RUSSIA): GENETIC SPECIFICITY AND MINERALOGICAL COMPOSITION

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Palevye (Pale) soils (Cambisol (Gelic, Calcaric) or (Gelic, Calcaric, Sodic) due to (WRB, 2006) of Central Yakutia are the permafrost affected soils developed from calcareous deposits of different textures including loess-like ones. Soil formation has been taking place in the conditions of the minus mean annual temperature and its high season amplitude, and low annual precipitation. The profiles are characterized by acid pH value in the upper part of profile, especially in the raw-humus horizon, and alkaline in the lower ones due to calcareous new formations. The fine size fraction (<1µm) of the set of studied soils is characterized by common mica – chlorite association of individual phyllosilicates and kaolinite presence as a trace and the mica–smectitic (vermiculitic) and chlorite–smectitic (vermiculitic) association of mixed-layered minerals. Supposedly parent substrates of studied soils despite the texture difference were derived from the mineralogical common source. The interesting fact is that the loess-like parent substrate differs from loess-loam loams of European Russia by considerably higher share of chlorite. The distribution of phyllosilicates in the soil profiles can be described as (i) undifferentiated in the loamy variants and (ii) differentiated in the loamy-sandy variants. The latter is characterized by the appearance of pedogenic smectitic phase resulted from inherited phyllosilicates transformation in the upper (under litter) horizon, which is close to phyllosilicate distribution in Podzols on the fluvioglacial deposits of European Russia. In the Palevye (Pale) soils the phyllosilicates distribution has been taking place despite the presence of carbonates, which migration in soil profile is generally typical of the soils of East Siberia and is related to the alternation of the downward migration of dissolved carbonates in the wet seasons and their upward migration toward the freezing front.

DIATOMITE AND DIATOMITIC CLAY AS POTENCIAL ADDITIONAL MATERIAL FOR CEMENT

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Nowadays concrete is the most widely used construction material. The manufacture of Portland cement (main component of concrete) has a significant effect on the environment due to its high energy demand and the emission of greenhouse gas into the atmosphere, mainly CO_2. The use of mineral additions (e.g. metakaolin or zeolite) as a partial substitution of Portland cement clinker has become one of the main ways to obtain more eco-efficient cements (Janotka et al., 2010).

The main goal of presented results was the characterization of diatomite and diatomitic clay from Jelšovec (Veľká nad Ipľom) before and after calcination as the first step of the project to explain the mechanism of synergic effect of two different additives – calcined kaolin sand and diatomite or calcined diatomite in cement composites on the basis of Portland cement.

The Jelšovec diatomite deposit comprises the filling of basalt fossil maar. It is located in Lučenská kotlina Depression that belongs to the larger South Slovakian Basin. It is sporadically mined by surface mining. It was used as material for light building construction with favourable thermo-insulation properties (Vass et al., 1998).

Diatomitic material is composed of variable content of amorphous matter (in our samples from 72 to 28 wt %) and clay minerals (14 to 68 wt %). Smectite and kaolinite predominate over illite and chlorite. The samples were calcinated at 700 to 1000 °C. The most promissing calcination temperature seems to be at 900 °C when the smectite and kaolinite were collabsed and about 70 wt % of amorphous SiO_2 material was determined. Kaolinite was still observed after calcination at 700 °C.

Acknowledgments

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PREPARATION AND STRUCTURAL CHARACTERIZATION OF VERMICULITE/POLYETHYLENE COMPOSITES

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The polymer nanocomposites exhibit new and sometimes improved properties that are not displayed by the individual phases or by their conventional composite counterparts. Significant improvement of mechanical properties, thermal stability, resistance to solvent swelling and suppression of flammability have been achieved with the only up to 5 wt.% exfoliated layered silicates nanoparticles in polymer matrix.

Polyethylene (PE) is one of the most widely used polyolefins. When mixing PE with hydrophilic clay minerals the additives can play a role of a polymeric surfactant, or they may act as a compatibilizer. The polar additives or charge of carriers introduce dipole moments in PE.

Literary sources report the results about vermiculite (VER) nanofiller intercalated with the maleic anhydride into polyamide, polyethylene, and polypropylene. Nanocomposites containing vermiculite particles partly intercalated and exfoliated in polyethylene (PP) were prepared without compatibilizer by solid-state shear compounding using pan-mill equipment.

The study aimed with the VER/PE composites with the 7 wt.% and 3.5 wt.% of VER nanofiller that were manufactured using melt compounding procedure without additives. The vermiculite nanofillers of two size fractions were prepared in a planetary ball mill and in the jet mill. The structure of VER in PE and the composites plates VER/PE were characterized using the X-ray powder diffraction methods and atomic force microscopy. The structural relations between VER and PE were simulated using the Molecular modeling. Survival of the colonies of bacterial strain on the surfaces of the VER/PE platelets was monitored at time intervals from 1 to 96 hours.

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Computational methods in clay science

Poster presentation

MOLECULAR SIMULATIONS OF CLAY MINERALS

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Molecular simulations were applied for detail structure analysis of several types of intercalated layered structures of layer double hydroxides (LDH) with different anions and cationic clays like montmorillonite with various organic cations and polar molecules. Calculations show a detailed insight into the arrangement of the interlayer space and on the surface. We can study mutual relations between inorganic layers and organic species, their charge distribution, energy characteristics, calculated X-ray diffraction, influence of water on the stability of structure etc. Properties of predicted models were carefully compared with the experimental results and resultant structures are in a good agreement with them. Advantages and disadvantages of molecular calculations applied for hybrid materials will be shown. Simulations were done in *Cerius^2* and *Materials Studio* modelling environment.

MECHANICAL PROPERTIES OF THE GRAFTED KAOLINITE – DFT STUDY

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Kaolinite ($Al_2Si_2O_5(OH)_4$) is a layered 1:1 dioctahedral aluminum silicate with layers formed from linked tetrahedral and octahedral sheets, where the octahedral side is terminated by surface hydroxyl groups of μ-OH type. Although the layers are held together via hydrogen bonds, kaolinite can be relatively easily intercalated with various molecules. The intercalation process opens an access to basal surfaces, which can be modified by further treatment. It was observed that the interlayer aluminol groups are susceptible to grafting with different organic molecules. Grafting of aluminol surface with methanol can lead to a modification of hydrophillicity/hydrophobicity of clay surfaces and can change physical-chemical properties of the parent material. Therefore, methoxy-kaolinite complex (KM) is an interesting material which may be successfully used as a precursor for obtaining e.g. kaolinite-amine derivatives and kaolinite-polymer nanocomposites.

Five models of the kaolinite-methanol complex were supposed in the previous study of the grafting process (Matusik et al., 2012). In the present work these models were used for a theoretical study (density functional theory, DFT) of mechanical properties of this perspective material. The elastic constants and bulk modulus were calculated for models of pure kaolinite (K), kaolinite intercalated with two methanol groups (K-INT), kaolinite grafted with methoxy group (K-MTX), kaolinite with intercalated one methanol molecule and one grafted methoxy group (K-MIX), and K-MIX containing one additional water molecule (K-MIXW). The numbers are related to the computational unit cell used in DFT calculations. The calculated bulk modulus is the highest for K model (40.3 GPa). For the intercalated/grafted models bulk moduli are lower decreasing in following order: 38.0 GPa (K-MTX) > 36.6 GPa (K-MIX) > 30.8 GPa (K-MIXW) > 30.2 GPa (K-INT).

Acknowledgment

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AB-INITIO CALCULATIONS OF INTERACTION OF PORPHYRINE WITH CLAY SLAB

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Ab-initio calculations of interaction of substitued porphyrine with mineral slab. Energy and geometry optimizations of subtitued porphyrine cores interacting with mineral surface were calculated.

Using DFT method, there were found ground state energies of isolated and clustered porphyrine moleculens on clay surface.

WETTABILITY OF MINERAL SURFACES - MOLECULAR DYNAMICS SIMULATIONS

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Wettability of minerals is primarily related to an energetic characteristic of surfaces affecting physical processes such as adhesion, friction, detergency, biofilm growth, etc. The wetting ability of a solid surface is mainly determined by its chemical composition, structure and topography (Bachman et al., 2000). Solid-liquid contact angle method is often used to characterize wettability of surfaces and to determine its surface free energy.

In order to elucidate structural and compositional factors affecting hydrophilic/hydrophobic character of minerals, interactions of water nanodroplets with basal surfaces of selected minerals (particularly kaolinite, goethite, lepidocrocite, and phlogophite) were investigated by means of classical molecular dynamics simulations at room temperature. Simulations were performed using LAMMPS program package (Plimpton, 1995). Mineral layers were described by CLAYFF force-field potential (Cygan et al., 2004), specifically developed for simulation of hydrated and multicomponent mineral systems and their interfaces with aqueous solutions. In a description of water molecule, two force-field models were used – two point charge models SPC and SPC/E, respectively. From temporal evolution and averaged shape of the water nanodroplet on the surface it was possible to characterize hydrophobic/hydrophilic character of studied mineral surfaces.

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Geology and mineralogy of clays

Poster presentation

EFFECTS OF ISOSTATIC UPLIFT ON CLAY MINERAL TRANSFORMATION ON ALNÖ ISLAND, SWEDEN

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The aim of this study is the research of clay mineral transformation due to the isostatic uplift in a chronosequence of eleven soil profiles on Alnö Island on the East coast of Sweden.

Since the island is situated in the centre of the isostatic uplift of the Baltic Shield, it is an ideal investigation area for studying mineralogy in a chronosequence of soils that have developed on surface of known age.

During Quaternary the northern parts of Europe were characterized by three main ice ages, Weichselian, Saale and Elster glacial. The Swedish landscape is mainly affected by Weichselian ice sheet, which amounted up to 2.500 meters in the area of the Gulf of Bothnia. By reason of weight of the continental glaciers the Baltic Shield was pushed down. In consequence of climate warming glacial melt occurred and isostatic uplift took place. Even though the area around Alnö is ice free since about 9.600 years, postglacial uplift is taking place to date. Since the uplift rates in the Alnö area have been nearly constant with values of about 7mm/year, approximate ages can be calculated for the soil profiles in question.

Due to highest elevation above sea level on Alnö is 128 m at present, it was calculated that the emergence must have taken place between 7.400 and 7.700 years BP. As this is the same time for beginning of terrestrial soil formation, the oldest soils on the island are of corresponding age. By considering uplift and development of the shoreline, the age of soils at a certain elevation above sea level can be determined.

Every single soil profile developed on granite and gneiss and can be classified as podzol.

As clay minerals are sensitive to changes of their environment, they can be used as indicators for soil development during pedogenesis. All samples are dominated by the sand size fraction whereas only minor amounts of clay were found.

Illite is the predominant clay mineral which indicates a low rate of alteration. The main transformation during pedogenesis is the neoformation of vermiculite from illite. The amount of primary chlorite decreases with the soil age, whereas secondary chlorite increases. Vermiculite, chlorite and illite are also components of mixed layer minerals, which are found in high concentrations in all soil profiles.

THE INFLUENCE OF CLAY MINERALS ON SLOPE STABILITY IN LANDSLIDE AREAS OF THE POLISH FLYSCH ZONE

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Landslides are one of the most common events that cause natural disaster. Major landslides in Poland occur in the southern part of the country in the Polish Flysch (Outer) Carpathian Mountains. Till now, 20.000 places of appearing landslides have been counted. This is more than 95 % of all landslides in Poland, which represents only 6 % of the country.

Sliding is a common process in the Beskid Wyspowy Mountain range. Slides occupy approximately 3 % of the total area of mountain range (Bober, 1984). The widespread is caused by local geology, which is dominated by flysch-type formations alternating layers of shale and layers of shale and sandstone as well as by presence of shale and debris cover that had evolved via weathering processes.

Generally two locations in the Beskid Wyspowy (the landslides in Kłodne and Łososina River Basin) were chosen to show different ways of looking at the problem of slope instability. A very intensive and chaotic building construction in the Carpathian valleys and on the slopes adds to larger and larger damages in the area every year.

In all above, mentioned locations the relatively fresh material of the landslide head was sampled and investigated. The composition of the bulk samples and the clay fraction, grain size, water content, pH values, electrical conductivity, cation exchange capacity and carbon content were measured and the soil type was described. The mineral composition of the less than two microns of this material was determined by X-Ray diffraction. High amounts of mixed layer minerals, vermiculite and illite were found. Additionally the Atterberg limits were determined.

The aim of this project is to make an assessment based on the methodological background and case study to explain the mass movements, which cause structural damages. The analysis of the results of the laboratory studies and field surveys should give information about the landslide problems in the Beskid Wyspowy.

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CLAY MINERALOGY, A USEFUL TOOL FOR THE IDENTIFICATION OF A DOUBLE LAYER SOIL PROFILE

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Eluvial and illuvial horizons of a pseudogley on flat terrain, primary, middle deep, distric at Laudonov Gaj locality were analysed by X-ray powder diffraction (XRD). The mineral composition of the following size fractions was analysed: <2 mm, 63-125 μm, 32-63 μm, 2-32 μm and clay fraction (<2 μm). The dominant mineral phases in eluvial and illuvial horizons are quartz and mixed-layer clay minerals. Samples also contain micaceous minerals (including illitic material), kaolinite (well and poorly crystallised kaolinite), potassium feldspar, plagioclase, goethite, amorphous matter, possibly chlorite and vermiculite. In the eluvial horizon, the amount of quartz is almost twice the amount of quartz in the illuvial horizon. In contrast, the amount of clay minerals in the illuvial horizon is twice the amount of clay minerals in the eluvial horizon. Compared to the illuvial horizon, the eluvial horizon is enriched in potassium feldspar. The clay fraction of the eluvial horizon is dominated by mixed-layer clay minerals, presumably interstratified chlorite-vermiculite. It also contains significant amounts of kaolinite minerals (approximately similar amounts of both well crystallised and poorly crystallized kaolinite), illitic material and vermiculite. The clay fraction of the illluvial horizon is dominated by mixed-layer clay minerals and kaolinite minerals. The amount of the irregularly interstratified chlorite-vermiculite dominates over regularly interstratified chlorite-vermiculite. The share of poorly crystallised kaolinite is substantially higher than the share of well crystallised kaolinite. This fraction also contains illitic material, and, possibly, irregularly interstratified illite-smectite. The diffraction lines of chlorite and vermiculite are also discernible, but it cannot be taken for granted due to their very low content. It is important to stress that the 2-32 μm and 32-63 μm fractions of the illuvial horizon contain kaolinite minerals. The same fractions of the eluvial horizon do not contain kaolinite minerals. The diffraction lines of dolomite in the 32-63 μm fraction of the eluvial horizon are visible. This mineral phase was not observed in the same fraction of the illuvial horizon.

Given the great texture contrast between the two horizons and the differences in their mineral composition, it can be assumed that the proluvial deposit could be the source material for the development of younger sediments, which were later, as a coarse textured material, deposited on the soil formed on proluvial clays, and the double-layer soil profile was formed.

BENTONITE BED IN THE DINANTIAN LIMESTONES OF THE SOUTHERN POLAND

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A thick (1.10 m) K-bentonite bed has been found in the Lower Carboniferous limestones succession in southern Poland, forming eastern marginal part of the carbonate platform in the Moravian-Silesian Basin. This K-bentonite, herein defined as the Czatkowice Bed, crops out in the wall of the limestone open pit in Czatkowice near Kraków. The Dinantian limestone (up to 1100 m thick) here are on the western limb of the Dębnik Anticline, and the beds deep WSW at 50^o-90^o. The Czatkowice bed lies within the 50 m thick sequence of medium-bedded black limestones with numerous spongia spicules, which is the Tournaisian in age. Although some bentonites are described from this interval in platform carbonate succession in eastern Belgium, this paper reports the first set of data for a bentonite of this age discovered in Poland.

The Czatkowice Bed consists of pink massive clay deposits (10 cm) overlain by an olive-grey one (100 cm). The later show fissility in the lower part (55 cm). The limestones are silicified as well as reddish and whitish in the contacts with the bentonite beds.

X-ray diffraction and microscopic data document vertical variability in grain-size of the Czatkowice Bed that resulted in the change of its mineral composition. The pink massive deposits consists of numerous splinters and crystal euhedra of quartz as well as lath-shaped potassium feldspars up to 0.5 mm across, scattered in a matrix of former volcanic glass shards that have been altered to clay. The outlines of glass shards locally are readily recognizable. The olive-grey deposits showing fissility are closely similar in texture but splinters and crystal euhedra are less numerous, finer grained (up to 0.1 mm) and feldspar-dominated. The olive-grey massive deposits are devoid of crystal chips and consist manly of glass shards altered to clay.

The clay minerals are homogenous throughout the profile of the Czatkowice Bed. They are dominated by low smectite mixed-layered illite-smectite. It is supposed that the homogeneity of clay through the profile is a signature of early alteration process in a shallow water and of burial diagenesis in K-rich system in which illitization was enhanced.

The K-bentonite described above (Czatkowice Bed) represent a big and probably one of older Carboniferous volcanic events that was associated with the closure of Rheik Ocean.

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SEDIMENTARY FABRICS AND CARBONATE COMPOSITION OF THE HADER AND MITTERSBERG BENTONITE DEPOSITS

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The sedimentary fabrics and carbonate composition of two terrestrial bentonite deposits (Hader, Mittersberg) in the Upper Freshwater Molasse (UFM, Middle Miocene) near Landshut, Germany, were investigated and compared to previously studied deposits (Landersdorf, Gabelsberg). Detailed profile sections are combined with sedimentary fabrics, carbonate morphology and composition. Bulk sample and carbonate compositions were determined by XRD. The Hader deposit has a simple stratigraphic succession of gravels at the base, partially altered volcanic tephra ("Harte Platte"), sandy bentonite with carbonate lenses at its base, and gravel beds at the top. Few carbonate nodules are present in the bentonite. These carbonates occur as white-grey, soft and hard nodules, as well as, white sugar-like granular nodules, soft powder or friable carbonate lenses. Preliminary XRD results show calcareous, dolomitic and mixed compositions. Dolomite appears to be more abundant towards the top of the bentonite bed. The Mittersberg deposit has grey marls at its base followed by two bentonite beds and a chaotic horizon that laterally grades into partially altered tephra, grey-green sand-rich bentonite and/or carbonate-rich clay. Joint surfaces in volcanic tephra are covered by powdery carbonate with tiny root traces. Carbonate content increases towards the top and laterally carbonate replaces the clay. Carbonate nodules from this layer have shrinkage cracks with calcite crystals implying repeated wetting and drying. The previously studied Gabelsberg deposit shows an almost identical stratigraphic succession to Mittersberg but the volcanic tephra is devoid of bentonite nests and carbonate-rich joints. Very rare calcite is present. The Landersdorf deposit is almost identical to the Hader deposit, except for carbonate composition which is dolomitic with little calcite in Hader. We interpret footwall marls, bioturbation, and intense rooting (Mittersberg/Gabelsberg) of volcanic tephra and carbonate content as deposition in shallow freshwater bodies and subsequent pedogenesis, while foot- and hanging-wall gravels (Hader and Landersdorf) indicate a more fluvial influence. We suggest that depositional differences in relief and a meandering river system account for different sedimentary fabrics and carbonate composition, consistent with previous research on palaeosols in the UFM.

NATURAL PENCIL CLAY DEPOSITS IN GERMANY

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Germany is a leading producer of natural clays used with graphite in the manufacture of pencil leads. The Klingenberg deposit in Northern Bavaria had a 270 year-old mining history and was the World's most important pencil clay deposit before its closure in December 2011. The Kärlich blue clay from the Neuwied basin is the present-day successor. Here we present a comparison of geological settings, mineral compositions and geochemical characteristics of the two deposits to better understand the genesis of natural penci clays.

The Klingenberg deposit is located in a small isolated Tertiary half-graben filled with lacustrine fine-grained sediments within the red sandstones of the Bunter (Lower Triassic) in the southern Rhönarea. The economic clay bed has a maximum thickness of about 30 m. New palynological data (M. Hottenrott, pers. comm.) infer a Middle to Upper Oligocene age of the clay, opposed to the previous views of an Upper Pliocene age. The black to grey pencil clay is extremely fine grained with up to 98wt.% in the <2 µm fraction. It mainly consists of disordered kaolinite and a smectite-rich illite-smectite with minor contents of illite, anatase and quartz. The Klingenberg blue clay shows a Fe_2O_3 concentration of about 2.5 to 3.5 wt.% and an Al_2O_3 content around 28-32 wt.% very similar tothe composition of theKärlich clay. The Ti, Co, Cr, Cu, Ni and Nb concentrations are within the range of values of average shale.

The Kärlich blue clay is hosted within an Upper Oligocene brackish to lacustrine sequence of the Neuwied basin in the Variscan Rhenish Massif. The bluish black refractory clay with a thickness of about 6 m show a gradual transition to the underlying bentonite (*Kärlich Grünton*). The main constituent is disordered kaolinite, with minor smectite or smectite-rich illite-smectite and discrete illite. The high content of expandable clay minerals and rather low illite content is unusual for Tertiary lacustrine clays in the Rhenish Massif, such as the classic Westerwald clays. High V (300 ppm) and Cr (250 to 300 ppm) as well as unusually high TiO_2 (3.5 to 4 wt. %) and Nb (about 150 ppm) contents are unique geochemical features that imply specific alkaline and mafic protoliths in the source area.

The German pencil clays are characterized by similarly high contents of disordered kaolinite and expandable 2:1 clay minerals, as well asby the extremely fine grain size related to an efficient sedimentary grain size sorting process and a quiet lacustrine depositional environ-ment. Specific protolithsin the source region(mafic and alkalinerocks)are indicated by trace element geochemical data for the Kärlich blue clay, but not forthe Klingenberg pencil clays.

BENTONITES IN THE NEUWIED BASIN AND THE ADJACENT WESTERWALD

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The Upper Oligocene alkaline intraplate volcanic province of the Westerwald, Siebengebirge and Eifel region is host to a number of small bentonite deposits. The igneous rocks range from picrobasalts and basanites to trachyites and phonolites and are associated to limnic mostly illitic-kaolinitic clays. We present preliminary geological, mineralogical and geochemical data on the Kärlich bentonite (*Kärlich Grünton*) in the Neuwied basin and the Salz bentonite in the southern Westerwald area.

The 0.5 to 2 m thick green Kärlich bentonite bed is underlain by a 50-m-thick brackish series of Fe-rich clays of the Maifeld Formation. It shows a gradational transition to the overlying lacustrine kaolinite-rich Kärlich blue clay. The Upper Oligocene sedimentary sequence ends with smectite-bearing trachytic tuffs and tuffites. The bentonite consists of dominating Fe-rich smectites (50 to 60 %) with a minor interstratified illitic component, disordered kaolinite, illite and quartz. The Fe-rich nature of the expandable clay mineral contrasts with the Al-rich smectite of the overlying altered trachytic tuff and implicates a Fe-rich protolith. The Fe_2O_3 contents scatter around 10 wt.%. The presence of illite, kaolinite and quartz indicates a sedimentary component of weathered metapelites of the Rhenish Massif and excludes an in situ formation from volcanic products. The bentonite is characterized by high Ni, Co, Cr and Zn contents as compared to average shales.

In contrast, the reddish brown Salz bentonite formed by alteration of a massive amphibole-phyric mafic stock. The altered rock poorly disaggregates in aqueous solutions. The bentonite mainly consists of Fe-rich smectite (about 70 %) with minor amphibole, kaolinite, feldspar and quartz. The Salz smectite has a higher Fe content compared to the smectite from Kärlich. The Salz bentonite shows very high TiO_2 (about 4.3 wt.%) and Fe_2O_3 (about 14 wt.%) contents and similar to the Kärlich bentonite elevated Co, Cr, Ni and Zn, but also high Nb and Zr concentrations.

We conclude that while the Salz bentonite is an in situ alteration product of an alkaline mafic volcanic rock, the Kärlich bentonite has to be considered rather a smectite-rich sediment. The geochemical fingerprint, however, also shows a mafic signature for the latter. But it remains unclear whether the Fe-rich smectites in the Kärlich bentonite derived from altered mafic rocks of Oligocene or even Devonian age in the source region or from the Fe-rich clays of the underlying Maifeld Formation.

Clays in environment and in radioactive waste applications

Poster presentation

COMPARISON OF STANDARD SHRINKAGE TESTS AND FIRST SHRINKAGE PARAMETERS OF SLOVAK BENTONITES

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In a previous research on the deep geological repository of radioactive waste, the swelling potential of bentonites from Slovak deposits was evaluated by indicative parameters and by swelling pressure tests (more details in Adamcová, Frankovská, Durmeková, 2009). The noticed absence of data on shrinkage behavior initiated a pilot research of bentonite shrinkage parameters in Slovakia. Comparison of Slovak, Austrian, German and British Standards for shrinkage test methods showed that Slovak Technical Standards (STN) pertain to undisturbed soil samples, where shrinkage depends not only on the current moisture, but also on the grain size distribution and porosity (pore number and size). On the other hand, shrinkage limit w_s (%) and percentage of linear shrinkage L_s (%) determined according to the foreign technical standards are independent from those properties, because sample preparation brings all soils to equal starting conditions: sieved to size below 0.5 mm, moisture w at the Atterberg liquid limit w_L, i. e. $w = (1 \text{ to } 1.1).w_{L,}$ smeared without bubbles into standard moulds. We used the Austrian ONORM B 4411: 2009, that offers three test procedures for w_s. First, shrinkage limit w_s was determined by manifold weight and volume measuring followed by calculation from the moisture-to-relative volume linear trend-line. Results were compared with data from the other two methods.

High linear shrinkage L_s (up to 32.5 % of the initial length) was observed in bentonite J250 from the Jelšový Potok deposit, the best Slovak bentonite because of highest swelling potential. L_s is good for comparative studies when searching for material less sensitive to shrinkage, but it does not indicate the final shrinkage of bentonite blocks. To test the absolute shrinkage of compacted bentonite, we suggest to use methods described in STN 72 1019. Reaching of the shrinkage limit w_s at 11 % moiture was indicated also by bentonite color change from light brownish grey (2,5Y 6/2) to light grey (2,5Y 7/1 - Munsell Soil-Color Charts, 2009). Because w_s is lower than the usual equilibrium moisture of the bentonite J250 under room conditions (14 %), bentonite blocks might shrink and gaps between them open due to high temperature around the containers with radioactive waste until water from the host rock mass intrudes and bentonite swells. In this manner, the necessity of further shrinkage tests, this time on compacted bentonite, was indicated.

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THE ROLE OF CATION EXCHANGE ON THE SWELLING BEHAVIOUR OF MX80 BENTONITE: AN XRD STUDY OF MODELED BENTONITE-CEMENT AND BENTONITE-GROUNDWATER INTERACTIONS

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MX80 bentonite, composed mainly of Na-montmorillonite, is one of the prime candidates as a buffer for the Swedish spent fuel repository in Forsmark. In the repository the buffer is expected to come into contact with groundwater from surrounding rock and with cement-altered solutions derived from areas that use concrete. This study aimed to characterize the swelling behavior of MX80 montmorillonite after exchange with ideal solutions of Na^+, K^+, Ca^{2+}, Mg^{2+} or with a saturated cement solution derived from white Portland cement. Bentonite samples were treated, with one of the solutions each, four times to attain complete saturation and then washed. Afterwards all samples were micronized and orientated samples were prepared for X-ray diffraction (XRD). XRD measurements were made from 4 to 32° 2θ using a Bruker D8 Advance diffractometer equipped with a hot humidity chamber at 40° C that could attain relative humidites between 0 and 85 %. The swelling behavior of all samples was reconstructed using the complete sequence of 00*l* montmorillonite reflections.

The untreated original MX80 showed a stepwise swelling from the zero, through the first to the second layer hydration state, as did the Na-exchanged MX80. In contrast, Ca and Mg-exchanged montmorillonite swelled continuously from the first to the second layer hydration state, whereas the K-saturated sample did not reach the first layer hydration state under any of the humidity conditions tested. The cement-solution-altered MX80 behaved most like the Ca-montmorillonite, with continuous swelling from the first to second layer hydration state, which was interpreted to reflect simple cation exchange by Ca^{2+} derived from the cement. This was in agreement with the observed differences in the cation concentrations in the cement solution before and after it was in contact with bentonite. The transitions between hydration states were best modeled assuming randomly ordered mixed-layered structure, which could be quantified using NEWMOD. Fixed scans of the montmorillonite 001 reflection also indicate the montmorillonite reached steady state within just minutes after a change in humidity. This quick reaction time is attributed to the thinness of the clay film used in this study. Based on our results it is apparent that that infiltrating waters with varying types and abundance of cations change the swelling behavior of the MX80 bentonite backfill and that contact with altered cements induces widespread exchange by Ca^{2+} that could reduce the barriers effect.

SURFACE PHYSICO-CHEMICAL PROPERTIES OF TERRA ROSSA AND CALCOMELANOSOL DEVELOPED ON HARD LIMESTONE

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Two different soils developed on hard limestone in Istria, Croatia, were investigated in order to evaluate the relation between their composition and surface physico-chemical properties. Terra rossa bearing typical Fe-oxide characteristics (e.g., Fe_d and Fe_d/Fe_t) and calcomelanosol enriched in organic matter were analysed. Kaolinites (Kl_D and Kl), illitic material and Fe-oxides are main mineral phases in the clay fraction of terra rossa while calcomelanosol contains kaolinites, chlorite and vermiculite as main mineral phases in the clay fraction. To define relation between the individual constituents and properties of soils, samples were selectively dissoluted. Granulometric composition, the specific surface area (SSA) and the cation exchange capacity (CEC) were measured on the following subsamples: original samples, samples treated with H_2O_2, samples treated with H_2O_2+NH_4-oxalate, samples treated with H_2O_2+NH_4-oxalate+Na-dithionite-citrate-bicarbonate. The morphology of samples and size of aggregates and particles were examined by scanning field-emission electron microscopy. Differences were observed between the surface properties of terra rossa and calcomelanosol that are the result of particle-size distribution, mineral composition and different share of organic matter. The distribution of CEC values among subsamples of terra rossa and calcomelanosol is different. On the contrary, the trend of SSA is same in the first three subsamples of analysed soils. The SSA increased proportionally to the amount of the removed organic matter in both soils. Following the dissolution of amorphous Fe-oxides, the SSA decreased. After the removal of well crystallized Fe-oxides the SSA decreased in calcomelanosol and highly increased in terra rossa due to major soil aggregate decomposition and accordingly, increased fine clay content.

PILLARED MONTMORILLONITES AS CATALYSTS FOR REMOVAL OF CHLORINATED VOLATILE ORGANIC COMPOUNDS FROM AIR. STRUCTURAL CHARACTERIZATION

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Chlorinated volatile organic compounds (CVOCs) constitute an important part of hazardous solvent wastes released into the environment by industry. Catalytic combustion offers efficient means to control this emission. In the present work Ti, Zr and [Ti,Zr]-pillared montomorillonites (referred to as Ti-PILC, Zr-PILC and [Ti,Zr]-PILC, respectively), doped with Pd, Cr and Pd/Cr, were synthesized as potential catalysts for full oxidation of chlorinated organics.

Pillaring of montmorillonite (sodium form of the less than 2 μm particle-size fraction extracted by sedimentation from Milowice bentonite, Poland) was carried out by means of cation exchange with aqueous solutions of Ti polycations (from $TiCl_4$ as a source), Zr polycations (from $ZrOCl_2 \cdot 8H_2O$ as a source) and a mixture of Ti and Zr polycations (Ti and Zr aqueous solutions mixed in a 1:1 ratio), followed by calcination at 400° C. Ca. 1 wt.% of Pd, Cr or Pd/Cr was introduced by impregnation/calcination method. Physico-chemical characterization showed that pillars generated in [Ti,Zr]-PILC differed from those formed in either Ti-PILC or Zr-PILC. In particular, both before and after calcination, they were larger than Zr and smaller than Ti species. Doping with Pd, Cr and Pd/Cr did not affect the diffraction pattern of pillared clays in any significant way. After calcination at 400^o C all pillar-forming oxides were amorphous, but upon further thermal treatment at 800^o C crystallization of anatase in Ti-PILC, orthorhombic zirconia in Zr-PILC and $ZrTiO_4$ compound in mixed Ti,Zr-PILC was observed.

Catalytic tests of CVOCs combustion demonstrated superior properties of catalysts derived from [Ti,Zr]-PILC solid. The effect was interpreted as due to advantageous catalytic properties resulting from the interaction of Zr and Ti within the common crystal lattice of mixed [Zr,Ti]-pillars.

RAMAN SPECTROSCOPY STUDY OF CEMENT/PET COMPOSITES

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The increasing amount of poly(ethylene terephthalate) (PET) waste is a worldwide problem which has induced requirements for its recycling and reusing. PET fibres have been used as a dispersed micro-reinforcement in a cementitious matrix. A new application, the Raman microspectroscopy mapping technique, was successfully used to study of the interfacial transitionzone (ITZ) around poly(ethylene terephtalate) (PET) reinforcement in concrete. Waste from PET bottles has been used in form of fibers as a reinforcing element in Portland cement concrete. Raman spectra represent the compositional variation of the cement matrix within the distance range of 5 to 200 µm from the PET fibre. The Raman band at 357 cm^{-1} corresponding to the vibrations of Ca–O bond at $Ca(OH)_2$ was used for quantitative distribution of portlandite within the ITZ area. The contact zone is characterized by a higher porosity (both air and water pores) and occurrence of newly formed mineral phases, particularly portlandite, hydrocarbonate, ettringite, and lower Ca^{2+} saturated C–S–H gels.

DETAILED STUDY OF CLAY MINERALS IN BODA SILTSTONE FORMATION, POSSIBLE REPOSITORY OF HIGH LEVEL NUCLEAR WASTE IN HUNGARY

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Boda Siltstone Formation (BSF) is the potential site for high level nuclear waste repository in Hungary. Although, BSF is a 600-800 m thick homogeneous, red clayey-sandy siltstone, at least three typical rock varieties can be differentiated based on their mineral composition: 1) BSF with high illite content, 2) albitic and 3) analcime bearing facies of BSF. Clay minerals in these three rock varieties were characterized by X-ray powder diffraction (XRD), high resolution transmission electron microscopy (HRTEM) and thermal analysis (DTA-TG).

Mineral composition of bulk BSF samples varies between 5–35 % albite, 35–70 % illite, 5–15 % calcite, 0–6 % dolomite, 5–10 % hematite, 0–5 % quartz, and 1–2 % chlorite. Analcimous BSF contains 15 % analcime. In the albitic sample, besides the dominant illite, few percent of chlorite represents the layer silicates in the clay fraction. This illite does not contain more than 5 % swelling component. Illite is the dominating phase in the illitic sample, a few percent of chlorite is present beside it. Half-width of illite 001 reflection is the largest in this sample. The broad peak is not related to smectite interstratification, but to the very small crystallite size of illite. HRTEM study revealed that the thickness of illite particles rarely reaches 10 layers, usually are of 5-6 layers thick. Illite crystals are generally thicker (sometimes more than 100 nm) in the albitic sample than in the illitic one. The sharpening of 001 peak upon heating to 350 and 550° C suggests significant water content (interlayer H_3O^+). This is supported by the 2.7 % weight loss between 35–235° C, which is the highest among the three samples. The most important difference between the clay mineral characterisitics of the analcimous sample and the other two samples is that it contains 10-20 % regularly interstratified chlorite/smectite beside the dominating illite. The amount of swelling component (smectite) in illite is max. 5–10 %, in chlorite/smectite mixed layer mineral it is around 50 %. According to the Green-Kelly test the layer charge of smectite is originated from the tetrahedral sheet.

Based on the crystal structure and chemical composition two kind of illite are present in BSF: 1M polytype 10 Å phyllosilicate always contains Fe and Mg besides Al, 2M polytype illite is free of Fe and Mg. Chlorite contains some illite interstratification. Close association of very thin illite plates and nanosized hematite crystals is typical textural feature in BSF.

New findings of this study on the clay mineralogy of BSF are indispensable for further studies focusing on radionuclide sorption properties of this claystone.

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HEAVY METALS AND THEIR HOST PHASES IN THE AIRBORNE DUST IN BUDAPEST, HUNGARY

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Airborne particulate matter has been widely associated with health disorders. They can be both ingested and inhaled causing health damage due to their size, shape or toxic components. Our aim was to identify and characterize the mineral phases associated with heavy metals in the total suspended particulate matter and gravitational dust samples from Budapest, Hungary.

Total suspended particulate matter samples were collected from the air filters placed in the respiration channels used for the air supply of the methane-heated turbines in five thermal power stations. Gravitational dust samples were collected in glass pots containing distilled water on the front and the back sides of a building at a busy street at four different heights. Detailed mineralogical (XRD, TEM), chemical (XRF) and magnetic analyses were carried out on the samples.

The major dust mineral components are characteristic of the surrounding geology. Both types of samples show significant enrichment in Zn, Pb, Cu and Mo. Statistical analyses based on their concentrations, that of other elements and the magnetic properties of the samples showed that they can be associated to not only one common anthropogenic phase. The nano-sized magnetite particles are supposed to be the major host for Cu and Mo. Additionally, transmission electron microscopy analyses showed that such particles also may contain significant amount of Zn and Pb. However, these latter metals may be associated also with layer silicates (smectites, micas) and carbonates too. Moreover, Zn also appeared as major phase constituent in carbonates and oxides.

Magnetite particles are resistant to weathering releasing its toxic components slowly to the environment, while layer silicates (and carbonates) may be the potential source of mobile toxic metals in the airborne particulate matter from Budapest.

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Properties of clays (catalysis, pore systems, transport properties in organic rich shales, ...)

Poster presentation

MODIFICATION OF CLAY MINERAL PARTICLE EDGES WITH REACTIVE FLUOROPHORES

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The synthesis of fluorescent hybrid materials based on clay minerals and reactive fluorescent dyes was investigated. The clay and reactive dye components included fluorohectorite (Corning), laponite (Laporte) and two silanes functionalized with fluorescent rhodamine or naphthalimide groups. The grafting of clay mineral particles took place selectively at the particle edges.

Small amounts of grafted silanes were detected by neither infrared spectra nor X-ray diffraction (XRD) patterns. XRD proved the absence of the significant amounts of adsorbed fluorophores at the basal surface of the silicate particles. Only larger loadings of cationic rhodamine-based silane led to a partial intercalation of the dye in the interlayer spaces.

All the samples were apparently colored. Both the absorption and fluorescence spectra were measured. The spectral properties of the materials' colloids were not much different from those of dye-silane precursor solutions. No significant aggregation and fluorescence quenching were observed which was confirmed by steady-state and time-resolved fluorescence spectroscopy.

Confocal fluorescence microscopy and fluorescence lifetime imaging detected optical heterogeneity of the fluorohectorite-naphthalimide monolayer films that was attributed to the selective location of the bound naphthalimide moieties at the particle edges. No optical heterogeneity was observed for the films of modified laponite with smaller particles.

Our research work currently continues with the modification of other clay minerals as well as other silicate materials.

RESONANCE ENERGY TRANSFER IN THE SYSTEMS BASED ON LAYERED SILICATES AND ORGANIC DYES

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The research of the energy transfer phenomenon is of high importance in various processes or phenomena in industry, e.g. in a photoactivation, photochemical initialization in organic-type solar cells, etc. Resonance energy transfer (RET) is a phenomenon of radiationless transmission of energy between energy donor and acceptor molecules. Our objective was to prepare supramolecular systems that will exhibit the process of energy transfer. Various systems were investigated based on the energy transfer between two dyes adsorbed on the two-dimensional space of layered silicates. In a first part we studied the colloidal systems composed of synthetic saponite and adsorbed rhodamine and oxazine dyes. The RET from the donor dye molecules to the acceptor dye molecules was proved by fluorescence spectroscopy. Molecules of rhodamine play a role of molecular antennas absorbing green light. The transfer was detected as a quenching of the light emission from the rhodamine (580 nm) in favour of the red light luminescence from oxazine (near 635 nm). The second part was based on the preparation of thin films of saponite and conseqeunt adsorption of two dye cations. For the preparation of thin films spin coating and layer-by-layer assembly was used. Preparation of photoactive hybrid systems mainly in a solid state is a challenge due to the formation of non-fluorescent H-aggregates; which are the efficient quenchers of luminescent and photoactive dye species. This problem was solved by appropriate modification of the inorganic host with hydrophobic alkylammonium cations was used to achieve a higher luminescence. Due to the higher tendency of Ox4 to form non-luminescent aggregates at higher concentrations, the lowering of the Ox4 concentration further improved the luminescent properties of the films. In this case, the energy transfer occurring in the solid film from R3B to Ox4 was clearly proven. The construction of layer-by-layer (LBL) assembly is one of the most promising routes to prepare thin films with controllable structure and arrangement of the components, and alternating oppositely charged particles or ions. The LBL films investigated in this work were prepared using sequential deposition of the components from ionic polymer (polydiallyldimethylammonium chloride) solution and saponite/laser dyes (rhodamine 3B and rhodamine 6G) colloid. RET measurement provided the evidence on correctness of the structural models of deposited components in prepared LBL films.

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OPTICAL OXYGEN SENSORS BASED ON CLAY/PORPHYRIN SYSTEMS

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In this work, hybrid clay/porphyrin systems as prospective oxygen sensing materials were investigated. These systems consist of two parts: a synthetic clay and metalloporphyrin molecules, suitable for the construction of the efficient oxygen sensors. Considering the complexity of these systems, the choice of suitable starting materials is of primary importance. The synthetic clay – Laponite – was chosen as a best candidate because of its excellent properties, e.g. swelling ability and resulting formation of stable homogeneous colloidal suspensions. Moreover, it has a well defined structure with absence of any impurities, what is extremely important when performing the spectroscopic studies. As a guest materials, metalloporphyrins with Pt- and Pd were chosen. These are known to be very efficient for the sensing applications because of "heavy atom effect". This effect promotes a "spin-orbit coupling", resulting in the fact that almost all of the radiation from singlet excited state undergoes the intersystem crossing, followed by the de-excitation via triplet state. A a result, a phosphorescence from these systems can be observed in a presence of an inert gas, e.g. nitrogen. However, in a presence of a reactive oxygen the collisional quenching takes place, resulting in a diminish of phosphorescence. By changing the nitrogen-to-oxygen atmosphere and vice versa, one can study the behaviour of an "on-off" type sensing. Using the above described approach, we managed to prepare an efficient oxygen sensing hybrid system, despite the fact there is a lot of space to improve some details.

DEHYDROXILATED ILLITE/SMECTITE AS A PRECURSOR FOR GEOPOLYMER BINDERS

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Geopolymers are inorganic binders formed by alkali activation of aluminosilicate materials such as furnace slag or metaclays. These aluminosilicate precursor materials are alkali activated to partially dissolve aluminium and silicon which condenses and polymerises while hardening to form a strong inorganic polymer network.

Dehydroxylated kaolinite (metakaolinite) is the most commonly used precursor for geopolymers. Initial studies using mixed layered illite-smectite (I/S) clays, which are more abundant and less expensive, showed promising results (Buchwald et al., 2009; Sperberga et al., 2011). However, there are problems related to the low amount of Al dissolved from this type of clay, as Al is necessary for rapid condensation and polymerisation.

In this study we investigated the dehydroxylation of I/S rich Eocene Friedland clay, from N Germany with 75 wt.-% clay minerals, in decreasing abundance R0 I(0.4)/S, well crystalline illite-muscovite, kaolinite and minor chlorite. We aim to determine the optimal temperature at which I/S becomes dehydroxylated and X-ray amorphous before neocrystallisation of alumosilicates i.e. mullite starts. We compare heating experiments using high speed in situ X-ray diffraction (XRD) measurements with simultaneous thermal analysis (STA). Our results show a small temperature window between completely X-ray amorphous clay minerals and neocrystallisation of new phases. The illitic minerals are X-ray amorphous by about 1110° C, whereas mullite appears at about 1190° C, in agreement with the illite studied by Jiang et al. 2008. In addition we are studying the effects of grain size, heating rate and dwell times. First results indicate that more cost effective "flash heating" with about 10 K/s leads to higher amounts of X-ray amorphous phases compared to 0.75 K/s or 3 K/s.

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RELATION BETWEEN SOME STRUCTURAL FEATURES OF KAOLINITE AND CLAY SORPTION PROPERTIES

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Kaolins usually contain kaolinite with different characteristics and quality defects which influence the main properties of clays. Kaolinite and halloysite have almost identical chemical formulas – Al4[Si4O10](OH)8 for kaolinite and Al4[Si4O10](OH)8*nH2O, where n=2 for 10Å-halloysite and n=0 – for 7Å-halloysite. Identification of highly defective kaolinite from 7Å- halloysite is usually difficult and which can be solved only by using both structural and sorption methods.

The aim of this research was find the influence of the kaolinite structural features on physical and chemical properties of clays. For the study 10 samples were collected from three Portuguese deposits (Barqueiros, Vila Fria and Vila Cha). The first two represent a redeposited material and the last one a residual weathered crust.

The characterization of clays composition and structure was carried out by X-ray diffraction, scanning electron microscopy (SEM), infrared spectroscopy, and X-ray fluorescent analysis. Furthermore, sorption properties were investigated by measuring the cation exchange capacity and the methylene blue adsorption kinetics by UV spectroscopy in the visible range.

The samples can be subdivided in three groups: 1) relative well ordered kaolinites; 2) highly defect kaolinites and 7Å- halloysites; 3) mixture of well-ordered kaolinites and 7Å-halloysites (highly defect kaolinites). The subdivision was based in the similarity and distinction of the diffraction patterns and micromorphological analysis using by SEM.

These three groups have different cation exchange capacity. For high-defect samples the value is about 8-10 mg*meq/100 g, while the ordered samples not exceed 5-6 mg*meq/100 g.

The most interesting and informative evaluation of the sorption properties were obtained by studying the behavior of methylene blue on the surface of clay particles. During the experiments optical spectra were analyzed after 1 minute and 5 days of interaction of dye molecules and the kaolinite. For each group, the specific adsorption curve was described and interpreted. The distinction between them is due to the dynamics of the methylene blue adsorption which is caused by the presence of different types of defects.

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INFLUENCE OF SYNTHEIS CONDITIONS OF PCHs ON THEIR STRUCTURAL, TEXTURAL AND CATALYTIC PROPERTIES

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Montmorillonite is a very attractive material for the synthesis of catalysts. Various methods were used for the activation of their catalytic properties [e.g. 1, 2]. The 2:1 clay minerals can be relatively easy intercalated and pillared with metal oxide pillars (e.g. Al_2O_3, TiO_2, ZrO_2) using ion-exchange methods, which increase their surface area and microporosity. The other group of pillared clay materials, called Porous Clay Heteroctructures (PCH), can be obtained by the surfactant directed method. Such materials are characterized by developed surface area, uniform porous structure and increased thermal stability. These properties of PCH materials make them efficient in various catalytic applications (e.g. Chmielarz , 2011; Chmielarz, 2009).

Montmorillonite was used as a starting material for the preparation of a series of PCHs. In the first step parent clay was transformed into sodium form of montmorillonite (Mt-Na) by its treatment with a solution of NaCl. Intercalation of Mt-Na with hexadecyltrimethylammonium (HDTMA) cations was done by ion-change method for the non-calcined samples of clay mineral and for montmorillonite calcined at 600° C. In the next step the deposition of surfactant were done using the five various ratios of clay to surfactant. Then the samples were separated from a solution and washed with demineralized water. In the next step, each sample modified with surfactant was added to melted hexadecylamine (HDA), which played a role of co-surfactant. Subsequently, tetraethylorthosilicate (TEOS) was added into each suspension and was allowed to react for 4 h under continuous stirring. The molar ratios of CEC/HDA/TEOS was 1/40/300. Finally, modified clays were separated from solutions, dried at room temperature and calcined at 600° C. The obtained materials were characterized with respect to composition (XRF), structure (XRD, FT-IR, UV-vis-DRS), texture (BET), surface acidity (NH_3-TPD) and tested in the role of catalysts for the selective catalytic reduction of NO with ammonia (DeNOx). It was found that catalytic performance of the PCH samples depends on the synthesis conditions used.

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THE EFFECT OF PREPARATION METHODS OF KAOLINITE ORGANOCOMPLEXES ON THE MORPHOLOGY OF CLAY NANOSTRUCTURES

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Synthetic halloysite nanotubes (HNTs) have promising application possibilities. They can be used for controlled release of entrapped bioactive molecules from the halloysite lumen under *in vivo* conditions, as well as for the prolonged effect of active components in cosmetics and different pesticides/fungicides (Du et al., 2010). In addition, halloysite nanotubes can be used as a nanoreactor to host reactants for biomimetic synthesis and various enzyme-catalyzed reactions (Shchukin, 2005). With the encapsulation of different cationic/anionic metalloporphyrins immobilized catalysts capable of performing selective oxidation reactions can be obtained. The application of halloysite as a selective nano-adsorbent is of high significance in environmental protection (Lu et al., 2006), while the delaminated structures and their nanohybrids are used as additives in the paint and plastics industry.

Synthetic HNTs are prepared from kaolinite organo-complex precursors via multiple intercalation. During the synthesis process the type of reagents used and the sequence of the subsequent steps are of primary importance. Since only a limited knowledge is available on the structure of intercalation complexes, on the complex-stabilizing parameters and on the nature of displacement reactions, the process of NHT preparation is based on experience, rather than on a solid physico-chemical approach.

In this work it was demonstrated that the morphology of the nanostructure to be produced is basically determined by the way of preparation of the kaolinite organocomplex precursors. It was found that from the same precursors but with different preparation methods (co-grinding, solution reaction, vapour-phase contacting) nanostructures of different morphology can be obtained, even if the steps of multiple intercalation are exactly the same. Water present in the organocomplex not only increases complex stability, but also hinders the formation of a halloysite-type nanostructure. Water can be expected to form even during dry grinding or microwave treatment, and its elimination from the complex with simple thermal treatment is not always possible. The complex-stabilizing role of water can be proved via the molecular mechanical modeling of the precursors and the relative values of the system energy.

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KINETICS OF METAKAOLINITE REHYDRATION

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The kinetics of rehydration of metakaolinite was studied from 150 to 250° C under autogenous pressures. A natural kaolinite was calcined to metakaolinite and than rehydrated at different temperatures to a highly porous kaolinite. The kinetics of this process was studied, with subsequent IR characterization of arised phases. The surface area and pore distribution of new phases were also assigned. Equilibrium adsorption isotherms of nitrogen were measured at 77 K using static volumetric adsorption systems (ASAP 2020 analyser, Micromeritics). The adsorption isotherms were fitted to produce the BET surface area, the micropore volume was derived by the t-plot method and the pore size distribution by the BJH method and DFT method. The surface area of the newly prepared kaolinites was much larger than raw kaolinite and metakaolinite (from 15.8 to ~103.1 $m^2\ g^{-1}$). It was observed that the median pore size of the samples was similar (diameter of pore 3.8 nm). The volume of these pores increased with the reaction time of rehydration at the temperatures of 150 and 175° C. The porous structure of new kaolinites was not fully developed at a rehydration temperature of 150° C. In the kaolinites prepared at 175° C, the volume of pores with diameter 3.8 nm was at a maximum, while the volume of pores with the same diameter was lower in samples prepared at 200 and 250° C. Between the first and seventh day of rehydration we recorded a decrease in the volume of pores with a diameter of 3.8 nm at rehydration temperatures 200 and 250° C. From the IR spectra of samples treated at 175° C the characteristic kaolinite bands have developed. The Al - OH stretching (3800 - 3500 cm^{-1}) and bending modes (940 and 910 cm^{-1}), along with $Al\text{-}O_6$ stretching, are useful for monitoring kaolinite rehydroxylation. In our study the intensities of the $Al\text{-}O_6$ stretching band at 523 cm^{-1} were used as a check of the rehydration process. Since the tetrahedral deformation of Si-O-Si band near 460 cm^{-1} did not shift significantly throughout the rehydration process, it could be used as a semiquantitative internal standard for comparison purposes. The rehydration of metakaolinite to kaolinite strongly depended on the temperature and time of hydrothermal process. The optimum transformation from the point of view of the surface properties was observed after longer-term autoclaving (4-7 days) at 175° C, when the specific surface S_{BET} of raw kaolinite increased more than three times.

PHOTOCATALYTIC ACTIVITY OF MONTMORILLONITE?

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Many papers have been dedicated to the photodecomposition of organic compounds by using clay catalysts in literature. The catalytic activity was ascribed to the photo-Fenton reaction of ferric ions located in clay structures or leached to the aqueous phase. In general, the Fenton reaction consists in the oxidation of Fe^{3+} to Fe^{2+} by hydrogen peroxide in the presence of strong acid. In the photo-Fenton reaction hydrated Fe^{3+} ions absorb photon forming hydroxyl radicals that are very strong oxidation agents with the high standard electrochemical potential of $E^o = 2.6$ V to 2.8 V. They are often used for the decomposition of organic compounds at e.g. wastewater treatment processes.

Ferrous ions are then back oxidized to ferric ones by oxidants such as dissolved oxygen and hydrogen peroxide. The reaction of $Fe(OH)^{2+}$ is based on absorption of UV irradiation which can be often decreased by the presence of other absorbing compounds. This condition is very limiting for the decomposition of organic compounds especially in real systems containing also solid particles. Some comprehensive reviews on application of clays for the Fenton (Navalon et al., 2010) and photo-Fenton (Herney-Ramirez et al., 2010) reactions have been published in literature.

Photocatalytic activity of Na-rich montmorillonite (MMT) was evaluated by means of the photodecomposition of phenol. The decomposition under UV irradiation (medium pressure Hg lamp) with and without MMT proceeded according to the second order reaction of phenol and hydroxyl radicals. Hydroxyl radicals were produced by the reactions of dissolved oxygen and electrons released from exited phenol molecules. MMT decreased the photodecomposition reaction rate because of scattering of UV irradiation on its particles and, therefore, no catalytic activity was observed. The photo-Fenton reaction of free iron ions leached from MMT was not observed as well. On the other hand, the nanocomposite of ZnS and MMT (Kozák et al., 2010) used for comparison exhibited significant photocatalytic activity indicated by a higher photodecomposition efficiency and the pseudo-first order reaction kinetics. The change of the reaction kinetics from the second order to pseudo-first order one indicates the production of high concentrations of hydroxyl radical by the ZnS nanoparticles.

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PHOTOCATALYTIC DECOMPOSITION OF N_2O ON NANOCOMPOSITE OF ZINC SULPHIDE NANOPARTICLES AND MONTMORILLONITE

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The decomposition of nitrous oxide (N_2O) is an important reaction for reducing the global air pollution because of its contributions to stratospheric ozone destruction and greenhouse effect. The photocatalytic decomposition of N_2O under UV irradiation on semiconductor photocatalysts is one of the candidate methods for its removal.

ZnS nanoparticles were prepared and deposited on montmorillonite (MMT) in the presence of cetytrimethylammonium (CTA). UV spectrometry and transmission electron microscopy proved the formation of nanoparticles with diameters ranging from 3 nm to 5 nm (Kozák et al., 2010). The photocatalytic reaction was carried out in a homemade apparatus at ambient temperature. A batch annular reactor was filled with 990 ppm N_2O/He mixture and illuminated by an 8 W Hg lamp with a peak light intensity at 254 nm (Kočí et al., 2012). The reaction products were analyzed by gas chromatography.

The effect of irradiation time on the photocatalytic decomposition of N_2O was studied for the nanocomposite of ZnS nanoparticles and MMT (ZnS-MMT) and for commercial TiO_2 catalysts (Evonik P25). The UV irradiation of both ZnS-MMT and TiO_2 led to the photocatalytic decomposition of N_2O into N_2 and O_2. ZnS-MMT was more photocatalytic active than TiO_2. The N_2O conversion of 79 % after 24 hours was reach over ZnS-MMT. Its reaction kinetic corresponds to the first-order reaction rate, which is in agreement with plausible reaction mechanisms.

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CHARACTERIZATION OF ALUMINO-SILICATE HYDRATE GELS FORMED IN ALKALINE MEDIA

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Alkaline activated binders (geopolymers) contain alumino-silicate hydrate phases which strongly differ in their composition and structure. The solidification of the binders is cause by the chemical reaction of a reactive alumino-silicate with an alkaline solution via a sol-gel transformation and polycondensation. As a result of this, amorphous and semicrystalline phases will be formed, depending on the composition of the reactive solids and activator solutions. This reaction process requires high concentrations (up to 6 mol/l) of hydroxid ions in the starting solution.

Aim of this study was to investigate how the composition of the starting mixture influences the formation of the alumino-silicate hydrate gels in alkaline media. Alumino-silicate hydrates were produced from mixtures of alkali-aluminate solution and nanosilica powder at temperatures from 20 to 60° C. A few experiments were repeated by addition of kalcium components to the mixtures, respectively. Further experiments were made using metakaolin as partial alumino-silicate source. The molar ratio Si : Al in the mixtures was varied from 1.0 : 1.1 to 1.0 : 5.5. The pH value of the starting mixture was varied from 12 to 14, by adding of NaOH or KOH. After the reaction, the solid phase (gel) was separated from the liquid phase and subsequently frozen and lyophilized. The resulting solids were characterized by means of chemical analysis, molybdate test, FTIR, XRD, NMR. ICP-OES was used to analyze the supernatant solutions.

The reaction process is influenced by the amounts of soluble silicate and aluminate in the mixture. Although, the solubility of the nanosilica is depending on the pH value generated in the system. Increasing the pH value (12 to 14) of the starting mixture and increasing the temperature during the synthesis (20 to 60° C) enhanced the formation of solid phases and zeolite like structures could be obtained in the solids. By all means, the solid phase is predominantly composed of amorphous alumino-silicate hydrate phases with high amounts of alumina in their structure (Si : Al ≈ 1). Calcium ions, present during the synthesis can be embedded in the geopolymer gel or in calcium silicate hydrate phases formed. Changes in the composition and structure of the resulting solids will be discussed in respect to the stability of building materials made of alkaline activated binders.

ADSORBENTS FOR HEAVY METALS REMOVAL OBTAINED BY SELECTIVE LEACHING OF VERMICULITE

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Vermiculite is natural clay mineral with layered structure. It consists of octahedral alumina or magnesia sandwiched between two tetrahedral silicate sheets. Net negative charge is compensated by interlayed cations such as K^+, Mg^{2+}, Fe^{3+}. Due to low cost and availability mineral has been exploited in many applications: accumulation of water, adsorption of heavy metals, oil, humic acids and pesticides (Vieira dos Santos, Masini J.C., 2007; Abate et al., 2006). However, as it is in the case of other clays and clay minerals, many techniques, such as: pillaring with polycations or selective leaching, were proposed to improve chemical properties of the mineral, its morphology and texture (Chmielarz et al., 2009).

In presented work, acid treated vermiculites were used as low-cost and active adsorbents for reducing of environmental pollution with heavy metals. Treatment was performed at elevated temperature (45 or 95° C) for 2 and 24 h in three different solutions of the following acids: HCl, HNO_3 and H_2SO_4. Starting material and modified samples were studied using physicochemical methods: XRD and FT-IR (structure), chemical analysis, DRS-UV-Vis (leaching of Fe), N_2 adsorption (surface area). Adsorption capacity towards heavy metals (Fe, Cu, Cr) was studied in column and semi-batch mode. It was shown that acid-modified samples are effective in removal of heavy metals due to formation of porous structure during acid treatment.

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Cu-Mg (Zn)-Al (Fe) HYDROTALCITE DERIVED MIXED OXIDES AS CATALYSTS FOR AMMONIA OXIDATION INTO NITROGEN AND WATER VAPOUR

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The process of low-temperature selective catalytic ammonia oxidation to nitrogen and water vapour (SCO): $4\ NH_3 + 3\ O_2 \rightarrow 2\ N_2 + 6\ H_2O$, seems to be the most promising method for elimination of ammonia from oxygen contaning waste gases. Catalysts dedicated for this proces should be active, selective and stable in a broad temperature range.

Hydrotalcites (HTs) with intended Cu-Mg(Zn)-Al(Fe) molar ratios of 0:1:1, 0.6:1.4:1.0 were used as precursors of catalysts for the SCO process. Precursors were synthesized by co-precipitation method using aqueous solutions of the metal nitrates and then calcined at 600 or 900°C in order to obtain mixed metal oxides with spinel phases. XRD, BET, UV-vis-DRS techniques were used for characterization of the obtained materials. Detailed studies of thermal transformation of obtained HTs into metal oxide systems were performed using: HT-XRD, TGA-DTA-MS, TPR. The HTs calcined samples were tested in the role of catalysts for the SCO reaction. Catalytic tests were performed in a fixed-bed flow microreactor system. Some of the results of catalytic tests are shown in Fig 1.

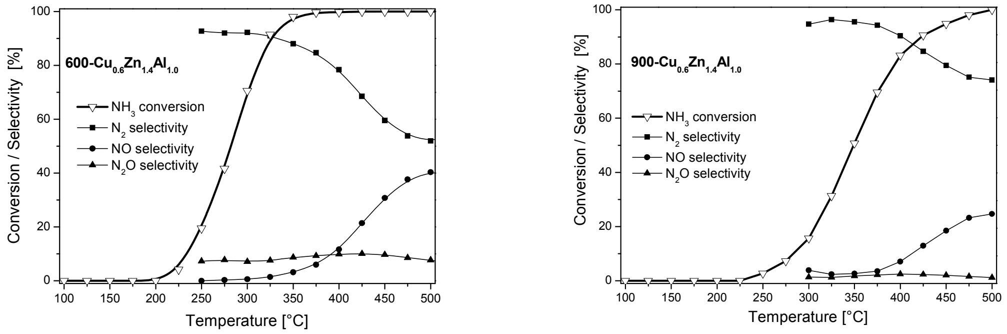

Fig. 1. Selective catalytic oxidation of ammonia over hydrotalcite derived catalysts

Mixed metal oxides obtained from hydrotalcites have been found to be very interesting systems for the SCO process. It was shown that chemical, phase composition of the catalysts as well as the temperature calcination determine their performance in the studied process. Conversion of ammonia increases with an increasing substitution of Mg^{2+} by Cu^{2+} or Zn^{2+} cations as well as Al^{3+} by Fe^{3+} cations.

HYDROTALCITE-DERIVED Cu-Mn-Al AND Co-Mn-Al MIXED OXIDE CATALYSTS FOR TOTAL OXIDATION OF TOLUENE: THE ROLE OF Ce AND Zr ADDITIVES

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Cu- Co- and Mn-containig mixed oxides belong to the most active oxide catalysts for the total combustion of volatile organic compounds (VOCs). Of particular interest are catalysts derived from hydrotalcite-like (Htl) precursors, which upon thermal decomposition yield nanocrystalline mixed oxides with high dispersion of all metallic components. The aim of this work was to determine the influence of the addition of cerium and zirconium on the physico-chemical and catalytic properties of two catalytic formulations based on Cu-Mn-Al and Co-Mn-Al mixed oxides, with Cu(Co):Mn:Al ratio = 4:4:1. Both dopants are modifiers frequently used in commercial total oxidation catalysts.

Htl precursors were synthesized by the co-precipitation method at constant pH=9, at 55° C, with the use of nitrate salts of metallic elements – Cu, Co, Mn, Zr, Ce, Al. Subsequently the precursors were converted to mixed oxides by calcination at 450° C for 3 h and used as catalysts for the total oxidation of toluene. Apart from the basic formulations, the following compositions were synthesized: Cu(Co):Mn:Al:Zr = 3.5:4:1:0.5, Cu(Co):Mn:Al:Ce = 3.9:4:1:0.1, Cu(Co):Mn:Al:Zr:Ce = 3.4:4:1:0.5:0.1.

Physicochemical properties of precursors and mixed oxides were determined using XRD, ICP OES chemical analysis, FTIR spectroscopy, MS EGA thermal analysis, N_2 adsorption/desorption at 77K, SEM-EDS, H_2 TPR. XRD patterns of all precursors indicate the presence of the carbonate form of HTl structure. In Co-containing samples some amount of $MnCO_3$ (rhodochrosite) is present as well. In calcined materials the most intense reflections of the spinel-like oxides are visible - $Cu_{1.5}Mn_{1.5}O_4$ in Cu-containing samples and $CoMn_2O_4$ – with significantly lower crystallinity – in materials containing Co. The replacement of Cu with Co leads to the formation of the mixed oxide systems with the specific surface area values significantly higher (up to 80 %) than in the case of Cu-based precursors.

All tested catalysts are very active in the total oxidation of toluene, showing 100 % conversion of toluene already at the temperatures approaching 200° C. Influence of the modification of the catalysts composition on their catalytic activity is different for Cu and Co-based series. In the case of Cu-containing catalysts, both additives, but particularly Zr, worsen to some extent the catalytic performance. No such phenomenon is observed in the Co-based series. In contrast, both additives improve slightly the catalytic performance in the low temperature range (100-150° C). The effect is discussed in terms of the catalysts physico-chemical properties.

Acknowledgement

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INFLUENCE OF SELECTED SYNTHESIS PARAMETERS ON THE PHYSICOCHEMICAL PROPERTIES OF HYDROTALCITE-DERIVED Cu-Mn-Al MIXED OXIDES

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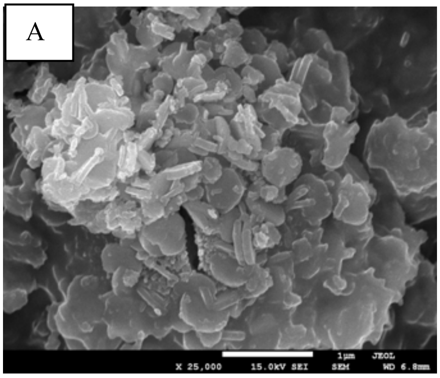
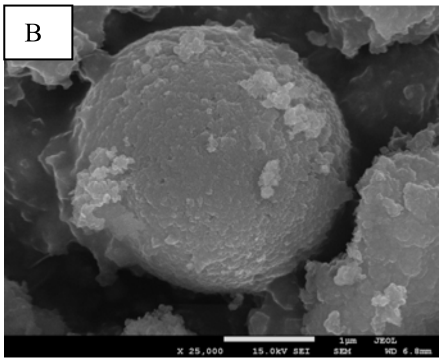
Hydrotalcite-like (Htl) precursors are often used in the synthesis procedures of the mixed oxide type catalysts, because of their ability to produce, after thermal decomposition, nanocrystalline oxidic phases with homogeneous dispersion of metallic elements. The purity of hydrotalcite-like phase, crystallinity of the precursor and the specific surface area value of the calcined materials are factors of key importance in determination of the catalysts properties. In the presented study the role of two synthesis parameters was followed in detail: the saturation level of the mother liquor and the synthesis temperature.

The series of Htl precusors with the nominal composition CuMnAl (1:2:1) were obtained at high or low saturation (the reagents were, respectively, either mixed quickly or slowly added dropwise at constant pH). Synthesis was carried out at 7, 22, 55 or 90° C. The Htl precursor were then calcined at 450°C. The samples were characterized with XRD, FTIR spectroscopy, ICP OES chemical analysis, thermal analysis (MS EGA), N_2 adsorption/desorption at 77 K and SEM measurements.

XRD of precursors shows the presence of well crystalline main phase of the carbonate form of Htl CuMnAl compound (61-99 % - A) and the rhodochrosite ($MnCO_3$) side phase (1-39 % - B). The results of both FTIR and SEM-EDS analyses also show that in all samples some amount of $MnCO_3$ appears next to the main Htl component. The samples obtained at high saturation of reagents contain more of Htl phase (81.5-99 %) and less of highly crystalline rhodochrosite (16-28 nm), than the materials synthesized at low saturation. Synthesis at 90° C leads to the formation of the practically pure Htl phase (relative content ≥ 98 %). The specific surface area values of obtained Cu-Mn-Al mixed oxides are in the range 103-145 m²/g. Results of this work allowed for the optimization of the phase composition, phase crystallinity, and specific surface area of a Cu-Mn-Al mixed oxide combustion catalyst.





Acknowledgement

This work is a part of an ERDF financed project POIG.01.01.02-12-065/09 "VOX".

Clays in absorption and intercalation processes

Poster presentation

ALTERNATIVE SORBENTS FOR ARSENIC REMOVAL: PUMICE AND SEPIOLITE

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Arsenic is usually found in the environment combined with other elements such as oxygen, chlorine, and sulfur. Arsenic combined with these elements is called inorganic arsenic. Inorganic arsenic occurs naturally in soil. The concentration of arsenic in soil varies widely, generally ranging from about 1 to 40 parts of arsenic to a million parts of soil (ppm). The natural occurrence of arsenic in groundwater is directly related to the arsenic complexes present in soils. Severe human health effects have been observed in populations that are exposed to persistent arsenic in groundwaters destined for potable, drinking water applications. Generally, trivalent arsenic compounds are more toxic than pentavalent arsenic compounds. Due to the high toxicity of As, remediation of As contaminated groundwater, therefore, is necessary to protect the environment and the public health.

Pumice and sepiolite are inexpensive and natural minerals available locally, coated by iron oxide and used as adsorbents for the removal of arsenic ions from drinking waters in batch experiments. The kinetics of the adsorption process was tested for the pseudo-first order and pseudo-second order and intra-particle diffusion models. The rate constants of adsorption for all these kinetic models were calculated. The comparison among the models showed that the pseudo second-order model best described the adsorption kinetics. Langmuir, Freundlich and Dubinin-Radushkevitch isotherm models were applied to the experimental equilibrium data and the isotherm parameters were determined.

The results indicated that the iron oxide coated pumice and sepiolite could be alternative adsorbents for arsenic ion removal.

THE IMPACT OF EC AND pH ON THE ADSORPPTION OF Zn AND Cd BY PALYGORSKITE MINERAL

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In this study, a natural palygorskite clay from (Dogtown, Florida USA) was selected as an adsorbent, and the adsorption capacity of Cd (II) and Zn (II) onto the adsorbent was investigated. The effects of parameters such as EC, pH of suspension solution, and amount of particle size of the adsorbent on adsorption capacity for Cd (II) and Zn (II) were studied. To understand the adsorption mechanism, the variation of the pH and EC (S·m-1) of the Cd (II) and Zn (II) solution in the adsorption process and the different adsorption models that can describe the adsorption of Cd (II) and Zn (II)) onto natural palygorskite were determined.

The effects of various experimental parameters were investigated using a batch adsorption technique. Adsorption of Cd and Zn by pure palyorskite as a function of pH (pH 6, 8 and 10), EC (EC 4, 6 and 8) and the amount of Cd added range from 0-100 mg/L to this mineral were studied. The shape of the isotherm were L1 and L2 type isotherm for the sorption of Zn (II) and L2 type isotherm only for the sorption of Cd (II). The basic mechanism governs the Cd adsorption characteristics of palygorskite at studied pH is adsorption and ionic exchange. However, for Zn (II) the adsorption on the pure palygorskite show similar trend as Cd at low pH and EC but at high pH values the adsorption of Zn was minmal comparing with Cd suggesting a precipitation. The results were fitted to both the Langmuir and Freundlich isotherms. Satisfactory agreement between experimental data and the model-predicted values was expressed by the correlation coefficient (R2). The fitness of the adsorption data of the adsorption of Cd and Zn on palygorskite into the Freundlich isotherm confirmed its heterogeneous nature. Data from this study proved that metal cations from aqueous solution can be adsorbed successfully in significant amounts by palygorskite.

INVESTIGATION OF MONTMORILLONITE HYDRATION BY NEAR IR SPECTROSCOPY

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Hydration properties of smectites are very important for many natural and industrial processes. The interaction of water with montmorillonite saturated with different exchangeable cations was investigated by near-infrared (NIR) and gravimetric techniques. The objective of this study was to evaluate the effects of exchangeable cations on the amount of water adsorbed on montmorillonite. The < 2 μm fraction of JP montmorillonite (Jelšový Potok, Slovakia) saturated with Li^+, Na^+, K^+, Mg^{2+}, Ca^{2+} and Zn^{2+} cations was used for the study. NIR spectra were obtained by UpDRIFT accessory enabling the measurements of the samples directly in closed glass vials. Combination band of water molecules, $(\nu+\delta)_{H2O}$, near 5250 cm^{-1} was used to follow the hydration of the samples. Difference in the area of this band at 52 % and 0 % relative humidity (RH) reflected the quantity of adsorbed water. The influence of time on the extent of hydration was examined. The NIR spectra showed the most pronounced increase of the water content within first three hours. For K-montmorillonite the hydration reached maximum after 12 hours while for Mg at least 24 hours was needed. To be sure that each sample adsorbed the maximal amount of water at 52 % RH, 48 hours was chosen for the experiments. Both, NIR spectra and gravimetric analysis demonstrated the evident effect of the exchangeable cations on the hydration of montmorillonite. The water content increased in order $K^+ < Na^+ < Li^+ < Ca^{2+} < Mg^{2+} < Zn^{2+}$ in dependence on the hydration energy of the cations. Gravimetric analysis detected the highest amount of water for Zn-form (15 mass %) and the lowest for K-form (7 mass %). The $(\nu+\delta)_{H2O}$ band areas plotted as a function of water content obtained from the gravimetrical analysis showed good correlation ($R^2 = 0.9039$) indicating that NIR spectra can be used for estimation of water content within the sets of similar samples. The exchangeable cations affected also the strength of hydrogen bonding between water molecules and thus also the position of $(\nu+\delta)_{H2O}$ band. The increasing ionic potential (ratio of valence to ionic radius) of the exchangeable cation caused shift of this band from 5253 cm^{-1} (K^+) to 5242 cm^{-1} (Zn^{2+}) in order: $K^+ \Rightarrow Li^+ \cong Na^+ \Rightarrow Ca^{2+} \Rightarrow Mg^{2+} \Rightarrow Zn^{2+}$. The obtained results confirmed that NIR UpDRIFT technique is very useful method giving information on hydration of montmorillonites.

Acknowledgement

This contribution is the result of the project implementation: Centre for materials, layers and systems for applications and chemical processes under extreme conditions supported by the Research & Development Operational Programme funded by the ERDF.

EFFECT OF HEATING ON PHYSICO-CHEMICAL PROPERTIES OF Cu-MONTMORILLONITE

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Smectites with their exceptional sorption and swelling abilities are important components of the barriers for toxic and nuclear waste deposits. Several factors, such as the temperature, pH, presence of competitive ions and organic ligands, etc., affect their properties. The exchangeable cations get dehydrated upon heating and migrate towards or into the smectite layers, subsequently affecting the sorption and swelling. The effect of thermal treatment on the sorption and spectral properties of Jelšový Potok (Slovakia) montmorillonite saturated with Cu^{2+} cations (CuJP) was examined. Infrared spectroscopy and powder X-ray diffraction analysis were used to investigate the changes in the structure upon heating. The interlayer distance decreased with the increasing temperature of heating, causing a move of the d_{001} diffraction to higher 2θ values. The shift of the Si–O vibration bands to higher wavenumbers, as well as the changes in the bending vibrations of the OH groups indicated that Cu^{2+} ions got trapped in the ditrigonal cavities of the tetrahedral sheet. Fixation of Cu^{2+} was dominantly irreversible, as can be seen from the cation exchange capacity value for CuJP heated at 300 °C reaching only 18 % of the parent clay value. Water, dimethyl sulfoxide (DMSO) and acetonitrile (AN) were utilized to depict the solvation ability of heated CuJP samples. The amount of adsorbed solvent was determined by gravimetric analysis and compared with the changes in the interlayer distance. The amount of adsorbed solvents (mg/g) on unheated CuJP decreased in the order DMSO > AN > water. The amount of adsorbed water decreased with the temperature of preparation, while only a small decrease in the amounts of adsorbed DMSO and AN was observed, in accord with higher dipole moments of these solvents. Heated and solvated samples were also studied by electron spin resonance spectroscopy. The Cu^{2+} complexes in the interlayer space showed a weakly rhombic distortion and distinctive hyperfine coupling constants not observable in the spectra of the samples heated above 150 °C. The broadening of spectral lines as well as the loss of hyperfine structure was mainly caused by the dipole-dipole interactions of unpaired electrons on Fe (III) in the mineral layers.

REMOVAL OF Cu^{2+} FROM COPPER FLOTATION WASTE LEACHANT USING SEPIOLITE: FULL FACTORIAL DESIGN APPROACH

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With rapid growth of industrialization, there is pressure all over the world on available land, not only for housing and industrial complexes, but for land-filling as a means of disposing huge quantities of waste generated from industrial and mining-mineral processing operations. The release of large quantities of heavy metals into the natural environment has resulted in a number of environmental problems. The metals of most immediate concern are Cu, Cr, Mn, Fe, Zn and Cd. Copper flotation waste which is the product pyrometalurgical production of copper from copper ores contains materials such as iron, alumina, calcium oxide, silica, etc. 1.5-2 million tons of slags and copper flotation waste were collected in Samsun Copper Factory in Turkey. Up to now this waste is disposed without controlling to open land. The toxic metals present in the copper flotation waste such as Cu, Zn, Co and Pb affect rich underground water resources and surface waters by leaching with precipitation which is very high in the region. A variety of techniques can be used for decontaminating and remediating copper slag. Environmental remediation technologies include in situ or ex situ techniques for decontaminating the polluted fields, such as soil-washing, physical separation, phytoremediation and leaching.

The aim of the present study is to investigate the safe disposal of the copper flotation waste by using sepiolite. 2^3 full factorial designs were employed to study the effect of three factors which are contact time, adsorbent dosage of the sepiolite and pH at two levels.

FACTORIAL EXPERİMENTAL DESIGN FOR ADSORPTION SILVER FROM WATER ONTO MONTMORILLONITE

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This research work involved the use of factorial design technique to investigate the adsorption of silver from water onto montmorillonite. There is a growing interest in using low-cost and commercially available materials for the adsorption of heavy metals. Of all the various water-treatment techniques, adsorption is generally preferred for the removal of heavy metal ions due to its high efficiency, easy handling, availability of different adsorbents and cost effectiveness. Attention has been focused on the development of the substitutes from natural clay minerals. This shift in attention is predicated on the surface properties of these materials. Clay particles are strongly anisotropic and exhibit faces and edges, which are very different in surface area and in chemical behavior. It has been reported that the abundance of clay minerals and their low cost has posed them a strong candidate as adsorbent for removal of heavy metal from wastewater. In this study, a factorial experimental design technique was used to investigate the adsorption of silver from water onto montmorillonite. Factorial design of experiments is employed to study the effect of two factors montmorillonite dosage (0.1 and 1.0 g/L) and initial concentration (20 and 100 mg/L) at the levels low and high. The efficiency of silver adsorption was determined after 60 min of treatment. Main effects and interaction effects of two factors were analyzed using statistical techniques. A regression model suggested and it was found to fit the experimental data very well. The results were analyzed statistically using the Student's *t*-test, analysis of variance, F-test and lack of fit to define most important process variables affecting the percentage silver adsorption.

CLAY MINERALS IN DECONTAMINATION PROCESSES OF AQUEOUS SYSTEMS

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Clays have many useful properties which can be used in decontamination processes of aqueous systems. Due to their high specific surface area, high ion-exchange capacity or purchase cost they are very often used as effective adsorbents.

This work deals with comparison of sorption effectivity of two problematic contaminants - arsenic and antimony oxyanions. Arsenic and antimony are toxic elements of natural origin but their occurrence in environment is also caused by various branches of industry. Sorption of arsenic oxyanions has been deeply described but there are very limited informations about sorption, toxicity and behavior of antimony in environment so far.

The aim of this work is to find optimal conditions and suitable materials for the removal of arsenic and antimony oxyanions from model aqueous solutions. For this purpose, clay materials (especially bentonite and kaolinite) and iron oxide-hydroxides have been used.

All materials have been characterized by X-ray diffraction and X- ray fluorescence. Sorption capacities of adsorbents have been determined and sorption effectivities have been calculated. The kinetic of sorption reaction has been also measured for determination of optimal reaction time. Antimony very often follows arsenic in environment, that´s why competitive sorptions have been measured eventually.

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INTERCALATION OF PARACETAMOL INTO THE HYDROTALCITE-LIKE HOST

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Hydrotalcite-like compounds are often used as host structures for intercalation of various anionic species. The product intercalated with the nonionic, water-soluble pharmaceuticals paracetamol, N-(4-hydroxyphenyl)acetamide, was prepared by rehydration of the Mg–Al mixed oxide obtained by calcination of hydrotalcite-like precursor at 500 °C. The successful intercalation of paracetamol molecules into the interlayer space was confirmed by powder X-ray diffraction and infrared spectroscopy measurements. Molecular simulations showed that the phenolic hydroxyl groups of paracetamol interact with hydroxide sheets of the host via the hydroxyl groups of the positively charged sites of Al-containing octahedra; the interlayer water molecules are located mostly near the hydroxide sheets. The arrangement of paracetamol molecules in the interlayer is rather disordered and interactions between neighboring molecules cause their tilting towards the hydroxide sheets. Dissolution tests in various media showed slower release of paracetamol intercalated in the hydrotalcite-like host in comparison with tablets containing the powdered pharmaceuticals.

THE ADSORPTION PROPERTIES OF DIFFERENT SOIL TYPES

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Soils represent the dynamic natural system created by pedogenesis processes including especially weathering of parents materials. They are multicomponent formation containing solids, liquids and gaseous components. Soils have important role in the storage and circulation of chemical elements in the environment. Five standard soils have with different texture, structure and density have been used in these work. The clay and sand portion, Fe, Al and organic C content, CEC (cation exchange capacity), hydrolytic acidity, pH and pH_{ZPC} and specific surface (A_{BET}) of these soils have been measured. In Table 1 you can see some soil characteristic.

Tab. 1. Characteristics of investigated soils

	$C_{org.}$	Fe	CEC	pH_{CaCl2}	pH_{ZPC}	A_{BET}	Soil type
	%C	mg. g^{-1}	meq. $100g^{-1}$			$m^2\ g^{-1}$	
1	0.68	2.9	4	5.1	8	1.9	sand
2	1.93	4.3	10	5.5	8	3.0	loamy sand
3	0.99	8.73	10	6.7	7	10.7	sandy loam
4	2.53	20.42	29	7.1	7	16.9	loamy sand
5	1.66	28.73	23	7.1	9	42.5	clay

The model sorption of toxic As, Se and Sb oxoanions have been investigated subsequently. Dependence of soil adsorption properties on their characteristic were measured and compared. It was found that adsorption capacities of each investigated soil are dependent on Fe content especially. The specific surface values and amount of organic Carbon are important in adsorption processes too. The dependence of adsorption effectivity on clay content was not observed.

Acknowledgments

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METHOXY-KAOLINITE: A PRECURSOR FOR THE INTERCALATION OF METHYLENE BLUE AND BENZOIC ACID

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Kaolinite is a 1:1 layered, dioctahedral phyllosilicate with $Al_2Si_2O_5(OH)_4$ chemical composition. In contrast to 2:1 smectites, the inner surface OH groups of the octahedral sheet are available for grafting reactions with selected organic molecules. Kaolinite reaction with methanol leads to formation of a methoxy-kaolinite (Matusik et al., 2012). Such modification of the octahedral sheet changes its character to hydrophobic. Thus the intercalation of several organic molecules becomes possible. Spectral properties of the dye-intercalated clays and structures containing aromatic molecules which can be used as fillers for the polymer nanocomposites preparation are of interest. Therefore, the research objective was to investigate the possibility of methylene blue (dye) and benzoic acid (carboxylic acid) intercalation into kaolinite using methoxy-kaolinite as a starting material.

For the experiments a Maria III kaolinite from Polish deposit (Lower Silesia region) was selected. It is a highly ordered kaolinite with Hinckley index equal to 1.31. In the first step a pre-intercalate with dimethyl sulphoxide was prepared (MDS). Afterwards the dried MDS was washed 6 times with methanol to obtain a methoxy-modified kaolinite (MM). The wet MM was reacted with a methanol solution of methylene blue (MB) and benzoic acid (BA) which led to formation of MBM and MBA samples, respectively.

The results indicated that the use of the MM enabled the intercalation of MB and BA in contrast to MDS pre-intercalate where the intercalation was not successful or took place to a very small extent. The d_{001} value of the MBM was equal to 17.5 Å (wet sample) and 15.1 Å (dried sample). The decrease of the d_{001} was due to removal of mobile methanol molecules from the interlayer during drying. Simultaneously the 11.2 Å peak of the wet MM was shifted to 8.7 Å which is characteristic for the dried MM. The presence of the 8.7 Å peak suggested that part of layers was not intercalated. In turn, for the dried MBA the d_{001} value was equal to 14.4 Å and the MM peaks were not found indicating high intercalation ratio. For both intercalates the changes attributed to the incorporation of the organic molecules into the interlayer were observed in the IR spectra: OH groups and Si-O vibration bands were altered in comparison to the MM precursor. The C-H stretching and bending vibrations assigned to the MB and BA were observed. The DTA/TG analysis showed that in addition to the intercalated MB the material contained also an excess of the MB which crystallized on the mineral surface. The approximate models of the intercalates were proposed.

Acknowledgments

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THE INFLUENCE OF SWELLING CLAY MINERALS ON THE BEARING CAPACITY OF SOIL

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The municipality of Pulkau, a small town with only 1600 inhabitants, is situated in the north of Lower Austria, near the border to the Czech Republic. People tend to move to larger cities, mostly Vienna. An important contribution against migration to cities is the creation of jobs and the provision of land for building plots. Major problems to find appropriate building plots are the clay-rich subsoil in this area, as well as floods caused by the river Pulkau.

The investigation area, the so-called Pulkautal, is located in the north-eastern part of the molasse and is underlaid by the Crystalline of the Bohemian Massif. The molasse consists of clay schists and conglomerates, further marine sediments of the Pielacher Tegel, Melker Sands, clay schists, marly clay of the Zogelsdorf Formation and the Zellerndorfer Schlier. Zellerndorfer Schlier in particular is very problematical for building construction, because high amounts of the fine fraction of the Zellerndorfer Schlier consist of smectite. Since decades the Zellerndorfer Schlier is responsible for settlement, landslides and causes severe damages on buildings.

By means of bulk and clay mineral analysis with X-Ray Diffraction (XRD), Simultaneous Thermal Analysis (STA), Fourier Transform Infrared Spectroscopy (FTIR) and grain size analysis the clay minerals and the amount of swelling clay minerals in the soils were characterized. Further important parameters and analyses are the actual water content, Atterberg limits and shearing test.

The content of swelling clay minerals is an important matter in terms of construction stability. Plots with a high content of smectite are not suitable as building plots. Expensive construction measures are necessary to provide stability. Results of investigations provide information, which sites are suitable for building and which are not.

HDTMA MODIFIED NATURAL CLAYS IN REMOVAL OF AFLATOXIN B1

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Aflatoxins are acute carcinogenic substances that cause mutations in genes of human organs. They are prevalent especially in tropical regions, like Thailand. Aflatoxins occur as contaminants of grain worldwide. An adsorptions of Aflatoxins by modified clay minerals with surfactant to increase their hydrophobicity are very interesting. Therefore, the aim of this work was to characterize and evaluate the affinity of clays modified with hexadecyltrimethylammonium chloride(HDTMA) for in vitro adsorption of aflatoxin B1. Under modification of bentonite, kaolin and halloysite with different concentrations of HDTMA: 0.3, 0.6, 1.3, 2.0, 4.0 and 6.0 mM, the extended interlayer spacing (d_{001}) of an organobentonite related to the concentrations of HDTMA was found to be an S-curve. The d_{001} of organobentonite was extended from 14.68 Ã to 23.33 Ã at 6.0 mM, while the value of d_{001} was almost constant for organokaolin (7.17 Ã to 7.29 Ã) and organohalloysite (7.33 Ã to 7.40 Ã). DTA profiles showed that at high HDTMA concentrations, there were at least three different interactions of adsorbed HDTMA on organobentonite. In the adsorption study of aflatoxin B1 (AFB1), the chromatogram of standard solutions showed only one peak of AFB1 with retention time of 6.9 min. But in the presence of clay minerals or H+, a new peak appeared at around 4.4 min. The new peak was the enol form of AFB1 which could exist in both acidic and basic aqueous suspension of clays. In all cases, the organoclays could tremendously adsorb AFB1 as comparing to the clay minerals. The ability of organobentonite to adsorb AFB1 depended significantly on the amount of adsorbed HDTMA within the clay layer.

ADSORPTION PROPERTIES OF LOESS AND OVERLYING TOPSOIL OF THE CONTINENTAL LOESS SECTIONS IN NORTHWESTERN CROATIA

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Four loess sections situated in northwestern Croatia (Gušćerovec, Rovišće, Ludina and Kloštar Ivanić), approximately 10 m in depth, were investigated for their adsorption properties. In each section the samples were collected at three horizons: topsoil excluding the uppermost 15 cm, intermediate zone (soil-loess transition) being 40-50 cm in depth, and loess horizon at various depths. A change in bulk mineralogical composition, iron and manganese oxyhydroxides and organic matter content was monitored and compared to a change in cation exchange capacity throughout the investigated sections.

Granulometric analysis of the loess samples showed that the silt fraction predominated ranging 55-75 %. Clay fraction ranged between 24-43 %. The sediment can be classified as very fine grained silt.

Bulk mineral composition was determined by X-ray diffraction, and clay minerals were mutually differentiated upon saturation with ethylene glycol, and heating at 400 and 550° C. Content of iron and manganese oxyhydroxides was determined by oxalate method (in darkness), and that of organic matter by heating at 375 °C overnight. Cation exchange capacity (CEC) was determined by copper ethylenediamine complex at pH 7.

Mineral composition of topsoil, intermediate zone and loess comprises quartz and illite-muscovite as main constituents with subordinate plagioclase, chlorite, kaolinite and, in some cases, vermiculite. In the investigated profiles the mineral composition does not vary significantly with only illite-muscovite being slightly more abundant in loess than in topsoil. Iron and manganese oxyhydroxides, with iron compounds being more abundant (1.12-7.02 % Fe_2O_3), decrease with depth. Their higher content in topsoil can be related to mineral weathering and pedogenesis. Organic matter content changes irregularly through the sections. CEC values range from 7 to 21 mEq/100 g, and generally increase with depth. Topsoil CEC values range 7-11 mEq/100 g, those in intermediate zone 8-14 mEq/100 g and in loess 14-21 mEq/100 g.

The observed trends of CEC value distribution throughout the investigated loess sections indicate its predominant relation to the phyllosilicate content, especially illite-muscovite. Also, the CEC values correspond well to the mean CEC values of phyllosilicate minerals determined in both topsoil and loess horizons.

PREPARATION OF PHOTOACTIVE LAYERED DOUBLE HYDROXIDES ON AL_2O_3/AL SUPPORT

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Layered double hydroxides (LDHs) are often used as host structures for intercalation of various anionic species. Incorporation of organic photofunctional guests has attracted considerable interest as a means of achieving controllable luminescence and other photofunctional properties. Photoactive molecules such as porphyrins can be excited by visible light to the triplet states that rapidly interact with molecular oxygen by energy transfer to form singlet oxygen, a highly reactive oxidation agent with cytotoxic effects. The LDH films can show novel properties and performances compared with LDH powders. We recently reported the structural and photophysical properties of LDHs intercalated with porphyrin sensitizers; the formation of singlet oxygen followed by its diffusion to solid-liquid or solid-gas interfaces was proven (Lang et al., 2007; Jiřičková et al., 2011).

In this work the Mg-Al and Zn-Al LDHs were prepared on the surface of Al_2O_3/Al support (anodized aluminum foil) during reaction with aqueous solution of magnesium or zinc nitrate under hydrothermal conditions. The deposited products consisted of thin curved LDH platelets with nearly perpendicular orientation to the support. The 5,10,15,20-tetrakis(4-sulfonatophenyl) porphyrin (TPPS) was intercalated into LDH hosts by anion exchange in TPPS aqueous solution. The rehydration of mixed oxides obtained by calcination of deposited LDHs in the aqueous TPPS solution was also applied. Powder XRD patterns of the samples modified with TPPS showed characteristic LDH diffraction lines and increasing d_{003} basal spacing confirmed TPPS intercalation in the interlayer. In the rehydrated Zn-Al samples ZnO was also found. The morphology of LDH crystals persisted after calcination; SEM images of rehydrated products showed formation of very small LDH platelets on the original mixed oxide crystals. The porphyrin photoactivity persisted after its incorporation into the LDHs deposited on Al_2O_3/Al support and production of singlet oxygen after irradiation was detected.

Acknowledgements

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Identification of clay minerals

Oral presentation

CLAY AND IRON MINERALOGICAL STUDY OF MEADOW SOILS FROM A HUNGARIAN WETLAND AREA

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Meadow soils usually characterised by periodic or sustain saturation of water, therefore enhanced mineral weathering, typical organic matter formation and variable redox conditions. These soil forming processes with the presence of reduced iron and decomposition products of organic matters create special conditions for clay mineral formation and transformation. Wetland areas with variable microrelief and ground water levels indicate diverse mineral weathering, clay and iron mineralogy in different pedons within short distances. Seasonal dynamics are also characteristic, iron minerals dissolve or precipitate according to the redox conditions. As a result, spatially and temporally varying mineral features of soils determine trace element flows in wetland systems.

We have investigated three meadow soil profiles from a 8 ha wetland developed on alluvial carbonate sediments between the rivers Danube and Tisza. Soils have been sampled seasonally for a year. We focused on understanding the mineralogical and geochemical changes in the studied area by XRD, XRF and thermal analysis. As iron minerals are sensitive indicators of soil hydromorphism, soil horizons with different iron minerals (goethite, vivianite and probably green rust) were selected for detailed clay mineralogy studies. The influence of fluctuating ground water was tested by wetting-drying experiments at laboratory conditions.

According to XRD results the distribution of illite and chlorite are found vertically homogenous, but in the profiles with the highest ground water level the illite was absent. It is generally found that amount of swelling clay minerals increases with depth in all studied profiles. These mineral distributions indicate alteration of primary silicate minerals to smectites. Swelling minerals are beidellitic and montmorillonitic according to Green-Kelly test. Samples contain low and high-charge smectites as K saturation was followed by 15 Å peak shift to a broad 12-10 Å reflection. Beidellitic character formed likely due to the reduced iron-rich soil pore water. Iron oxyhydroxides such as goethite accumulate in a periodically aerated horizon. These soil layers are also characterised by frequent wetting/drying events which are markedly reflected in the disintegration of smectite layers. Wetting/drying experiments show similar results, we observed the broadening of smectite 15 Å reflection and also transformation of vivianite into goethite. The geochemical analyses indicate that smectite associated with goethite accumulates multiple concentrations of trace elements (Ba, As, Co, Pb) than those which is iron (goethite) free.

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CHARACTERIZATION OF TALC BEFORE AND AFTER SONICATION AND MILLING

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Talc is one of the main strategic industrial minerals of Slovak Republic. Accumulations of talc belong to typical deposits with Mg-carbonates. Major deposits were evolved in Gemeric unit (Early Paleozoic Gelnica group) and in Veporic unit (Early Paleozoic Sinec belt). The main topic of presented results is characterization of talc material. The main method used was XRD. Quantitative XRD analyses of phyllosilicates can be very complicated due to preferential orientation of their crystals. For that reason a McCrone mill, to reach the best possible homogenization, and also side-loaded samples were used. To support the accuracy of analyses a set of talc and pyrite mixtures were utilised. During XRD pattern simulation (RockJock, Eberl, 2003) a systematic error was determined. The similar error was observed after Rietveld analysis (BGMN, Bergmann et al., 1997). The desired accuracy was reached after changing the talc standard in RJ and after preparation of non-oriented samples by shaking of the sample with vertrel and plastic balls (Omotoso and Eberl, 2009). Besides pure talc, talc raw materials with occurrence of varied minerals (mainly magnesite, dolomite, quartz, Mg-chlorite and pyrite) were analysed. Simultaneously with XRD electron microscopy the IR spectroscopy was applied to characterize talc.

The effect of coupled sonication and milling of talc crystals was also studied. Prolonged stand-alone milling may causes aggregation of talc particles. However, the sonication can delaminate crystals while preserving their structure. This behavior can be important in nanocomposites, where shape of filling material (talc) has major influence on nanocomposite properties.

Acknowledgments

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MINERALOGICAL AND CHEMICAL CHARACTERISTICS OF CROATIAN BENTONITES

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In Croatia several bentonite deposits are already described (Braun, 1991; Marković, 2002). The aim of the present study was to obtain additional information on mineralogical and chemical characteristics of bentonites from several deposits: Maovice-Štikovo (Middle Dalmatia, S Croatia), Gornja Jelenska (Moslavina, N Croatia), Bednja and Poljanska Luka (Hrvatsko Zagorje, NW Croatia), and Divoselo (Lika, SW Croatia). In addition bentonite from nearby deposit Šipovo in W Bosnia and Herzegovina was analyzed for comparison.

All of the investigated deposits have been formed by alteration of volcanic material. The deposits' ages range from Upper Jurassic (Maovice-Štikovo), through Lower Miocene (Gornja Jelenska and Bednja), to Upper Miocene (Poljanska Luka). The age of the Divoselo deposit is still unknown due to extensive erosion of the uppermost layers.

The samples (whole rock and <2 µm fraction) were analyzed by X-ray diffraction, FTIR spectroscopy, thermal and chemical (ICP-AES and ICP-MS) methods. The cation exchange capacity (CEC) of the samples was determined with two different methods (ammonia electrode and $[Cu(en)_2]^{2+}$), while the exchangeable cations were measured by atomic emission and absorption spectroscopy. Additionally, the ability of the studied bentonites to adsorb heavy metals (Pb, Cu and Zn) from aqueous solution was measured by atomic absorption spectroscopy.

According to the trace elements content, original volcaniclastic material was andesitic to rhyolitic in composition. As expected the main constituent in all the samples is dioctahedral smectite; montmorillonite in all the samples except in those from Divoselo and Šipovo deposits in which chemical analyses (primarily higher content of Al), lower dehydroxylation temperature as well as the results of the Greene-Kelly test revealed the presence of beidellite. Other constituents, type and quantity of which vary within and between deposits, are clinoptilolite, calcite, quartz, opal-CT and plagioclase. In all the samples the main exchangeable cation measured is calcium. Adsorption of Pb, Cu and Zn on studied bentonites is positively correlated with their CEC. The results showed that analysed bentonites preferentially remove Pb from aqueous solutions containing these heavy metals.

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ORIGIN AND BEHAVIOR OF THE CLAY MINERALS IN A FAULT ZONE: EXAMPLE OF THE POINT VERT FAULT IN THE ANNOT SANDSTONES (SE FRANCE)

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The behavior of fault is closely linked to fluid-rock interactions and newly formed minerals like clay minerals. They can favor the slip weakening behavior of the fault and they are able to modify the permeability of the rocks in the fault zone.

The present study focuses on clay mineral assemblages from the Point Vert normal fault zone located in the Annot sandstones, a Priabonian-Rupelian turbidite succession of the Alpine foredeep in SE France. In this area, the Annot sandstones were buried (6-8 km) below the front of Alpine nappes soon after their deposition and exhumed during the middle-late Miocene. The fault affects arkosic sandstone alternating with pelitic layers, and displays throw of about thirty meters. The fault core comprises intensely foliated sandstone bounding a gouge corridor about 20 cm thick. The foliated sandstones display quartz microfracturation, pressure solution mechanisms, dissolution of K-feldspar and clays concentration along S-C structures. The gouge is formed by a clayey matrix containing fragments of foliated sandstones. The damaged zones features fractures with quartz-calcite fillings.

The aims of the study are to determine the origin and behavior of clay minerals in the fault zone and to estimate their conditions of formation.

Optical and SEM observations show that the clay minerals fraction of the studied rocks is dominated by white micas and chlorite. These minerals have two different origins: detrital and newly-formed. Detrital grains are identified by their larger shape and by their chemical composition with a lower Fe-Mg content than the newly-formed white micas. Newly formed white micas are concentrated along C-S structures or replace K-feldspar. Both types of mica display the same chemical composition suggesting that they formed in same conditions. The newly-formed chlorites are associated with micas along the shear planes. According to microprobe analyses, they present the following structural formula: $(Al_{1,48}\,Fe_{2,50}\,Mg_{1,84})(Si_{2,82}\,Al_{1,18})\,O_{10}\,(OH)_8$. All these data suggest that these clay minerals are synkinematic and they registered the fault activity.

Illite crystallinity measurements and thermodynamical calculations from chlorite chemistry suggest that the main fault deformation occurred under temperature around 220° C, coherent with the maximal burial temperature of the Annot sandstones in this area (deduced from vitrinite reflectance). These data suggest that synkinematic clay minerals registered the fault deformation during the maximal burial of the Annot sandstones. However, the gouge samples have a higher IC index. These data could be explained by a reactivation of the fault at lower temperature (lower burial ?) during the exhumation of the Annot sandstones formation.

CLAY MINERALS FROM LOŠTICE QUARRY

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In North Moravia near the village Loštice by Mohelnice is active rock quarry in the Moravian-Silesian culm. It is the offal which is extracted to the aggregates. Refraction is violated several faults with clay and sand filling. In these filling were studied clay minerals.

In the quarry mined rock is breached several faults, which are both filled with rocks and rubble surrounding both clay and sandy material or healing quartz. Several faults were removed macroscopically different samples fillings. Total of 5 samples were taken. These are, first, the gray-black clayey fill with small pieces into 0.5 cm weathered rock fragments, followed by pure white clayey mass, filling with gray-weathered rock fragments up to 5 cm, reddish yellow panel with rock fragments up to 3 cm and finally filling ocher color with small fragments of rock.

The X-ray diffraction patterns were found diverse association of clay minerals of the kaolinite serpentinite group, mica group minerals, chlorite group and smectites. Specifically, identified kaolinite, illite, smectite and chlorite, and the two species, as 15 Å montmorillonite and probably end member smectite series - beidellit.

QUANTIFICATION OF MASS TRANSFERS RELATED TO CLAY MINERAL REACTIONS AND DEFORMATION IN THRUST FAULT: EXAMPLE OF THE MONTE PERDIDO THRUST

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In sedimentary environment, clays are mains components of rocks and they play a major role in the fault behavior. In the western part of the south Pyrenean zone, a detachment fault related to the Monte Perdido thrust affects the Millaris marls inside the Monte Perdido unit. Hanging wall and footwall of this fault are very homogeneous marls composed of calcite, illite, quartz and chlorite. The fault zone consists of a 10m thick shear zone bounded by two major shear surfaces. In the fault zone, intensely deformed marls are darker than the host marls and feature a well-developed S-C type structure (Lacroix et al., 2011). Scanning electron microscopic images revealed that cleavage is defined by alignment of clay minerals and shows mm-scale S-C geometry. Pressure solution is suggested by the indented morphology of quartz grains along cleavage surface and is probably also responsible for the absence of calcite grains relative to the protoliths.

The aims of the present study are to determine the origin and behavior of clay minerals in the fault zone, to quantify the mineralogical reactions related to fluid-sediment interactions and deformation and finally, to estimate the scale of the mass transfers related to the mineralogical changes in the fault zone.

An accurate mineralogical characterization has been carried out by X-Ray Diffraction, and microprobe analysis on the protolith and fault zone samples. XRD Rietveld refinement has allowed a quantification of the proportions of each mineral in 8 samples from the protolith (hanging and footwall) and 20 samples from the fault zone. Bulk chemical analyses of the same samples permitted an estimation of mineral proportions by modal composition. The very good correlation between these two methods allowed us to use this quantitative data for mass balance calculation. Mineralogical variations between the protolith and fault zone samples were estimated by Gresens calculation (Gresens, 1967).

Measured densities were homogeneous for all samples and according the Gresens formulae, $\Delta Ci = (MA/M0) * CiA - Ci0$, the volume variation is estimated up to 50 % reduction. The Gresens results show a calcite loss (up to 80 %) between protolith and deformed samples, an illite enrichment (up to 40%) while quartz and chlorite appear to be relatively stable.

Scanning electron microscopic images confirm that dissolution of calcite with deformation occurs in the highly deformed sediments. Clay minerals recrystallizations are also observed in deformed rocks, confirming transfer of fluids and mineralogical reactions. The origin of the fluids and the relation between clay mineral reactions and fault activity are discussed.

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MINERAL CHARACTERIZATION OF ADVANCED ARGILLIC ALTERATION OF THE BIELY VRCH AU-PORPHYRY DEPOSIT, SLOVAKIA – PRELIMINARY RESULTS

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The Biely vrch deposit is a new economic Au-porphyry mineralization discovered in Slovakia. The deposit is located in the central zone of the Neogene Javorie stratovolcano, situated in the eastern part of the Central Slovakian Volcanic Field. Advanced exploration and drilling have been realized at the area since 2006 by EMED Mining Ltd.. They calculated that Biely Vrch gold deposit contains Indicated Resources of 461,000 oz (17.7 million t at 0.81g/t gold) and Inferred Resources of 596,000 oz (24.0 million t at 0.77g/t gold; www.emed-mining.com). Au-porphyry deposits represent the relatively new type of deposits of the porphyry group with growing importance in the world. The Biely vrch deposit has many properties typical for Au-porphyry deposits in general. Based on the results of preliminary research it is known, that parental intrusion is intensively affected mainly by intermediate argillic alteration that replaces K-silicate and in deeper parts Ca-Na alterations. Zones of advanced argillic alteration are the youngest and the uppermost part of porphyry system. They are spread from surface to depth of several hundreds metres in shape of ledges. The basic aim of the contribution was to describe the mineralogy of advanced argillic alteration from two selected drillholes (DVE-10 and DVE-51) focusing the attention towards clay minerals.

The main clay mineral from studied samples was kaolinite. The average content of kaolinite determined by XRD quantitative analyses of 13 bulk samples from depth 2 to 205 m was almost 33 wt %. The amount of kaolinite varied from 3 to 54 wt % in the particular samples. Pyrophyllite is associated with the kaolinite as second clay mineral in the upper part of advanced argillic alteration. Dickite, as other index mineral of advanced argillic alteration, occurred with kaolinite more frequently than pyrophyllite but in smaller amount. The significant amount of illite was identified almost in the half of the studied samples. Clay minerals were investigated also by electron microscopy and IR spectroscopy. Quartz was determined as the main non-clay mineral. The first mineral quantitative analyses showed significant application potential of the product of advanced argillic alteration as secondary source of silicate raw material with high content of Al_2O_3. The models of distribution of selected elements were prepared simultaneously with mineralogical characterization. Several good correlations were observed between these distributions and alterations and their products.

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3D FIB-SEM STUDY OF CLAY MINERAL COATINGS IN FAULTED STAßFURT CARBONATE (Ca2) OF THE PERMIAN ZECHSTEIN, NORTH GERMAN BASIN

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The Staßfurt carbonate (Ca2) of the Permian Zechstein 2 located in the North German Basin is well known for its oil and gas occurrence and is a continuing target of exploration. The reservoir has been extensively studied over the last 50 years on the basis of over 225 exploration drill holes (Katzung, 2004). Despite been well studied, the precise nature of the complex fault and fracture mineralization and its relationships to reservoir history remains unresolved.

Of particular interest are the numerous polished and scaly fault surfaces enriched in sheet silicate mineral phases, which influence fluid-rock interaction in the reservoir. They can act as seals or pathways for fluid flow, dependent mineral fabric and porosity-permeability structure. Samples for the study were collected from key boreholes into faulted Staßfurt carbonate. X-ray diffraction study of the typically dark colored mineralized fault material revealed the present of abundant illite and Mg-chlorite phases.

Following initial characterization, focused ion beam and scanning electron microscopy (FIB-SEM) investigations were carried out using a Zeiss Auriga crossbeam microscope. Combining slice-and-view imaging (tomography) and automated energy dispersive X-ray mapping (EDX), we are able to make 3D reconstructions using the ImageJ software (http://rsbweb.nih.gov/ij/). Both microstructure and microchemistry can be displayed for a cutting depth and width of 10 µm for each block. The improved resolution of inlens detectors enables us to resolve mineral phases and pore spaces down to the nanometer-scale. Thus determination of micro-porosity pathways as achieved by Keller et al. (2011) on the Opalinus clay can be achieved.

Based on these first results, we discuss the diagenetic to secondary origin of fault-related mineralization in the reservoir rock in respect to fluid-flow and rock deformation history. Evidence will be provided for syn-tectonic clay mineral growth during strike-slip faulting events, similar to that documented by Schleicher et al. (2010) for the San Andreas Fault.

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CLASSIFICATION OF PRECAMBRIAN DIOCTAHEDRAL 2:1 PHYLLOSILICATES OF ILLITE-GLAUCONITE SERIES (NORTHERN SIBERIA, RUSSIA)

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Dioctahedral 2:1 phyllosilicates are characterized by a wide range of isomorphous cation substitutions in octahedral and tetrahedral sheets. Previously, the classification of these dioctahedral Fe^{3+}- and Al-containing fine-dispersed micaceous minerals was based on the ratio $n={}^{VI}Fe^{3+}/({}^{VI}Fe^{3+}+{}^{VI}Al)$. The Fe^{3+} and Al isovalent substitutions in the octahedral sites of these minerals result in the formation of a continuous series of solid solutions of glauconite ($n \geq 0.50$) to illite ($n \leq 0.25$) via intermediate Al-glauconite (or Fe-illite) (n=0.5-0.25) (Tsipursky, Ivanovskaya, 1988; Kossovskaya, Drits, 1991).

According to the recommendations of the Nomenclature Committees of IMA and AIPEA interlayer-deficient micas (interlayer charge ≈ 0.6-0.85 p.f.u.) include two series of glauconite and illite minerals (Rieder et al., 1998; Guggenheim et al., 2006). These two groups differ in the values for the ratio ${}^{VI}Al/({}^{VI}Fe^{3+}+{}^{VI}Al)$, which are ≤ 0.5 and ≥ 0.6, respectively.

The samples of dioctahedral 2:1 layer silicates from Precambrian sedimentary rocks of Olenek and Anabar uplift (Northern Siberia) were studied. The contents of octahedral tri- and di-valent cations vary within wide limits: Al = 0.48-1.26, Fe^{3+} = 0.31-0.98, Fe^{2+} = 0.07-0.43, Mg=0.18-0.63 p.f.u. Based on the contemporary classification, part of the studied minerals were identified as glauconite (${}^{VI}Al/({}^{VI}Fe^{3+}+{}^{VI}Al)$=0.34-0.50) and illite (${}^{VI}Al/({}^{VI}Fe^{3+}+{}^{VI}Al)$= 0.65-0.80). Other samples are represented by intermediate varieties (${}^{VI}Al/({}^{VI}Fe^{3+}+{}^{VI}Al)$=0.52-0.59), which were also found by the authors in other studied sections (Ivanovskaya et al., 1989, Ivanovskaya, 1996). Thus, on the basis of the classification recommended by the Nomenclature Committees of IMA and AIPEA, the studied Precambrian dioctahedral 2:1 layer silicates are shown to form a continuous series from illite to glauconite.

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MINERAL COMPOSITION OF RENDZIC LEPTOSOLS FROM THE CZECH REPUBLIC

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Rendzic Leptosol are shalow soils, showing evidence of soil development usually limited to the A horizon over a calcareous rock. Limestones are the most widespread parent material of these soils in the territory of the Czech Republic.

The main objective of this study is to provide an overwiev of Rendzic Leptosols developed on different Paleozoic limestones, evaluate basic soil properties and mineral composition.

The study was focused on protected areas of the Czech Republic. Three typical sequences were chosen on the basis of soil survey. The Cikánka National Nature Monument lies in the southwestern part of Prague (Lower Devonian Series, Lochkovian-Pragian stage of limestones). The second soil profile is located 232 km to the southeast of Prague in the Třesín National Nature Monument (Middle-Upper Devonian Series, Givetian-Frasian stage of limestones). The third soil sequence is situated 178 km to the south of Prague in the Vyšenské kopce National Nature Reserve (Paleozoic crystalline limestones). Particle-size distribution, chemical properties and soil organic matter were analysed using routine pedological methods. Mineral composition was assessed by micromorphological analysis and oriented preparations of the fraction < 0.001 mm by X-ray diffraction after a removal of organic matter and $CaCO_3$.

The results of particle-size distribution show a predominance of silt fraction at all localities and also a relatively high content of chiefly sand fraction in the Vyšenské kopce NNR. Soil profiles of Cikánka and Vyšenské kopce have a neutral reaction in the upper parts of the profiles and a basic one in horizons Crk. By contrast, the values of pH at the Třesín site range from very acid to acid in the upper part of soil and neutral one in horizon Crk. The lowest content of $CaCO_3$ was documented at Třesín and the highest one at Cikánka. The value of base saturation corresponds to the content of $CaCO_3$. Cation exchange capacity is relatively high in the upper parts of the soil profiles and decreases with deph. The contents of soil organic carbon and nitrogen are the highest in the upper parts of the profiles. Quartz and illite are dominant componets of the Cikánka profile. The proportion of kaolinite, chlorite and feldspars is low. The Třesín profile has a higher content of feldspars, which is probably conected with the presence of flysch sediments which contain the limestones. The high content of illite and the presence of smectite result from the weathering of feldspars. The content of chlorite is small. Kaolinite is present in some horizons. The locality of Vyšenské kopce is dominated by chlorite which originated from amphibole. Their presence is connected with the nearby occurrence of amphibolite. Kaolinte does not occur at this site.

The obtained results indicate a poor development of pedogenic processes in the studied soil, and a dominant role of parent material in the initial stage of pedogenesis.

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Properties of clays (catalysis, pore systems, transport properties in organic rich shales, ...)

Poster presentation

THERMODYNAMIC PROPERTIES OF NATURAL NONTRONITE

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Nontronite - ferriferrous dioctahedral smectite is widespread in weathering crusts of serpentinized ultramafic arrays, zones of oxidation, soils, as well as in modern ocean and marine sediments. The study of composition and structure of these minerals is complicated not only by extremely high degree of dispersion, but also by the processes of iso- and heterovalent isomorphous substitutions and formation of difficulty separated mixtures. For identification of nontronites we used the complex of physico-chemical methods: X-ray fluorescence spectroscopy, X-ray diffraction technique, thermal and thermogravimetric analyses in the range 25-1000ºC, FTIR spectroscopy in the range from 400 to 4000 cm^{-1}. We studied two samples of natural nontronites: (I) - from the field Pinares de Mayari (eastern Cuba) and (II) - from Kempirsayskii serpentine massif (Southern Urals, Kazakhstan). On the basis of these researches the crystallochemical formulas of minerals were obtained as follows: $Mg_{0.4}(Fe^{3+}_{1.5-x}Mg_{0.4}Ni_{0.1}Al_{y})_{\sum=2.0}[(Si_{3.7}Al_{0.3-y}Fe^{3+}_{x})_{\sum=4.0}O_{10}](OH)_2\cdot 4.0H_2O$ (I) and $Mg_{0.3}Na_{0.1}Ca_{0.1}(Fe^{3+}_{1.4-x}Mg_{0.5}Ni_{0.1}Al_{y})_{\sum=2.0}[(Si_{3.7}Al_{0.3-y}Fe^{3+}_{x})_{\sum=4.0}O_{10}](OH)_2\cdot 3.2H_2O$ (II). The presence of small amounts of Fe^{3+}_{x} in the tetrahedral positions and Al_y in the octahedral positions were recorded in the IR absorption spectra. Thermochemical study of nontronites was performed on high-temperature heat-flux microcalorimeter Calvet and included the study of the processes of dehydration (removal of low-temperature adsorbed and interlayer water) and the determination of enthalpies of formation from the elements. We obtained the following values of the enthalpies of dehydration: 22.8 ± 6.8 kJ (removal of 3.8 moles of H_2O) for the sample (I), which corresponds to the enthalpy of removal of one mole of molecular water, equal to 6.0 ± 1.8 kJ; and 18.9 ± 6.5 kJ (removal of 2.9 moles of H_2O) for sample (II), which corresponds to the value of 6.5 ± 2.2 kJ per 1 mol of water. Thus, the enthalpy of the process of removing of molecular adsorption and interlayer water in the studied nontronites is 6 ± 2 kJ per 1 mol of H_2O. Enthalpies of formation from the elements were determined by melt solution calorimetry using a thermochemical cycle, taking into account the dissolution of the mineral and its constituent components - oxides and aluminum hydroxide. The values of $\Delta_f H^o(298.15\ K)$ K were found for studied aqueous nontronites to be -6125±15 (I) and -5939±10 (II) kJ mol^{-1}, for dehydrated hydroxyl-containing nontronites to be -4958±13 (I) and -5003.6±8.0 (II) kJ mol^{-1}. The estimation of the enthalpy of formation of nontronite of theoretical composition $Mg_{0.15}Fe^{3+}_{2}[Si_{3.7}Al_{0.3}]O_{10}(OH)_2$ was made (-4750 kJ mol^{-1}). The data obtained in present work are the first calorimetric determinations of thermodynamic characteristics of dioctahedral ferriferrous smectites – nontronites.

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