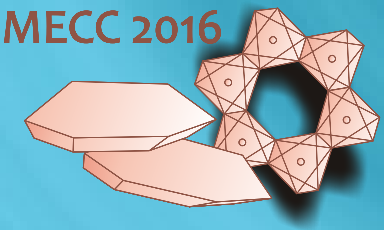
8th Mid-European Clay Conference



Book of Abstracts

July 4-8, 2016
Košice, SLOVAKIA

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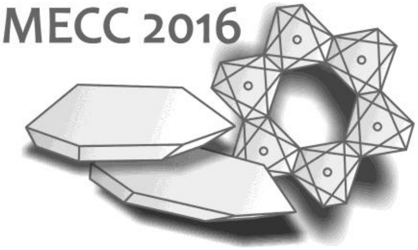

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Dear Colleagues,

It is a great pleasure to welcome you all to the **8th Mid-European Clay Conference - MECC2016** in **Košice**. This meeting belongs to the conference series organised biannually on behalf of the clay groups of the MECC countries to provide the newest knowledge in different areas of clay science. In this book you can find abstracts of 81 oral (plenary, keynote, regular) and 90 poster presentations submitted by the participants from 30 countries. The contributions are arranged in twelve technical sessions related to clays, zeolites and other layered and silicate materials.

We hope that you will find scientific program interesting, enjoy meeting your friends and new colleagues from all over the world. We encourage all young clay scientists to discuss with more experienced colleagues, seeking new information on advanced techniques and materials or innovative applications of clays. While the conference program provides a possibility for mental and intellectual exercise, the organised trips may offer some time for relax at discovering historical town Košice and its surrounding.

Substantial grow in the number of conferences organized world-wide is continuous. We are pleased and honoured that you have decided to attend our conference. Your selection obliged us to design pleasant and creative scene for sharing scientific ideas, establishing new professional co-operations and making new friendships.

We express our thanks to plenary and keynote speakers for accepting our invitations, the session conveners for reviewing all submitted contributions and putting together this great programme, International scientific board for support and especially to all of you arriving to Košice to present your results. The success of the conference is down to you. The last but not least we would like to thank to all our sponsors for their financial and/or materials support.

Slovakia was the first country which hosted the first and very successful MECC meeting in September 2001 in Stará Lesná. Now, 15 years later we are honoured to have a chance to welcome you again. We truly believe that all of you will fully enjoy your stay in Košice and the MECC 2016 will be as successful as the first one in 2001.

Jana Madejová
Conference Chair

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SESSION 1 - Theoretical methods and structure of clay minerals

SESSION 2 - Analytical tools and methods for characterization of clays

SESSION 3 - Modifications and synthesis of clays

SESSION 4 - Organoclays and nanocomposites

SESSION 5 - Clays in medicine, biological systems and the environment

SESSION 6 - Application and treatment of clays and other industrial minerals

SESSION 7 - Clay minerals in soils

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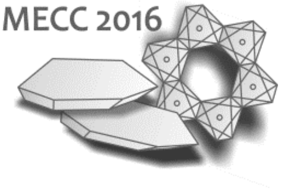
PLENARY LECTURES



Clay hydrogels and composites - potential medical and commercial applications

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Keywords: regenerative medicine, sustained release dressings

The development and application of a series of N-isopropylacrylamide (NIPAM) based hydrogels containing 1 to 10 wt% of the synthetic hectorite, Laponite® (Registered trademark of BYK Additives), will be described [1]. These highly processable NIPAM/Laponite hydrogels remain liquid indefinitely until they are cooled at a predetermined temperature, whereupon they form a hydrogel that does not melt upon re-heating. Their excellent biocompatibility is proven by the cell viability studies.

Human mesenchymal stem cells (MSCs) were used to investigate cell viability, cell migration characteristics, matrix production and the differentiation capacity of MSCs. The initial biocompatibility studies proved extremely successful; MSCs readily proliferate and produce matrix in the presence of the set hydrogels and, perhaps more importantly, the MSCs can be pre-mixed into the hydrogel precursor and subsequently injected into cadaver without any detriment to the ability of the cells to proliferate.

The second system considered is a novel wound dressing material based on a polymer-clay composite, which exhibits a significant advantage in that it shows a gradual and sustained release of the antimicrobial agent over 5-7 days, whereas its release from comparative dressings is complete within 24 hours [2]. The material has demonstrated in vitro activity against a range of common bacteria including Staphylococcus Aureus, Escherichia Coli, and Pseudomonas Aeruginosa, for up to 7 days. The dressing is particularly effective against Methicillin Resistant Staphylococcus Aureus (MRSA), an ongoing challenge to the UK's National Health Service, and has been shown to be active in vitro against two strains of hospital acquired MRSA and a strain of community acquired MRSA. The dressing shows an up to 100% kill rate of MRSA over 5-7 days, which is a remarkable result.

Acknowledgements: The authors would like to thank Smith and Nephew Extruded Films Ltd, the Materials and Engineering Research Institute, METRC (M9027), EPSRC grant (EP/H000275/1) and EPSRC grant (EP/I016473/1) for financial support.

[1] UK Patent GB2493933B, February 2016
[3] UK Patent Application GB1504305.2

Relevance of clay synthesis for environmental studies

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Keywords: clay synthesis, infrared spectroscopy, Mössbauer spectroscopy, crystal-chemistry, chemical series, smectite

Under the condition of the Earth's surface, clay minerals are issued from the weathering of silicate minerals. At pressures or temperatures higher than those of the Earth's surface, clay minerals are the result of recrystallisation processes. Aqueous solutions play a major role in the formation of clay minerals in natural systems. Using synthetic systems, the crystallisation of clay minerals can be controlled, and their environmental conditions of formation can be partially determined. Deduce the environmental conditions which favor formation of clay minerals from their observed crystal chemistry is challenging and particularly relevant in the case of Mars where clay minerals comparable to Earth's analogues were identified on its surface.

Furthermore, synthetic clay minerals are essential for acquiring spectral data when natural pure analogues are not available. They can be used as references for analytical calibration. In particular, the use of synthetic chemical series of well characterized clay minerals clearly improves the empirical approaches to attributing spectral features.

Advanced ecological applications of clay minerals

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Keywords: montmorillonite, sepiolite, bionanocomposites, graphene, pollutants removal

Nowadays advanced materials derived from clay minerals with potential applications in many diverse fields are under study and development following certain Nanoscience and Nanotechnology concepts [1]. So, novel approaches are being applying for the use of this natural resource in a rational and ecological way to prepare nanostructured materials and, *vice versa* to apply them in turn to reduce environmental impact. In this context some of them can be utilized, for instance, in the removal of pollutants and other kind of repair and green activities. In this context, clay minerals represent a paradigmatic example because they belong to the most widely spread type of silicates that are present in soils and ore deposits, being exploited since the dawn of humanity.

In this lecture it will be introduced recent contributions from our Research Group at the Materials Science Institute of Madrid (CSIC) related to diverse clay-based nanostructured materials, showing their ability for efficient elimination in a green way of pollutants, such as hexavalent chromium, radionuclides, pesticides, drugs in urban water, etc. [2,3]. Also, it will be considered examples of clay-based biohybrids provided of specific and predetermined behavior crucial to design materials of interest as sensing agents for selective ion-recognition, virus particles immobilization for improved adjuvant of vaccines or DNA non-viral transfection [4]. Finally, this lecture will also show the production of clay-carbonaceous materials containing carbon nanotubes and graphenes of great interest for the fabrication of conducting electrodes for potential uses in energy generation and storage as well as in biosensing devices. This methodology may open the way to a future large scale production of graphene-clay based materials in an ecological way [5]. The synthetic strategies here discussed concern layered smectites and vermiculites, as well as microfibrous silicates, such as sepiolite and palygorskite, which can be used as basic building units for the design and preparation of both structural and functional materials.

Acknowledgements: We thank financial support from the CICYT (Spain, projects MAT2012-31759 and MAT2015-71117-R) and the EU COST Action MP1202.

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Geomimicry: Harnessing the antibacterial action of clays

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Keywords: antibacterial, clays, illite-smectite, reduced metal, oxidation

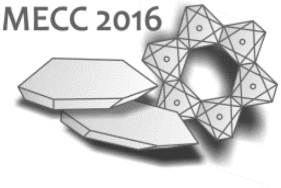
Our decade of research on clays that kill human pathogens, including antibiotic resistant strains such as methicillin resistant *S. aureus* (MR*SA*), has documented their common characteristics. Testing of ~100 clays worldwide has identified ~5% that are antibacterial when hydrated. Most of the antibacterial clays identified are from hydrothermal deposits, where volcanogenic fluids produce minerals containing reduced metals. Ferruginous illite-smectite (I-S) is the most common clay mineral, although kaolins dominate some samples. Bactericidal clays may contain soluble Fe-phases (e.g., pyrite) that drive production of reactive oxygen species (peroxide, hydroxide radical, superoxide) damaging cell membranes and intracellular proteins. Ion exchange with bacterial membranes also leads to a loss of membrane bound Ca^{2+} and Mg^{2+}.

Critically important is the role of the clay mineral assemblage in buffering the water pH to conditions <4 or >10, where Al and Fe may dissolve from various minerals in the clay. Nanometric particle sizes (<200nm) are a characteristic feature of antibacterial clays. Testing various size fractions of these clays showed that the <0.1μm fraction is antibacterial, while coarser fractions are not; implying that a high surface area aids solubility on the time scale of topical applications (~24 hrs). Smectite interlayers (and possibly halloysite) may absorb Fe^{2+} or other reduced transition metals, and act as a barrier to their oxidation in the natural environment. However, when the clays are mixed with deionized (DI) water, cation exchange occurs, releasing metals that lead to bactericide.

Different modes of action have been documented for different clay assemblages that kill bacteria by chemical transfer. In each case the role of the minerals is either to flood pathogens with toxic metals, or to rob bacteria of essential nutrients. By simply measuring the pH and Eh of the hydrated clay (100-300 mg/ml DI water), potential antibacterial clays may be identified in the field, although confirmation of their bactericidal effect requires antibacterial susceptibility testing. In general, if the pH is near neutral, the toxic metals are not soluble and therefore are not available for oxidation. However, where metals are soluble, oxidation reactions will increase the Eh of the water (>400 mV) leading to bacterial oxidation.

Our understanding of the antibacterial clay mechanism opens the field to design of new treatments for antibiotic resistant bacteria, with additional applications in wound dressings, medical implants (joint replacements, catheters), animal feed stocks, agricultural pathogens, and production of antibacterial building materials. This interdisciplinary research exemplifies how *Geomimicry* (e.g., mimicking mineralogical processes) may lead to new frontiers in clay science.

ORAL PRESENTATIONS



Simulating the clay mineral-brine-organic interface: implications for understanding enhanced oil recovery

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Keywords: molecular dynamics, kaolinite, montmorillonite, enhanced oil recovery

Enhanced oil recovery (EOR) is becoming commonplace in order to maximize recovery from oil fields. One EOR method, low-salinity EOR, has shown promise; however, the underlying chemistry requires elucidating. Here, mechanisms proposed for low-salinity EOR in sandstone reservoirs are investigated. In this study, classical molecular dynamics simulations have been used to understand the key interactions and surface structure of a set of organic molecules at the hydrated surfaces of the 2:1 clay mineral montmorillonite and the 1:1 clay mineral kaolinite. Decane, decanoic acid and decanamine have been modeled at both the hydroxylated and silicate surfaces of kaolinite, as well as the basal surfaces of both sodium and calcium exchanged montmorillonite. The effects of salinity and pH were studied.

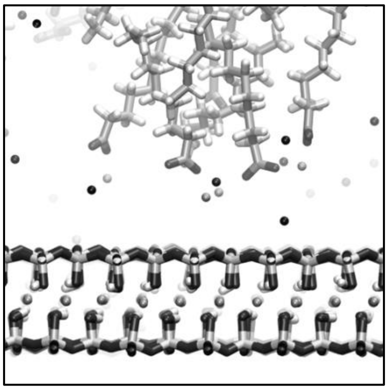

Fig. 1. Snapshot of simulation of decanoate at a hydrated surface of montmorillonite.

For montmorillonite, electric double layer expansion is not able to fully explain the effects of low-salinity EOR. The pH and hence the protonation and charge of acid molecules, is determined to be one of the dominant effects driving low-salinity EOR (see Fig. 1.). Further, results indicate that the presence of calcium cations can drastically alter the oil wettability of montmorillonite. Replacing all divalent cations with monovalent cations through multicomponent cation exchange dramatically increases the water wettability.

The relative affinity of the organic molecules to kaolinite may be readily switched between the hydroxylated and silicate surfaces according to the pH and the nature of the organic head functional group. Decane molecules readily form droplets atop the silicate surface and do not adsorb to the hydroxyl surface, as do protonated decanoic acids. In contrast, decanoate anions do not adsorb to the silicate surface, yet adsorb to the hydroxyl surface through an anion exchange mechanism. Decanamine readily adsorbs to both silicate and hydroxyl surfaces, though the hydroxyl-amine interactions are mediated through water bridges. Once charged, the decanamine remains adsorbed to both surfaces, however, both interactions are ionically mediated, rather than through van der Waals and hydrogen bonds.

A simulation study on the influence of anisotropy and crystal structure defects on small-angle neutron scattering/diffraction patterns

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Keywords: vermiculite, anisotropy, small-angle neutron scattering, porous media

Small-angle (X-ray or neutron) scattering techniques are powerful methods to investigate large scales organization of clay porous media as information on the density contrast between clay material and the pore network can be obtained. At short spatial scales, the internal organization of clay grain is typically obtained from the analysis of hkl diffraction bands. However, it is well known that defects in the crystal structure of clay minerals (e.g., stacking faults, mixed-layering, etc…) control both position and intensity of experimental diffraction bands. Information on the influence of these structure defects on the experimental profiles in the small-angle region is thus crucial in order to provide a continuous description of the scattering properties of clay porous systems over spatial scales.

Recently, we have been interested in the characterization of different size fractions of vermiculite (i.e., 0.1-0.2, 1-2 and 10-20 μm) obtained by sonication process [1]. Using neutron scattering/diffraction method, the degree of anisotropy in particle orientation for the different porous media showed significant size-dependency [2]. In parallel, representative 3D virtual porous media were obtained using a one-by-one particle deposition algorithm, similar to the one proposed by Coelho et al. [3]. The obtained results showed that the experimental data, such as the distribution of particle geometric factors (surface and aspect ratio) as well as particle orientation (rocking curves), were correctly reproduced for the three vermiculite size fractions [4].

Based on these virtual porous media, calculations of theoretical scattering/diffraction profiles are performed and compared to experimental ones. The comparison between experimental and calculated profiles provides sound constrains on the representativeness of the obtained virtual porous media. Moreover such close confrontation allows getting additional insights on the role played by crystal structure defects on the calculated intensities.

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Structure and dynamics of water-smectite interfaces: Hydrogen bonding and the origin of the sharp O-D_w/O-H_w infrared band from molecular simulations

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Keywords: clay-water interface, adsorbed water, smectite, molecular dynamics, infrared spectroscopy

A sharp high-frequency IR band at ~3615 cm^{-1} (in H_2O form) and at ~2685 cm^{-1} (in D_2O form) is a common feature of all smectites and can be used for determining their layer charge [1]. In order to explain the molecular origin of this band, a series of classical MD simulations were performed for several smectite models.

The smectite layers were described using the CLAYFF force field with non-electrostatic Lennard-Jones parameters of bridging oxygen atoms modified after [2]. The potential proposed by Toukan and Rahman [3] was chosen for H_2O. Power spectra were calculated for selected sub-sets of interlayer H_2O to quantitatively analyze their contribution to the observed spectral features. Statistics of interlayer H_2O hydrogen bonds were also analyzed to support the spectral calculations.

The data show clearly that interfacial H_2O in bidentate and monodentate orientation with respect to the surface are the only contributors to the experimentally observed sharp high-frequency band. In the bidentate orientation a H_2O donates two hydrogen bonds to the surface: one was found to be relatively stronger, and another much weaker. In the monodentate orientation a H_2O donates only one relatively weak H-bond to the surface. In all model structures investigated, the number of monodentate interlayer H2O was found to exceed greatly that of bidentates and is, thus, the predominant contributor to the high-frequency vibrational band.

The experimentally observed red-shift of the high frequency band upon increasing layer charge was found to arise from the decrease of the H-bonding distances of H_2O in both monodentate and bidentate orientation. In good agreement with experiment, the effect of charge localization was observed to have a small influence on the high-frequency peak position. On the other hand, the experimentally observed independence of the position of this vibrational band on the type of the (Na^+ or Ca^{2+}) interlayer cation was not explained.

Acknowledgements: The studies were supported with NCN (grant 2012/05/B/ST10/01948).

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Quantum Mechanical Engineering of Exfoliated Kaolinite

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Keywords: exfoliated kaolinite, molecular cluster modelling, water adsorption, structural iron, hydrogen sulphide reactivity

Conversion of crystalline kaolinite mineral to nano-kaolinite is possible by choreographed intercalation, exchange-intercalation, delamination, and exfoliation steps [1]. These reactions convert the periodic material into a molecular system. As secondary structure to the primary sequence of the Al-octahedra and Si-tetrahedra, new morphologies (tubular, chips, platelet) emerge.

We are focusing on developing computational models using quantum chemical methods for atomic scale description of nano-kaolinite for assisting parallel experimental studies. Our current interest is the structure and reactivity of transition metal ions that substitute Al- or Si-sites in kaolinite especially with hydrogen sulphide resulting in Fe-S motifs. A representative example for a quantum chemical model is shown in *Fig.1*. Using Fe-containing natural clays from Hungary, Japan, and Montana with high kaolinite content, we have carried out the exfoliation and investigated the reactivity of the surface exposed, structural Fe-sites in forming Fe-S clusters. Mössbauer and X-ray absorption spectroscopic results indicated the presence of Fe-S bonds when adopting an aqueous synthetic strategy that was successful for the conversion of FeO(OH) biominerals to Fe-S particles [3]. We report on the progress of creating Fe-S decorated nano-kaolinite and explain the observations through atomic scale computational modelling.

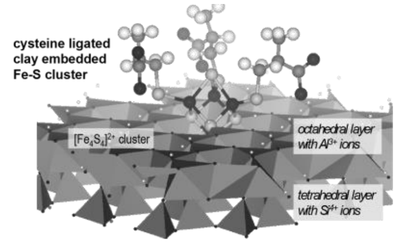

Fig. 1: Virtual chemical model for a [4Fe-4S] cluster with cysteine coordination embedded in a nano-kaolinite calculated with PM7 Hamiltonian inspired by Fe-S metalloprotein active sites

Acknowledgements: The MTA-ELTE Chemical Structure & Function "Momentum" Laboratory (ID 96122) is supported by the Hungarian Academy of Sciences, Budapest, Hungary (Contract No. LP2015-10/2015). Travel support from Office of International Programs at Montana State University is greatly appreciated.

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Terahertz time domain spectroscopy in study of alumino-silicate systems

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Keywords: layered alumino-silicates, organic moieties, nanohybrid materials, THz-TDS, Far-infrared

There are various types of organic moieties which can be useful for modification of natural and synthetic layered alumino-silicates with the aim to prepare nanohybrid materials having advanced and synergic properties. There are several well established experimental tools suitable for changes investigation induced by modification of these materials, such as spectral properties, thermal stability, enhanced adsorption or selectivity for molecular species used etc. The functionalized materials, however, require novel and advanced experimental techniques which simplify prove of the successful modification of layered materials. From those reasons it is believed, that among such techniques can be counted as well the Terahertz time domain spectroscopy (THz-TDS). This technique operates with the advance of femtosecond lasers, while it offers results in the far-infrared region, where interlayer cations have their spectral response at libration frequencies [1]. Hence, valuable information about changes in confined environment of the interlayer galleries can be investigated. In addition, THz-TDS has enhanced signal to noise ratio at frequencies 3.3-100 cm-1 in comparison to conventional FTIR spectroscopy. Several specimen prepared were investigated also by well established techniques such as XRPD, Mid-FTIR, TEM eventually Simultaneous TA, or MAS-NMR spectroscopy, to support results found by THz-TDS. It was found that THz-TDS can be used to collect supporting, complimentary or especial data easily and reliably, as any of above mentioned up to date techniques, used for investigation of layered alumino-silicate materials [2,3].

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Nonlinear optical responses of composites consisting of clay minerals and organic molecules

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Keywords: synthetic saponite, clay-organic hybrid material, nonlinear optics, SHG, two-photon absorption

Optical responses from organic molecules depend strongly on the surrounding media. Clay minerals have been attracted considerable interests as one of the surrounding media of photo-functional organic molecules [1]. For obtaining clay-organic "optical material", we have developed a technique for preparing a low light scattering clay-organic composite film. In the composite film, clay layers stack in a homogeneous layer-by-layer structure [2, 3]. In the present paper, specific nonlinear optical responses of organic molecules confined in the composite films will be discussed.

Second-harmonic generation (SHG) materials [3] - Since the interlayer space of smectites is centrosymmetric, the confined molecules typically orient in a centrosymmetric manner. However, by employing a chiral guest molecule, non-centrosymmetric molecular orientation can be realized in the interlayer space of smectites. We fabricated a composite film consisting of a chiral metal complex and synthetic saponite. The obtained composite films exhibited SHG behaviors similar to that of an SHG active 3-dimensional crystal.

Two-photon absorption materials [4, 5] - A two dimensional (2D) interlayer space of clay mineral forces the confined molecules to be a planar molecular conformation. As shown in Fig. 1, such flattering of molecular conformation can be often seen in diacetylene derivatives. This confinement suppresses a rotational motion of diacetylenic part and thus induces the extension of π-electron system. As a result, diacetylene derivatives confined in the interlayer space of clay minerals exhibit significantly enhanced two-photon absorption responses compared to the derivative in dimetylsulfoxide.

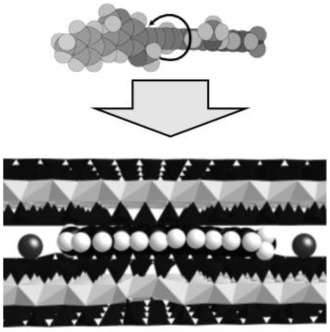

Fig.1 Schematic representation of a diacetylene derivative confined in an interlayer space of a clay.

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A new spectroscopic method of layer charge measurement in smectites

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Keywords: ATR, D_2O, infrared spectroscopy, layer charge, smectite

Layer charge (LC) is one of the most important properties of smectite. Available LC measurement methods are usually not free of certain method-specific drawbacks. Recent attenuated total reflection infrared spectroscopy (ATR-IR) study reported a correlation between the position of a high-energy O-D stretching band (νO-D) of D_2O saturated smectites and their LC, suggesting a new approach to LC measurement [1], which was further tested in the present study.

A collection of natural dioctahedral smectites in various cationic forms and the reduced-charge montmorillonites, all with LC measured by independent methods, was examined in a D_2O-wet state by the means of ATR-IR. The samples covered the full range of smectite LC *e.g.* 0.2 to 0.6 *e* per formula unit. Statistically significant, equally good correlations were found between νO-D and LC determined with structural formula method and with the alkylammonium method. Interlayer cation type was found to have a negligible effect on the correlation with νO-D when comparing Mg, Ca, Na, and Li *i.e.* cations with relatively high hydration enthalpy. For K- and Cs-exchanged smectites the νO-D vs. LC correlation trend line slope corresponded to virtually lower LC than the LC of the samples studied and the correlation was noticeably worse [1]. The difference was more pronounced for high-charge smectites and was explained by strong interactions between the siloxane surface and the cations with low hydration enthalpy, causing neutralization of the charge distributed among basal oxygen atoms.

The proposed new method of LC measurement requires only a small amount of material (~5 mg), is relatively fast, and can be easily implemented in laboratories with ATR-IR setup. The O-D method, however, requires calibration to a set of samples with accurately measured LC, which is a possible source of error.

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Optical properties of organic dyes after excitonic coupling in clay mineral hybrid film

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Keywords: clay mineral, synthetic saponite, organic dyes, J-aggregates

Excitonic coupling is a phenomenon which can occur when the molecules are in close proximity. Due to relative orientation of molecules and Van der Waals interactions is the transition energy of dimers and higher aggregates shifted with respect to monomeric species to higher or lower energies [1]. In the case when the excitonic coupling results in in a shift to lower energies, then the aggregate is called J-aggregate. Depending on used conditions J-aggregates can be organized in 2D brickwall fashion which is more advantageous than the 1D arrangements, because the 2D brickwall arrangement has better electron-hole and exciton transport properties [2]. Materials with these kind of properties are essential in applications like thin-film organic semiconductors or light harvesting systems [2, 3].

In this study we have prepared thin hybrid films consisting from synthetic saponite (SSA) and cationic organic dyes. The formation of monomeric and J-aggregate species in the interlayer space of SSA can be controlled by changing the height of the interlayer space of SSA. Proposed method is based on the swelling properties of SSA and was developed to gain control over the formation of monomeric and J-aggregate species in the interlayer space of SSA. Swelling procedure has been done with dimethyl sulfoxide (DMSO), and the optical properties of prepared film under presence and absence of DMSO were investigated in the meaning of conventional UV-Vis and fluorescence spectroscopy.

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Local manipulation of colloidal liquid crystals of oxide nanosheets by optical tweezers

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Keywords: colloidal liquid crystals, oxide nanosheets, optical tweezers

Inorganic nanosheets prepared by exfoliation of layered crystals have around 1 nm thickness and several micrometers lateral size. They form liquid crystals (LCs) in colloidal state by the exclude volume effect. We have investigated LC behavior of the inorganic nanosheets prepared from layered oxides such as clay minerals and semiconducting oxides. The nanosheet LCs are macroscopically structured under external forces such as bulk electric fields. If we can locally organize the LCs, we may control their structures more precisely. Hence, we report herein local alteration of the nanosheet LC structure by optical tweezers, the technique which traps and manipulates particulate objects by focused laser beams.

Nanosheet LCs of exfoliated layered hexaniobate was irradiated by a focused beam from a CW laser operated at 532 nm and observed with a polarized optical microscope. By the laser irradiation, the nanosheet LC injected in a thin layer (~ 100 μm) cell caused a local alignment change as represented by Figure 1. Although the nanosheets were homogeneously aligned parallel to the cell surface before the irradiation, their alignment turned to orthogonal to show cross-shaped birefringent area. The birefringent area appeared only at around the focal point. This result evidences manipulation of the nanosheets by the laser beam. The generation of cross-shaped texture suggests the formation of a nematic domain by manipulating the nanosheets. Collective nature of the LC state will contribute to the generation of a local nanosheet domain. We experimentally estimated the minimal laser power required for the manipulation as 20 mW, and compared the alignment change with that realized by a bulk electric field.

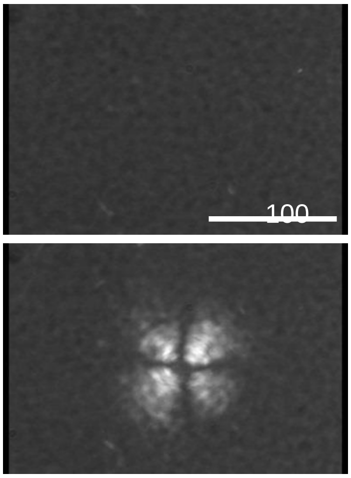

Fig. 1. Polarized optical microscope images of the nanosheet LCs in a thin layer cell before (upper image) and after (lower image) the irradiation of laser beam.

The coupled processes of dehydration and Si-O phonon mode deviation in Na$^+$-saturated montmorillonite

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Keywords: infrared spectroscopy, water, silicon wafer

The purpose of the present study is to investigate the coupled processes of dehydration and changes in Si-O vibrations of a Na$^+$-exchanged dioctahedral smectite using in situ infrared transmission spectroscopy by adopting the tethering by aggregation and growth (T-BAG) preparation [1]. Further on, using differential transmission spectra and combining the results with the findings of the simultaneous thermal analysis make it possible to distinguish between the OH-stretching modes of structural hydroxyls and interlayer water. The changes of the SiO stretching vibration during dehydration can be recognized from the peaks $(SiO)^{LO}$ and $(SiO)^{TO}$. Their shifting behavior as well as the shift of $\nu(Al\cdots OH)$ at 3630cm^{-1} describe the changing dimensions of the tetrahedral and octahedral sheet during dehydration.

The present Fourier transform infrared spectroscopy (FTIR) study has shown that the release of water affected both the OH stretching and the SiO phonon modes. Both spectral changes are coupled as the interlayer water releases. The major release of water is observed in low temperature regime < 60 °C. These results provided that at least two H_2O species exist in the interlayer of the clay mineral. One of these H_2O molecules must have a different character as bulk water since we observe a sharp OH stretching band. Furthermore, these H_2O molecules are more strongly bound than bulk water since they have a higher release temperature. In addition to the differentiation of the H_2O species, we quantify the amount of water in dependence of their releasing temperature.

In agreement with early and recent IR studies on smectite – water interactions [2], we fill the gap between crystalline swelling at low water contents ($< 6\ H_2O\ /\ Na^+$) and swelling at high water contents.

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Heating of chamosite causes H_2 release

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Keywords: chamosite, dehydroxylation, H_2 liberation, oxidation

A natural chlorite-rich sample has been studied using simultaneous thermal analysis that includes evolved gas analysis by mass spectrometry (MS). Special focus was drawn on monitoring low molecular gaseous products e.g. molecular hydrogen. The sample contains massive aggregates of small chlorite crystals. Its bulk mineralogical composition was determined by XRD to 61% Fe-rich chlorite, 22% siderite, 13% quartz, 2.3% apatite, 1.2% gypsum, and 0.5% rutile.

The structural formula was calculated to $[Fe(II)_{1.66}Mg_{0.07}Al_{1.05}Fe(III)_{0.22}(OH)_6]$ $[(Si_{2.73}Al_{1.27})Fe(II)_{2.49}Mg_{0.51}O_{10}(OH)_2]$ based on the chemical analysis to be classified as chamosite having Fe dominantly as Fe(II) (95%) and with a Fe(II) distribution ratio between the interlayer octahedral sheet (IOS) and the 2:1 layers of 1:1.5.

It has often been suggested that the oxidation of Fe(II) during heating of clay minerals [1] induces a transfer of an electron to OH groups in the octahedral sheets ultimately forming H_2. Our results showed for the first time that H_2 is released during heating a chamosite under N_2 atmosphere and that under synthetic air the released H_2 reacted further to H_2O.

The liberation of H_2 was proved by a peak at 512 °C in the MS curve of $m/z = 2$. This peak has no corresponding peak in the MS curves of $m/z = 16$, 17 or 18. Thus, the peak in the MS curve of $m/z = 2$ was not related to the cracking pattern of H_2O. Under synthetic air, the released H_2 reacted with O_2 from the gas atmosphere to H_2O, which was deduced from the lower intensity of the peak at 547 °C compared to the peak at 528 °C in the MS curve of $m/z = 16$ due to the O_2 consumption.

After heating at 1100 °C Fe(II) was fully oxidized under synthetic air and partially oxidized (>50%) under N_2. The color changed from brown to red under synthetic air and to black under N_2. The red material was nonmagnetic while the black material was magnetic. Hematite, spinel phases, cristobalite and amorphous SiO_2 were the high temperature phases (HTP) after heating under synthetic air. In contrast, under N_2 magnesioferrite, Fe-Mg-pyroxene phases, cristobalite, tridymite and amorphous SiO_2 were formed as HTP.

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Swelling of montmorillonites in liquid water - the balance of cation hydration, layer charge and temperature

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Keywords: montmorillonite, swelling, temperature, layer charge, cations

Most montmorillonites with divalent interlayer cations are known to form a 19 Å basal spacing when placed into water, but have been observed to sometimes swell and partly form a 21 Å basal spacing upon cooling [1]. The current study aimed at investigating the variation in swelling in liquid water using synchrotron X-ray diffraction and three montmorillonites with different layer charges, ion-exchanged with divalent Ca, Cu, Mg, Sr, and Zn (Wyoming, USA) or with Ca, Mg, and Zn (Milos, Greece; Kutch, India). The temperature was cycled between +20 and -50 ºC, or between +20 and +90 ºC, and the solid/water mass ratio was kept constant at 30 wt.% solid. It was observed that Ca and Sr Wyoming montmorillonite formed the 21 Å phase during cooling while in Mg, Cu and Zn Wyoming montmorillonite the phase was partly present already at 20 ºC, and at lower temperature the amount of 21 Å increased while 19 Å phase decreased, until ice was formed and dehydrated to 16 Å. Milos and Kutch montmorillonites did not form the 21 Å phase at any temperature. Lower charged montmorillonite (Wyoming) expanded further compared to montmorillonites with higher charge (Milos and Kutch). Lower temperature (above freezing point) expanded the montmorillonites to different extent. Higher Gibbs hydration energy of the interlayer cation allowed further hydration and greater basal spacing (Sr < Ca < Mg < Zn < Cu). The results contribute to an improved understanding of the crystalline swelling of montmorillonites with divalent interlayer cations in complex applications and can be input for validation of model calculations.

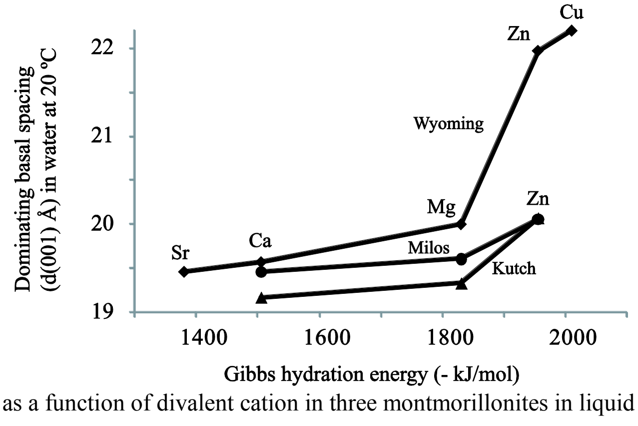

Fig. 1. Swelling as a function of divalent cation in three montmorillonites in liquid water at 20ºC.

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Random lasing from hybrid materials consisting of clay minerals and organic molecules

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Keywords: random laser, stimulated emission, synthetic saponite, fluorophore, clay-organic hybrid material

Stimulated emission occurred by propagation of a multiply scattered fluorescence beam in a strongly scattering medium is called random lasing [1]. To realize efficient random lasing, a fluorophore should be densely doped in a scattering medium so as to exhibit intense fluorescence. Clay mineral can densely incorporate fluorophores without aggregation into its interlayer space. Consequently, the fluorophores maintain fluorescence efficiency in the interlayer space [2, 3] even at a high density. In addition, typical hybrid materials are strongly scattering materials. Therefore, a clay / fluorophore hybrid material should be a promising medium for random laser. In this study, we investigated stimulated emission from Synthetic saponite (SSA) / fluorophore hybrid materials.

Fig. 1 shows emission spectra of SSA / 4,4’-[4,1-phenylenedi-(1*E*)-2,1-ethenediyl]bis[1-methylpyridinium] dichloride (bisBz) hybrid material excited by using a femtosecond pulsed beam. The full width at half maximum (FWHM) at an incident power of 0.05 mW was 54 nm. On the other hand, when excited at a relatively strong incident beam of 0.40 mW, the FWHM was 13 nm. In addition, emission intensity showed dependence on the incident power, which is typical for a random laser medium. Thus, we observed random laser behavior from clay / fluorophore hybrid materials. We will also discuss a random laser behavior of hybrid materials consisting of other fluorophores.

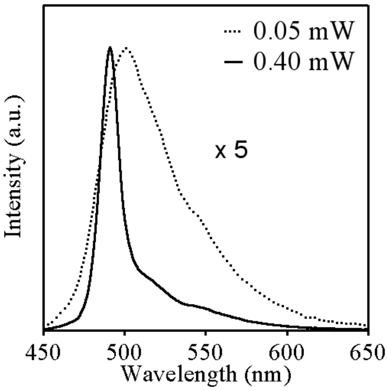

Fig. 1. Emission spectra of SSA / bisBz excited at 0.05 mW (dotted line) and 0.40 mW (solid line). The intensity of emission spectra at 0.05 mW is 5 times larger than original one.

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Surface species of lanthanum ion on montmorillonite

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Keywords: lanthanum-bentonites, cationexchange, X-ray diffraction (XRD), scanning electron microscopy (SEM), Mössbauer spectroscopy

Lanthanum-bentonite was prepared from Ca-bentonite (Istenmezeje, natural) by three consecutive ion exchange [1]. XRD, SEM and ^{57}Fe Mössbauer spectroscopy were used to study the surface of the modified montmorillonite.

The result show the intercalation of lanthanum ions in the interlayer of smectite. In the case of trivalent lanthanum more ion bounded on bentonite surface than the Cation Exchange Capacity (CEC) [2].

As a result of the exchange of bivalent Ca^{2+} ion to trivalent La^{3+} ion, the basal spacing of montmorillonite increase from 14.656 Å to 15,535 Å. So, the growth of basal spacing confirms the ion exchange. In the SEM-EDX spectrum of La-bentonite, the appearance of La peaks can be well seen when no peaks of Ca could be detected at all, proving the total exchange of Ca^{2+} by La^{3+}.

For La-bentonite, Mössbauer spectroscopy studies [3] show an unexpected magnetically split component associated with interlayer Fe, which was observed in the Mössbauer spectra at 78 K. During the formation of La-bentonite a part of the octahedral iron atoms can move into the interlayer space, leaving place for the accommodation of lanthanum ion. This could cause the incorporation of higher amount of La^{3+}-ion in bentonite than expected based on the CEC, however the phenomenon needs further investigations.

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Influence of surface composition of Fe-doped porous clay heterostructures on catalytic properties

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Keywords: Laponite, Porous clay heterostructures, HRTEM, ^{57}Fe Mössbauer spectroscopy, NIR and MIR spectroscopy

In the present work we demonstrate the study on the development of novel approach to clay derived support modification in order to obtain materials containing transition metal oxides dispersed on the extended PCH surface. The effect of temperature transformation and high pressure treatment on the alteration of the surface composition and structure evolution of crystalline-amorphous porous clay composites upon iron doping from the metal-organic C_6H_5FeO and inorganic $Fe(NO_3)_3$ Fe-sources were investigated. Detailed information on the character and lattice positions occupied by iron, the extent of their incorporation, its local structure and symmetry within samples were provided by comparing the transmission and reflection FTIR techniques in the MIR and NIR regions with the ^{57}Fe Mössbauer spectroscopy and ^{29}Si MAS NMR data.The nature and nanocrystalline structure of the surface Fe species was observed in the cross-section of the calcined Fe-PCH powders. HRTEM analysis of the organic derived Fe-PCH revealed that the sample consists of slightly disordered layered areas of the composite grains and small (about 5 nm) crystallites of Fe_3O_4 and α-Fe_2O_3 phases**.** The surface of inorganic derived Fe-PCH was enriched into α-Fe_2O_3 phases. High pressure treatment resulted in the alteration of sample morphology and better, more homogenous dispersion of the Fe species in the composite lattice. FTIR indicated slight impairment of the clay structure in the PCH network followed by surface enrichment with Mg species due to Mg cations leaching from the octahedral sheets as confirmed by XPS study. The Mg pronounced surface concentration in composites, depended on the synthesis approach, as well as the different distribution of Fe species was well reflected in the ethanol dehydration/dehydrogenation reactions.

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Enhanced luminescence of cyanine cations NK88 adsorbed on saponite particles

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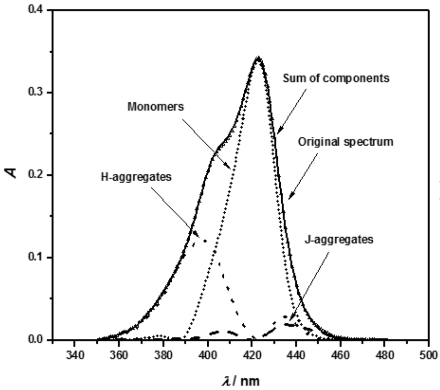
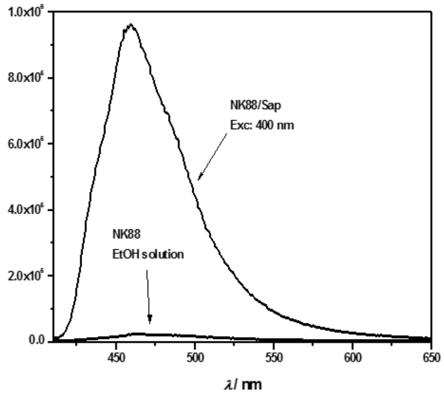
Keywords: cyanine dyes, smectites, adsorption, dye aggregation, hybrid materials

Hybrid colloidal dispersions based on cationic cyanine dye (NK88) and saponite (Sap) were prepared and their spectral properties were compared with dye solution. The effect of various NK88/Sap ratios were investigated by absorption and fluorescence spectroscopies. A detailed analysis of absorption spectra based on chemometric methods (principal component analysis and multivariate curve resolution - alternating least squares) revealed a very complex nature of these hybrid systems [1]. Presence of three relevant components (monomeric form, H- and J-aggregates) were identified [2]. NK88 luminescence was significantly enhanced upon the adsorption on Sap surface, but could not be assigned to a single dye form. Strong couplings, such as collective exciton delocalization in dye supramolecular systems formed on saponite surface, and weak coupling via excitation energy migration and transfer led to the emission spectra, whose profiles did not depend on the excitation wavelengths. These colloidal systems are perspective precursors for other hybrid materials.





Acknowledgements: This work was supported by the Grant Agency VEGA (2/0107/3)

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Cascade, multi-step energy transfer in hybrid systems based on saponite and organic dyes

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Keywords: smectite, fluorescence, laser dyes, FRET

Förster resonance energy transfer (FRET) is a phenomenon occurring in green plants to deliver light energy for photosynthesis. It is induced by resonance between two dye molecules transferring energy from an initially excited molecule representing energy donor (ED) to the second molecule, representing energy acceptor (EA). FRET will likely play a key role in future solar cells performing at a molecular level.

The objective of this work was to develop hybrid materials based on the mixture of luminescent dyes intercalated in synthetic saponite Sumecton (Sap), which would exhibit a multi-step FRET. Six cationic dyes (three rhodamines, pyronin and two oxazines) with spectral properties to match the resonance conditions were chosen. Fluorescence spectra proved cascade FRET in the experiments based on hybrid colloids. The colloids were used for the preparation of thin films, which were characterized by X-ray diffraction, absorption spectroscopy and linearly-polarized absorption spectroscopy. Dye molecular aggregation was relatively low. The photoactive forms such as monomers and J-aggregates were dominant in the prepared films. Emission and excitation spectra, fluorescence anisotropy and time-resolved fluorescence spectroscopy confirmed the occurrence of a multi-step FRET also for solid films. The effect of the concentration of intercalated dye molecules on FRET efficiency was proved. It affects the intermolecular distances between neighboring dye molecules intercalated in Sap film. Relatively low dye concentration (0.6% CEC) led to optimal distances below 5 nm, which was sufficient for efficient FRET.

Saponite with a low layer charge represents a suitable inorganic template for the design of hybrid materials preserving the photoactivity of the adsorbed dyes. Its films with organic dyes are affordable hybrid materials useful for the manipulation of light energy at a molecular level, thus mimicking a cascade energy transfer processes occurring in photosynthesis systems in green plants.

Acknowledgements: This work was supported by the Grant Agency VEGA (2/0107/13, 1/0278/16).

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Experimental and molecular dynamics modeling of poly(ethylene glycol) adsorption on to montmorillonite

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Keywords: organoclay, polyethylene glycol, montmorillonite, adsorption, molecular simulations

The adsorption of polyethylene glycol (PEG) or its larger molecular weight equivalent polyethylene oxide (PEO) onto clay has been studied for a number of years due to its wide use in different applications including drilling muds and pharmaceuticals. More recently a renewed interest has arisen since they have been investigated as plasticisers or compatibilising agents in clay-polymer nanocomposites [1,2].

Experimental adsorption isotherm data shows that PEG (molecular weight = 600) adsorbs strongly on to montmorillonite at low concentrations, which coincides with the formation of a single layer of PEG within the interlayer space. Increasing the PEG concentration then results in less strongly adsorbed PEG coinciding with the formation of a bi-layer structure. Additional amounts of PEG results in weaker and fewer adsorption processes and no further expansion in the interlayer spacing.

The intercalated PEG molecules as well as the cationic sites within the interlayer space of clay are considerably hydrophilic and as a consequence water is present and competes for the space within. Increasing PEG concentration generally results in less water being present due to stronger adsorption processes from the former.

Molecular dynamics modeling has been used to enhance the experimental data in order to provide an insight at an atomistic level into how the PEG molecules (molecular weight = 200) and water molecules are arranged within the interlayer space.

PEG molecule orientations are shown to be dependent on the extent of layer charge and the charge location (tetrahedral or octahedral). A ring-type formation of PEG molecules around cations occurs more frequently with low and octahedral charge, whereas crown-type structures occur more often with the same low charge, but located within the tetrahedral sheet. Planar structures are also more apparent when changing from an octahedral to tetrahedral charge for high charge montmorillonite.

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Lamellae ordering induced by nanosheets for organoclay materials

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Keywords: nonionic surfactant, organoclay, lamellar organization

The chemical modification of clay minerals through the adsorption of amphiphilic molecules containing n-$C_nH_{2n+1}(OCH_2CH_2)_mOH$ nonionic surfactants (abbreviated as C_nE_m) characterized by their self-assembled liquid crystalline phases (hexagonal; lamellar, cubic) has received particular attention. Indeed, the recent intercalation of a normal $C_{10}E_3$ bilayer in a natural Mt resulting to the condensation of a bulk lamellar phase above cmc points out the link between the packing of the surfactant and its bulk phase state [1-2].

In this contribution, the role of the surfactant state in bulk solution for the adsorption onto layered materials and niobite nano sheets, by focusing on the structure and the dynamics of aggregates made by various C_nE_m nonionic surfactants. The results obtained by a set of complementary techniques (X-ray diffraction, small angle X-ray scattering, solid state nuclear magnetic resonance, FTIR, thermo-gravimetry analyses) show for the whole studied surfactants the importance of the shape of the nanosheets that induce a lamellar monodomain ordering of the nonionic surfactants within the inorganic layered materials [3].

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From dopamine to melanin and back: A natural history of color change

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Melanin derivatives are among the most important classes of biopolymers but also among the least understood and least characterized ones. They are obtained by oxidation of dopamine and L-DOPA and are responsible for the pigmentation of several biomaterials: hair, skin, feathers, insect cuticles, etc. Eumelanins have a black color, phaeomelanines are brown to reddish and other modifications are still possible. The synthesis of melanin has inspired several researchers during the last decade to obtain bioinspired materials including hybrid organic-inorganic materials. Functionalized melanins are partially responsible for the presence of black spots in Lascaux frescoes[1] and on some Egyptian wall paintings[2]. Conversely, melanin seeds contributing to the black color in the hair or feathers can be degraded in presence of light or free radicals[3,4] which are able to induce a depolymerisation. These polymerization-depolymerization reactions have been considered to explain the taphonopy of colors in fossils[5].

The aim of the present work was to investigate the polymerization reactions producing melanin and the inverse depolymerisation reactions inducing a degradation of this biopolymer. The influence of some cations, and more specifically manganese and iron in presence of inorganic matrices such as clay minerals and zeolites, has been investigated. These reactions are of interest for cultural heritage applications (LASCAUX) since they can stabilize specific oligomers as has been previously reported[6]. A set of experimental and theoretical approaches (UV-vis, IR, RAMAN, solid state NMR, EPR, TG-DTA, XRD, TEM and DFT) allow the identification of the different species formed in different pH conditions and inform us about the interactions that occur between biomolecules and inorganic matrices.

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Nano-kaolinites/halloysites as potential photocatalysts

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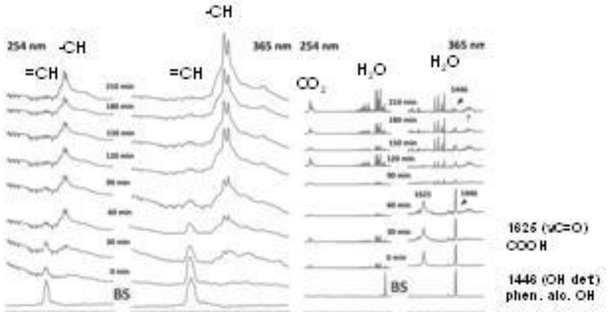
Keywords: kaolinite, halloysite, nanostructures, delamination, photocatalysis

Although the band gap values of kaolinites/halloysites (*3.82-3.96 eV, ~322 nm*) are close to those of TiO_2 (*anatase 3.20 eV; 387 nm; rutile 3.02 eV; 410 nm*), these minerals show rather low photochemical activity. After delamination a significant increase can be observed in the photochemical activity along with a little change in the band gap values, only. This phenomenon cannot be explained by the increased dispersity of photoactive contaminants and the increased mineral surface, since the activity of the contaminant-free minerals is increased, as well. The band gap values may indicate the semiconductive nature and the possible catalytic activity of the nanoclays, but give no information on the mechanism of the photochemical processes. UV/VIS fluorescence spectroscopy can be used for the identification of the photocatalytic nature of the nanostructures.

The fluorescence spectra of the book-type and the delaminated kaolinites are the same, independently of the excitation wavenumber. The only difference is in the intensity of the emission bands. This means the presence of local excited states between the valance and conductive bands. Based on their life-time, these local reactive states can be responsible for the increased photochemical activity. Since delamination is accompanied with the increase of the specific surface area, the activity is increased with the increase of the quantum yield. It is also very interesting that the distortion of the Al-centered octahedra in the delaminated structure and the change in the coordination number of the central atom result in the formation of (under normal conditions unstable) reactive sites stabilized by the new morphology. These two phenomena can jointly be responsible for the catalytic activity which can further be increased by the deposition of silver nanoparticles on the surface. To follow the decomposition (mineralization) process FT-IR(ATR) spectroscopy was used with sodium-benzenesulphonate (BS) as model compound.



BS mineralization upon UV irradiation (ATR vs. time curves)

Modified montmorillonites as materials for the cupric ions removal from aqueous solutions

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Keywords: montmorillonite, cupric ions removal, atomic absorption spectroscopy

Heavy metals pollution is a considerable environmental problem caused by the increasing global consumption. The most common metal pollutants include Cd(II), Cu(II), Cr(VI), Hg(II), Ni(II), Pb(II), and Zn(II) ions. Their presence in groundwater or soils significantly threats ecological systems and human health. Numerous techniques for the heavy metal removal have been developed, such as physical separation, extraction, immobilisation, etc. The need of cost-effective and environmentally safe processes has increased substantially because of high expenses and low efficiency of those currently used.

For the immobilisation and separation of metal species by adsorption, the use of clay minerals has been extensively studied because of their high adsorption capacity, cation exchange capacity, and specific surface area. In order to increase the heavy metal binding capacities, the preparation of organoclays containing metal-chelating functionalities has been intensively explored. To this end, amino acids have been chosen as surfactants of low toxicity, biodegrability, and various structures.

The aim of this work was to prepare novel adsorbents using Ca-montmorillonites and they were characterised by X-ray powder diffraction, infrared spectroscopy, and C, S content determination. Prepared materials were used as adsorbents of cupric ions. The effects of pH and metal cation concentration were investigated. The adsorption capacities were calculated from the equation:

$$q = \frac{(c_\mathrm{i} - c_\mathrm{f}) \cdot V_\mathrm{m}}{m_\mathrm{s}}$$

where q (mg/g) is the adsorption capacity, c_i (mg/L) is the initial concentration of Cu(II), c_f (mg/L) is the final concentration of cupric ions, V_m (L) is the volume of Cu(II) solution, and m_s (g) is the mass of adsorbent. The concentrations of cupric ions were determined using atomic absorption spectroscopy. Most importantly, the adsorption capacity of prepared organoclays was increased by >300 % compared to parent Ca-montmorillonites.

Surface and interface properties of BEC-montmorillonite

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Keywords: benzethonium chloride, montmorillonite, organoclay

In last two decades, the research on the development of new clay based materials has been very active due to their wide area of use from nanocomposite preparation to antibacterial agents. Montmorillonite is the most common type of clay used for the modification because of its high swelling and adsorbing properties [1-3].

In this study montmorillonite (Mt), from Turkey has been modified with benzethonium chloride (BEC), which is a quaternary alkyl ammonium cationic surfactant used as disinfectant. During the research, kinetic and isotherm studies were made as a first step and then Mt modified with BEC by using amounts equal to 50, 100 and 200% of the cation exchange capacity of the Mt were subjected to XRD, ATR-FTIR, zeta potential and DTA/TG analyses for their characterization. The prepared samples were named as 0.5 CEC-BEC-Mt, 1CEC-BEC-Mt and 2CEC-BEC-Mt. Two different heating methods, hydrothermal (traditional) and microwave were used. After the modification, percent adsorption of BEC was determined. The adsorption percentage was around at 99% except for 2 CEC-BEC-Mt. The washing caused an approximately 10% decrease in the adsorption percentage for all samples.

The kinetic studies indicated that adsorption was rather fast and was explained by a pseudo second order model. The adsorption isotherm fitted to a Langmuir model. The ATR-FTIR analyses showed the existence of BEC on the surface. According to the XRD analyses, the crude clay is a typical Na-Mt with d_{001}=1.22 nm. XRD analysis of the modified Mt showed an increase in the interlayer spacing compared to that of the crude clay. The interlayer spacing of the clay for 50% of CEC increased to 1.54 and 1.55 nm using microwave irradiation and hydrothermal heating, respectively. Zeta potential analysis indicated a similar decrease in negative surface charge with increasing BEC loading irrespective of the preparation method used. Thermogravimetric analysis showed a degradation maximum at around 299 °C associated with van der Waals interactions for 0.5 CEC-BEC-Mt decreasing to 285 °C with the 2 CEC-BEC loading.

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Playing with cation exchange capacity to aid in fighting *Helicobacter pylori*: results of in-vitro tests

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Keywords: Helicobacter pylori; cation exchange capacity; ammonium; clinoptilolite; mineral excipients

Helicobacter pylori is a bacterium present in the stomach of about half of the world's population. Infection with *H. pylori* causes 95% of duodenal ulcers and 70% of gastric ones, and 78% of all gastric cancer cases are estimated to be attributable to this chronic infection [1]. Urease, a surface protein component of *H. pylori*, enables ammonia production from the urea of the host. This process is important for the survival of the bacterium in the stomach, because NH_3 is protonated in NH_4^+, which results in a local raise of pH [2]. Clinoptilolite is a natural zeolite that combines cation exchange capacity, high selectivity toward ammonium ion and good stability in acid media, and is having a growing interest in studies for biomedical applications [3]. A clinoptilolite-based material, specifically prepared for the development of pharmaceuticals [4], has been used to study if this zeolite, due to the properties above reported, is able to develop an antagonistic activity against *H. pylori* growth and infection. In-vitro tests, performed with a reference strain of *H. pylori* (ATCC®43504™), have shown that clinoptilolite prepared in sodium form is able to inhibit bacterial growth (Minimum Inhibitory Concentration = 0.5 mg/ml); conversely, the same material, but in ammonium form used as control, has not determined effect on *H. pylori* growth up to the highest concentration used (15 mg/ml), meaning that inducing NH_4^+ decrease in the micro-environment of the bacterium can be a good strategy in supporting the fight against *H. pylori*. On the other hand, a set of tests, carried out with solutions of NaCl and in absence of zeolite, have shown that the bacteria also replicate in presence of high Na^+ concentration. These results demonstrate that the bacterial growth has been inhibited by the ability of Na-clinoptilolite to subtract ammonium ions by cation exchange.

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Paste of natural Cuban zeolite and its topical application in inflamed skin irritations

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Keywords: clinoptilolite, mordenite, mycosis, intertrigo, psoriasis

Natural Cuban zeolite has been well characterized by its mineralogical (combination of clinoptilolite and mordenite phases) and chemical compositions, microstructural harmlessness as well as histamine binding capacity suitable for human applications [1]. According to the adsorption capacity of these microporous crystalline aluminosilicates with channels and cavities, we have recently prepared an anhydrous zeolite paste for topical application (Detoxsan® Paste) able to adsorb water and low molecular weight compounds.

While the use of clays in health has its roots in prehistoric times, its present application on the skin focus attention to its bactericidal action [2], anti-inflammatory properties [3] and topical application as active carrier for antibiotics [4]. Our formulation of zeolite paste is based on petrolatum and contains additionally squalane as natural lipid component responsible for skin moisture. Advantage of the latter compound is the absence of a double bond within the molecule and therefore the paste cannot get rancid. Thus, Detoxsan® Paste can be applied topically, adhere to the skin surface and forms a thin mineral layer, which is able to fulfill its properties as adsorbent.

The paste is used in superficial dermatomycosis, mainly between toes, in intertrigo, inflamed skin folds and in psoriasis at different parts of the body surface. Application of this zeolite paste has been performed under the climatic conditions of Cuba and Germany.

In dermatomycosis and intertrigo improvement of skin irritations was visible after 2 to 5 days and they disappeared in most cases after 2 weeks. In psoriasis the effect depended from the size of the affected area. Significant improvement could be stated between 1 and 3 weeks, large areas needed more time [5].

The positive effect on skin irritations of zeolite paste seems to be due at least partially to the adsorption of histamine (an inflammation promoter) and water (a prerequisite for microbial growth) by zeolite. Thus, this formulation reduces inflammation promotors and prevents microbial growth and can be used therefore as care for skin affected by mycosis, intertrigo and psoriasis.

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Mechanochemistry immobilization of organic and inorganic pollutants into dioctahedral and trioctahedral smectites: a suitable technology for soil remediation

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Keywords: smectite, heavy metals, organic pollutants, mechanocremistry, remediation

The presence of organic pollutants as well as of heavy metals in the environment is a potential risk for water and soil quality due to their toxicity. Lots of technologies have been developed to remove them from the environment. Among these, mechanochemistry is quite suitable for it allows activation of chemical reactions by inducing different kinds of mechanical stress and without any other energy supply. Clay minerals have been employed in this technology due to their low cost, availability, and low toxicity. In the present study the effect of dry milling on the ability of dioctahedral smectites (BentoliteH) and trioctahedral smectites (LaponiteRD) to immobilize heavy metals cations (Cd and Cu) were investigated by using X-ray diffraction, FTIR, solid-state NMR, XPS, and TG-DTA. The mechanochemical reactions of both smectites with organic molecules (phenols) - as representative of pollutants with enhanced polarity, i.e. cathecol (CAT) and pentachlorophenol (PCP) – were also investigated. Strong milling treatments gradually reduces crystallinity in clay minerals by causing diffusion of atoms ("prototropy"), delamination, and layer breakdown, therefore affecting the surface and colloid properties clay minerals and causing the increase of their catalytic activities and sorption capability. Mechanochemical dry milling activates chemical reactions between clay minerals surface and heavy metals cations by inducing different kinds of mechanical stress. Long time experiments (24 h) showed otherwise that laponite RD exhibits stronger Cd retention capability than bentolite. Milling facilitates heavy metal sorption in sites in which the cation is relatively tightly bonded to the TOT layers of the smectite structure. The type of mechanochemical interaction of PCP with the trioctahedral smectite is weak, mainly occurs on the external surfaces, and does not involve the OH-phenolic group or any complexation of the interlayer cation. On the contrary, the dioctahedral smectite exhibits strong mechanochemical interactions with PCP molecules via the phenolic group. Prototropy, induced in BentoliteH by milling, is responsible for the PCP molecule perturbation and the enhanced capability of BentoliteH to promote formation of intermediate products via OH groups. Mechanochemical interactions of CAT with both smectites mainly occur in the interlayers. For the dioctahedral smectite they are stronger than for the trioctahedral one, and likely involve inner-sphere complexation of Bentolite interlayer cation by CAT phenolic groups.

Decontamination of wastewaters with the use of organically modified vermiculite

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Keywords: organovermiculite, sorption, organic compounds, decontamination, filtration

It was confirmed in many research studies that organically modified vermiculite is a very efficient sorption material for organic compounds with efficiency comparable to organically modified montmorillonites and bentonites.

In our previous studies the organically modified vermiculite was tested for removal of many organic compounds from aqueous solutions, for capture of one of the most known chemical warfare agents - yperite from the gaseous medium and for antibacterial properties [1,2].

In this study the organically modified vermiculite (with the use of hexadecyltrimethylammonium and hexadecylpyridinium salts) was used for removal of organic compounds such as aromatic and polycyclic aromatic hydrocarbons, phenols, chlorinated benzenes and phenols and oils from real contaminated waters in the laboratory and the field conditions. The activated carbon was also used for comparison of the efficiency. The optimization of dynamic sorption process was performed.

The efficiency of the modified vermiculites for most of identified organic compounds was proven to be very high, even higher than the efficiency of activated carbon.

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De-emulsification of oil emulsions by clays and nanocomposites

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Keywords: emulsion, clay, nanocomposites, bile salts, oil

Edible fats are hydrophobic, whereas their main digestive enzyme is soluble in water, and hardly interacts directly with fat molecules. Therefore, increasing fat apparent solubility forming an emulsion of small fat micelles increases the area of contact between the fat and the dissolved enzymes, and is a key to fat's digestion and absorption. Fat emulsification is aided by bile salts, which are amphipathic molecules secreted from the liver into the upper intestine. Emulsified fats and oils, present a large surface area to the surrounding solution, thus the water-soluble lipase can efficiently hydrolyze triacylglycerols into monoglycerides and two fatty acids. The influence of clays and polymer-clay biocomposites was tested on olive oil emulsions prepared with different emulsifiers. When using Triton-X100, a non-ionic surfactant, as emulsifier raw layered clays (as bentonite) didn’t influence whereas acicular clays (as sepiolite) efficiently de-emulsified the oil suspension. This can be explained by the high affinity of sepiolite to non-ionic surfactants. However, in suspensions that mimicked intestine conditions, were the emulsifiers are anionic bile salts, the effect of sepiolite was minor. The use of clay-cationic polymer biocomposites enabled the binding of bile salts, yielding efficient de-emulsification. The Fig. below shows that addition of 90-150 mg/L yields fast de-emulsification, whereas a slow process continues and after 24h clarified suspensions are achieved also at larger doses. Since the formation of an emulsion is considered a crucial stage at the fat and oil intestinal absorption, the de-emulsification shown here may contribute to reduce such absorption, lowering effects of the Metabolic Syndrome.

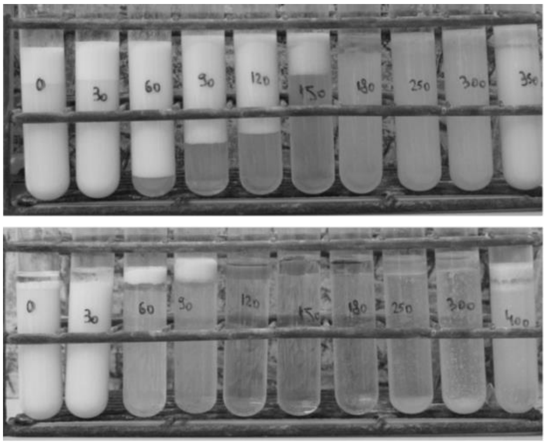

Fig: General appearance of buffer suspension mimicking intestine emulsion, with bile salts, phosphatidyl choline and 10% olive oil, 0.5 (top) and 24 h (bottom) after addition of a clay-cationic polymer biocomposite at amounts (in mg/L) shown.

Bentonite in waste repositories – a new application

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Geological disposal is the preferred option for the final storage of high-level nuclear waste and spent nuclear fuel in most countries. The selected host rock may be different in individual national programs for radioactive-waste management and the engineered barrier systems that protect and isolate the waste may also differ, but almost all programs are considering one or more engineered barriers. In most national concepts, the intention is to use swelling clay as a buffer that surrounds and protects the individual waste packages and/or as tunnel seal that seals off the disposal galleries from the shafts leading to the surface.

Bentonite and bentonite/sand mixtures are selected primarily because of their low hydraulic permeability in a saturated state. This ensures that diffusion will be the dominant transport mechanism in the barrier. Another key advantage is the swelling pressure, which ensures a self-sealing ability and closes gaps in the installed barrier and the excavation-damaged zone around the emplacement tunnels. Bentonite is a natural geological material that has been stable over timescales of millions of years and this is important as the barriers need to retain their properties for up to 10^6 years.

In order to be able to license a final repository for high-level radioactive waste, a solid understanding of how the barriers evolve with time is needed. This understanding is based on scientific knowledge about the processes and boundary conditions acting on the barriers in the repository. These are often divided into thermal, hydraulic, mechanical, and (bio)chemical processes. Examples of areas that need to be evaluated are the evolution of temperature in the repository during the early stage due to the decay heat in the waste, re-saturation of the bentonite blocks installed, build-up of swelling pressure on the containers and the surrounding rock, survival of bacteria within the clay, and degradation of the montmorillonite component in the bentonite. Another important area of development is the engineering aspects: how can the barriers be manufactured, subjected to quality control, and installed?

Geological disposal programs for radioactive waste have generated a large body of information on the safety-relevant properties of clays used as engineered barriers. The major relevant findings of the past 35 y are reviewed here.

Layered double hydroxide/sepiolite heterostructured materials: preparation and applications

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Keywords: heterostructured materials, sepiolite, layered double hydroxide, adsorbents, controlled release

There is an increasing interest in the development of nanostructured materials based on the combination of diverse type of inorganic particulate solids with the aim to produce a new generation of functional materials for diverse applications. In this context, fibrous clays have been used as support of nanoparticles, as for instance metal oxides (e.g., TiO_2, Fe_3O_4,..). This communication will introduce a new type of heterostructured materials in which layered double hydroxides (LDH) are assembled to sepiolite fibrous clay [1]. In this way, Mg-Al and Zn-Al LDH have been generated in presence of sepiolite clay, becoming linked to the fibrous silicate through the silanol groups present at its external surface. The synthesis procedure allows to tune the sepiolite:LDH relative ratio, being also possible to prepare the LDH in the presence of anionic organic species to produce the corresponding intercalation compounds. Changes in the textural properties deduced from the N_2 adsorption-desorption isotherms can be interpreted by the effect of sepiolite for providing a stable support where nanometric LDH particles remain attached decreasing the amount of N_2 adsorbed and therefore its specific surface area.

This methodology has been patented [2] and it is now applied to the preparation of diverse materials that can be of interest in diverse areas of application. For example, MgAl-LDH heterostructures show the preservation of adsorption properties ascribed to both type of inorganic components with the possibility of adsorbing simultaneously both cationic and anionic species. This has been tested in the removal of various dye pollutants. The thermal transformation of assembled ZnAl-LDH in the corresponding mixed metal oxide shows the presence of the generated nanoparticles that remain bonded onto the silicate, confirming the interest of the approach in view to prepare highly disperse metal oxide catalysts supported on sepiolite using LDH of different composition as precursors. The assembled LDH preserves its ion-exchange capacity which can be profited to incorporate anionic species useful for other applications. Thus, the anionic herbicide known as MCPA (2-methyl-4-chlorophenoxyacetic acid) has been intercalated in the supported LDH by ion-exchange as well by co-precipitation of the LDH in presence of MCPA and the clay. The release of the herbicide from these heterostructured materials has been tested in comparison to that from the herbicide intercalated in the LDH alone.

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Laponite® as a powerful compound to turn dark dye into fluorescent hydrid materials

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Keywords: clay, dye, photophysics, fluorescence

The combination of organic dye and clays minerals leads to very interesting hybrid materials showing original properties with applications in water depollution [1], solubilization [2], control of photochemical reactions [3] or optical properties [4]. In this work we used a synthetic commercially available 2:1 TOT phyllosilicate, namely Laponite®, to modify cationic triarylmethane dye spectroscopic properties. In this family, crystal violet (CV^+) absorbs in the red region with a high molar absorption coefficient and exhibits very complex ultrafast photophysics in which excited states decay in a few picoseconds [5]. This fast excited state deactivation is solvent viscosity dependent and involves phenyl ring rotations [6,7].

In this study demonstrate that electrostatic interactions between negatively charged basal surface of Laponite nanoplatelets and CV^+ cationic molecules can be used to tune the dye photophysics by steady state and time resolved femtosecond spectroscopy. Indeed, it is proposed that the strong electrostatic interaction hinders phenyl ring movements and consequently prevent the formation of either the twisted dark state or a twisted ground state isomer responsible of the fast decay of CV^+ excited state. As a consequence, light energy is stored in a singlet emissive bright state turning this non emissive dye into a fluorescent hybrid compound.

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Trivalent cations modified bentonites against eutrophication

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Keywords: phosphate, modified bentonite, eutrophication

Phosphorus is an essential and important element for all natural organisms [1]. Eutrophication is considered the most important water quality problem [2]. Nowadays there is growing interest in finding inexpensive and effective clays as phosphorus sorbents from natural water bodies. Certain anions (phosphate, nitrate, arsenate, etc.) are adsorbed onto clays via electrostatic attraction and ligand exchange [3]. Bentonite, as a low cost clay, is used in many applications for water treatment [4]. Montmorillonite clay mineral can be used as a model substance in the study of the interfacial processes of rocks and soils. It has many agricultural, industrial, and environmental applications [5].

In this study four modified bentonites (Y-, La-, Fe-, Ce-bentonite) were prepared and characterized, and their phosphate sorption capabilities were evaluated in batch experiments. Equilibrium time was also examined. The activation energy of the sorption process was calculated. The La-modified bentonite can be used for removing phosphate ions, but it is quite expensive, so we repeated the experiments with cerium (III), yttrium(III) and iron(III) ions modified bentonite. The iron was chosen because of the price, and the cerium was chosen because its relative abundance in Nature. In our work we have concluded that the Y-bentonite, La-bentonite and Ce-bentonite can bind similar amount of phosphate ions, while iron-bentonite only half as much phosphate that Y-, La-, and Ce-bentonites.

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Bioleaching effect on adsorption activity of Fe-rich clays

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Keywords: bioleaching, clay, iron, adsorption activity

A leaching of Fe-rich clays with acids or bacteria can transform Fe particles to active forms, which participate in adsorption process [1]. Three clays with different amount of Fe (1) – (3) (Table 1) were bio-leached with the heterotrophic bacteria of *Bacillus* sp. [2], and then used as the sorbents for As^V as AsO_4^{3-} and Pb^{2+} adsorption from model solutions ($c_{0(As,Pb)}$≈0.1mmol.L^{-1}; pH≈5.8-6.8).

Table 1: Characterisation of used clays

Sample	Mineralogical composition	leaching time (day)	Fe (before/after BL*) (mg.g^{-1})	S_{BET} (m^2.g^{-1})
(1) Kaolin Horní Bříza (West Bohemia, CR)	kaolinite (55 %), muscovite, quartz	60	4.4/3.5	7.5
(2) Kaolin Rudník (Slovakia)	kaolinite and smectite, muscovite, quartz, feldspar	30	7.7/6.4	10.8
(3) Bentonite Jelšovský potok (Slovakia) modified with Fe^{3+}	mostly montmorillonite (95 %)	16	463/218	82.8

*BL – bioleaching

The adsorption of Pb^{2+} was not significantly affected by a bio-leaching (Fig. 1a), as cations have been preferentially adsorbed to negatively charged O^- on the clay surface. Anions AsO_4^{3-} were adsorbed more effectively on bio-leached clays (Fig. 1b).

As anions are known by a strong adsorption affinity to available Fe oxides [3], the results indicated a promoting effect of bioleaching on adsorption activity of Fe in clays.

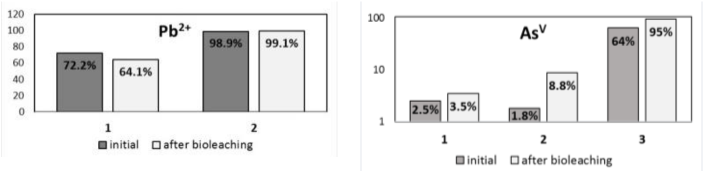

Fig. 1: Adsorption activity of initial and BL clays; a) for Pb^{2+}, b) for As^V

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Oxidative removal of an azo dye using clay and red mud

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Keywords: dye discoloration, clay, red mud, adsorption, Fenton process

In this study, Portuguese clay (Fe-impregnated clay), red mud and clay/red mud mixtures were used in the removal of Acid Orange 7 by Fenton and photo-Fenton (under UV light) oxidation processes. In comparison with purely adsorption, the catalytic activity of Fe-loaded clay showed an optimum removal rate (98%). This photo-assisted Fenton degradation of Acid Orange 7 azo-dye molecules was exploiting HO• radicals from generated H_2O_2 and clay supported iron species, following the pseudo-first order kinetic mechanism.

By using red mud pre-calcined at 400ºC, 10% improvement in overall discoloration was observed in comparison to the untreated clay. This improvement is attributed to the partial reduction of Fe^{3+} to Fe^{2+} species on the surface of the catalyst, and to the reaction with H_2O_2 to generate highly oxidative hydroxyl radicals. It was seen that the synergistic effect of photocatalysis due to the presence of TiO_2 in the red mud also contributed in this photo-Fenton process.

Furthermore, the use of red mud\clay catalyst mixes assured 38% dye discoloration at pH 7, but a lowering of solution pH to 3 resulted in a much higher discoloration rate (over 80% after 1 hour). The good fitting with a pseudo-second-order kinetic model (R^2 equal to 0.99) shows that adsorption processes could strongly contribute in the dye removal efficiency.

Characterisation of water in perlite from Milos, Greece

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Keywords: perlite, volcanic glass, water, Milos

The term perlite is used to describe hydrous volcanic glass. Scientifically the texture, type of water, and how water reached the perlite particle are important for the understanding of pre- and post-depositional alteration processes. From an industrial point of view it is more interesting to investigate the physical expansion behavior because some perlites significantly expand upon thermal treatment. The product is a light weight, fire-proof, and mechanically resistant material which can be used as thermal insulator in construction business. Interestingly not all perlites yield suitable products. Therefore, in order to bring some light into the open question why perlites behave differently, the water distribution in a Greece perlite was studied by various methods. Both, IR spectroscopy as well as thermal analysis proved the presence of a range of different water binding states. The spatial distribution of pores/water was studied by µ-CT (computer tomography), FIB (focused ion-beam electron microscopy), and IR-microscopy. Computer tomography (CT) showed large macropores (20 – 100 µm) and low density areas in the silicate matrix up to a few µm in diameter. FIB microscopy confirmed the presence of µm-sized pores and IR microscopy showed the filling of these pores with water. It remains unsolved whether the water in the µm-sized pores entered after or during perlite formation. However, the pores are sealed and no indications of cracks were found which indicated a primary source of the water, i.e. water was probably entrapped by quenching of the lava. The water in these pores may be the main reason for the thermal expandability which results in the extraordinarily expanded and porous perlite building materials.

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Acid activated clays: materials in continuous demand

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Keywords: bentonite, bleaching earth, acid activation, montmorillonite, non-swelling clay minerals

The purpose of this contribution was the review of literature on acid treatments of swelling and non-swelling clays and clay minerals, including materials based on smectites and vermiculites on one side and kaolinites and other non-swelling clays on the other. Acid activation is a chemical treatment traditionally used on clays, typically bentonites in hydrochloric or sulphuric acid, to obtain partly dissolved materials with enhanced surface properties suitable for new applications or displaying interesting behaviour. This contribution is a summary based mostly on experiments done in our laboratories [1-4], supplemented by recently published data from elsewhere [5-7]. Interest in these materials remains widespread, with several new developments of environmental relevance and in the area of clay−polymer nanocomposites. Acid treatment of vermiculites and of non−swelling clay materials is included to complete the overview on acid treated clays. The principal result of this comparison is that these materials are continuously demanded both in science and for traditional and new applications. The use of clay-based catalysts modified by ion-exchange and acid activation in the methoxylation of limonene, for the selective synthesis of α-terpinyl methyl ether was analysed. Mildly acid-activated SAz-1 was a promising catalyst, while the lack of activity of Ni^{2+}-SAz-1 with the Lewis acidity maximized provided evidence that the process occurs preferentially on Brønsted acid sites [5]. Saudi clay contains mainly smectite, and kaolinite and quartz as impurities. Acid activation causes decrease in contents of octahedral cations, increase in SiO_2 content, lower CEC and higher surface area, which is not the main factor affecting the removal capacity for basic blue-41 dye. The recycling of spent acid activated clay can be achieved by the sulfate radical oxidation [6]. H_2SO_4 treated Brazilian montmorillonite is a promising material in the catalytic esterification of oleic acid in the production of biodiesel, a renewable, biodegradable and environmentally friendly fuel [7].

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Modification of structure and adsorption properties by the thermochemical treatment

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Keywords: montmorillonite, acid treatment, nitric acid, adsorption properties, barrier applications

Montmorillonite clays are characterized by a high sorption capacity and can be used as a component of engineered barrier systems for radioactive waste disposal. The aim of this research is to assess the mechanism of transformation affecting the montmorillonite structure and its adsorption properties in processes that imply long-term interaction with nitric acid solutions.

The aim of this study is to describe features of structure and surface properties modification of different industrial Russian bentonite clays as a result of treatment with a nitric acid solution at an elevated temperature. Features of the composition and structure of natural and modified bentonite samples were studied with a set of methods (XRD, SEM, XRF, etc). Specific surface area and cation exchange capacity values were determined to characterize the adsorption properties. Staging transformation of the structure of montmorillonite under the influence of acid treatment was described. It was revealed that treatment with HNO_3 solutions results in partial leaching of interlayer and octahedral cations, which leads to protonation of internal surfaces, as well as the increasing microporosity due to partial degradation of the structure caused by the protonation of octahedral OH-groups followed with changing of the octahedral Al coordination and overall leaching of octahedral cations. The result of exposure to acid solutions is the reduction of the layer charge and modification of interactions between layers and sheets, and as a consequence, partial destruction of particles, which leads to a significant increase of the specific surface area. Whereas in contrast, with an increasing treatment duration, cation exchange capacity values decrease due to reduction of the layer charge.

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The role of clay minerals on non-aqueous solvent bitumen extraction

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Keywords: clay minerals, bitumen, oil sands, extraction, solvent

Clays (mainly clay minerals) cause problems in all stages of bitumen extraction from Alberta oil sands, it is thus of great importance to better understand the role of clay minerals on non-aqueous solvent extraction of bitumen. Previous studies have shown that it is difficult to determine a relationship among the individual parameters (e.g. mineralogy, chemistry and surface properties) of oil sands and rationalize their impact on bitumen extraction [1]. To overcome this problem, a set of experiments was conducted in the present study using natural standards of clays dominated by kaolinite, illite, chlorite, smectite and illite-smectite. These are known to be the main types of clay minerals comprising the Alberta oil sands [1]. Artificial mixtures of bitumen with clay standards were reacted for several days and washed three times each with cyclohexane to remove bitumen from the clays. The results showed that the total amount of residual cyclohexane insoluble organic carbon (CIOC) retained by clays is a function of intrinsic resistance of high molecular weight organic compounds to cyclohexane extraction and the nature of clays [2]. Swelling and non-swelling clay minerals reacted differently with bitumen. The non-swelling clays retained the residual CIOC primarily on the outer surfaces of clay mineral particles whereas the swelling clays retained the CIOC on both the outer and inner surfaces. The experimental results showed that the pre-treatment of swelling clays at various relative humidity conditions, swelling ability and number of swelling interlayers (i.e. expandability) affect the amount of CIOM retained on the swelling clays. On the other hand, the specific surface area was determined as a primary parameter controlling the amount of CIOM retained on the non-swelling clays [2].

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Broad bandwidth viscoelastic response of dilute clay mineral dispersions in different particle arrangements

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Keywords: rheology, clay mineral dispersion, viscoelasticity, particle interaction

Clay mineral dispersions display a rich variety of rheological behavior mainly because of complex arrangement of anisotropic disk-like clay mineral particles. Due to isomorphous substitution clay mineral particles gain negative charges on their faces and their edges are positively charged at $pH < pH_{PZC,edge}$ (point of zero charge at the edges) and negatively charged at $pH > pH_{PZC,edge}$. Accordingly, pH is decisive for electrostatic particle interaction and structure formation in clay mineral dispersions. In order to understand kinetics of structure formation of clay mineral dispersions at different pH values (8.5 to 12) and electrolyte concentrations (10^{-5} to 10^{-2} M NaCl) we applied oscillatory shear experiments at low deformation. Additionally, in order to Fig. out the effect of pH on particle interaction, linear viscoelastic response of clay mineral dispersions was analyzed in a broad frequency range (10^{-3}-10^{6} Hz) at pH 8.5, 10 and 12. We used synthetic and natural clay minerals, i.e. Laponite® *(registered trademark of BYK Additives)*, hectorite (0.2 μm fraction of SHCa-1 Source Clay) and montmorillonite (0.2 μm fraction of Volclay) with different lateral particle dimension of 20, 100 and 270 nm, respectively. Structure formation at pH = 10 takes longer than at pH = 12 for Laponite® dispersions with ion concentration lower than 10^{-3} M NaCl and curiously at high ionic strength (10^{-2} M NaCl) the gel-structure develops faster at pH 10 than at pH 12. We assume, the particles form face to face (FF) contacts at pH 12 in the presence of high ion concentration, but at pH 10 some edge to face (EF) associations between FF aggregates occur causing faster structure formation. On the other hand, Laponite® dispersions immediately form gel-like structure after setting pH = 8.5 irrespective of ionic strength. For all three types of clay mineral dispersions in arrested state, G' remains essentially constant in a wide frequency range and G'' exhibits a power-law dependence $G'' \sim \omega^{\alpha}$ with $\alpha = 0.75 \pm 0.02$ at high frequencies between 10^{3} and 10^{6} Hz. The loss modulus G'' is almost independent of the ionic strength of the dispersion, but changes significantly with pH in the frequency range between 10^{-3} and 10^{3} Hz. Since the plateau value of G' depends on strength of interaction among clay mineral particles, the crossover of G' and G'' shifts to higher values when increasing ion and solid concentration, e.g. it increases from 10 to 46 kHz by increasing electrolyte concentration from 10^{-4} to 10^{-2} M NaCl for the dispersion with 2 wt% of Laponite® at pH 10, and crossover frequency rises from 1 to 10 kHz by increasing solid concentration from 3 wt% to 5 wt% of hectorite dispersions with 10^{-2} M NaCl. For natural clay mineral dispersions this characteristic crossover occurs at lower frequencies than for Laponite® dispersions and decreases with increasing particle size.

Characterisation of raw and expanded perlite from Slovak deposits - water and texture

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Keywords: perlite, expanded perlite, porosity, Jastrabá deposit, Lehôtka pod Brehmi deposit

Perlite is acid volcanic glass with water content between 2-5 %. The most important deposits in Slovak republic – Jastrabá and Lehôtka pod Brehmi are related to rhyolite volcanism of the Jastrabá formation of the upper Sarmatian age. The purpose of this study is to compare raw and expanded perlite properties from the mentioned deposits.

The studied perlites contain about 6 % of mineral impurities (mainly phenocrysts and microlites of feldspars, biotite and quartz). Based on macro and micro observation and water content (loss on ignition, thermal analysis (TA)) two types of perlite have been identified at the Lehôtka pod Brehmi deposit – light-coloured with significant porosity and dark with low porosity. Light, grey perlite has average water content about 4 %, dark-coloured perlite contains about 3.5 % of water. Perlites from the Jastrabá deposit comprise two types of pores – oval in micrometrics scale (~1 µm) and elongated about 100 µm long. The amount of water is approximately 5 %. Molecular water dominates, content of hydroxyl water is only few tenth of percent (IR spectroscopy, TA). Process of water release from perlite glass was investigated at broad range of temperatures (from 150 to 900 °C), at different durations of treatments (3.5 and 15 hours), on three different grain fractions. The highest loss of molecular water was observed between 150 and 250 °C. Almost entire molecular water has been released during 15 hours treatments at 550 °C. The studied perlites were also expanded at 850 – 935°C in a labaratory furnace. Expansion ratio (bulk density of raw perlite/bulk density of expanded perlite) is between 17 and 20. Significant differences between studied perlite samples have not been detected. The porosity of raw and expanded perlite was studied also by scanning electron microscopy and X-ray computed tomography.

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Clay minerals and organic carbon persistence in soils

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Keywords: Carbon cycle, Soil organic matter, Clay minerals, Long-term bare fallow, STXM-NEXAFS

Soil clay-size minerals play a major role for soil organic carbon (SOC) stabilization. Among clay-size minerals, clay minerals (phyllosilicates) have been shown to protect efficiently SOC from decomposition. However, there is a wide variety of phyllosilicate types in soil and the respective abilities in protecting SOC of different phyllosilicates have not been clearly established.

Results of experiments carried out with simplified model clay minerals from geological deposits suggest that 2:1 clays protect more efficiently organic compounds from biodegradation than 1:1 clay minerals. However, soil clay minerals have different properties compared to model clay minerals. Studies dealing with “real” soil phases, using most often questionable methodologies, gave much more equivocal results.

To gain insights on the relative ability of differing clay minerals in protecting SOC, we decided to use the intrinsic mineralogical heterogeneity of the soil clay fraction. To do so, we compared soil organic matter associated with clay subfractions (<0.05 µm, 0.05-0.2 µm, 0.2-2 µm) having contrasted clay mineralogy recovered from the same soil. We applied our fractionation scheme to soils sampled in a long-term bare fallow experiment (79 years without plant inputs). We observed that C/N ratios of organic matter associated to clays decreased consistently with bare fallow duration, the steepest decrease being observed in the finest fractions. Bulk-scale C-NEXAFS data revealed that the speciation of SOC was similar across fractions and remained almost constant with bare fallow duration. STXM-based NEXAFS investigations at the submicrometer scale revealed that, contrary to smectitic clays, illite particles tended to lose SOM with bare fallow duration. Our study is the first direct *in situ* evidence that smectites are more efficient than illite in protecting soil organic matter over long duration.

Clay and iron oxide mineralogy, geochemical indicators and their paleoenvironmental interpretation in the southern European Russia loess sections

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Keywords: palaeosol, loess, clay mineralogy, iron oxides, climate change

Quantitative palaeoclimatic data (e.g. temperature, precipitation) are a prerequisite for understanding past and future climate change. Palaeosols may record, by changes in their physical, mineralogical and/or chemical properties, not only the soil forming climate prior to burial (and effective fossilisation) of the soil profile but also changes in soil evolution, vegetation, and environment. Paleosol chronosequences linked to global MIS events for the past ~1.0 Ma were investigated via analysis of loess/paleosol sequences in the North Caucasus and the Eastern Priazovie (Sea of Azov coast).The thickest loess/paleosol sequences in the Tersko-Kumskoy (N. Caucasus) depression, > 150 m thick, comprise one of the longest records of Quaternary paleoclimate change in Europe. Morphologically different types of palaeosol have been observed, indicating the regional climate has undergone several oscillations of as yet unknown extent. The loess/paleosol sequences in Eastern Priazovie provide Pleistocene climate records within the arid zone of southern European Russia. Here, exposed in the high cliffs of Taganroc Bay, subaqueous sediments (alluvial, from the Don, and estuarine-marine of the Sea of Azov) overlapped by subaerial sediments formed the parent materials for loess/soil formation. The southern Taganroc Bay sequences offer the most complete Pleistocene sequences within the whole Eastern Priazovie.

The aim of this study was to estimate the weathering status of the Pleistocene paleosols in the southern European Russia loess sections using iron oxide magnetic mineralogy, clay mineral assemblages and geochemical indicators (coefficients based on ratios of different element concentrations). We compare these data with other proxies available for these loess sections to incorporate them into the integral paleoenvironmental interpretation. The quantitative estimates of Quaternary climate changes enable us to obtain detailed environmental data for complete Pleistocene glacial-interglacial cycles across the steppic areas of the E. European plain.

Clay mineralogical evolution as a result of plant growth and potassium uptake

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Keywords: mineral evolution, potassium, quantitative analysis

Potassium (K), an essential plant nutrient, is found in different soil phases. In addition to K-micas and K-feldspars, it can be found in clay minerals. The effect of 110 years of continuous agriculture on the fate of soil K was investigated using samples from the Morrow Plots experimental fields. This long-running experiment represents a unique opportunity for quantitative assessment of the effect of plant growth and crop exportation on clay minerals in the field.

Topsoil samples from 1904-2014 are available, corresponding to fertilized (F) and non-fertilised (N) subplots under continuous corn (C) and corn-oats-hay (R) seeding rotations. Comparison of recent samples with samples from 1904 and 1957 allowed investigation of long-term differences and changes in fertilisation regimes, while the 2012-2014 series allowed establishment of the short-term alterations due to different cropping rotations. Samples were separated into <0.05, 0.05-0.2 and 0.2-2 μm fractions by centrifugation. X-ray diffraction (XRD) analysis was performed on Ca-saturated fractions under controlled relative humidity and ethylene-glycol solvated conditions. Full-pattern fitting of XRD data was carried out using a trial-and-error approach to determine a structure model quantifying the contribution of each clay phase.

A six-phase structure model for 2012 samples has been proposed, consisting of discrete illite, chlorite, kaolinite, and mixed-layer phases containing expandable layers (exp) interstratified with illite, chlorite or kaolinite layers. This structure model was used as a basis for the fitting of further samples. The proportion of mixed-layers in 2012 samples increased with decreasing particle size. Illite and illite-exp were found predominantly in the 0.2-2 μm size fractions, decreasing in proportion in finer fractions with a simultaneous increase in kaolinite-exp.

A greater proportion of illite-exp was found in C-subplots, with R-subplots more abundant in discrete illite. In addition to the variation with size, this suggests that degradation of illite in C-subplots over R-subplots occurred preferentially in finer fractions as a result of their greater reactivity. A variation between N- and F-subplots was also noted when considering the global proportion of illite layers from both discrete illite and illite-exp. While both N- and F-subplots contain similar amounts of discrete illite, F-subplots are shown to contain fewer total K-bearing layers indicating that fertilisation reduces the proportion of illite layers in illite-exp, possibly as the result of increased yield.

Non-clay mineralogy of the 2-50 μm fraction was quantified using Rietveld refinement. In addition to a dominant quartz phase (>70 %), fractions contained close to 20 % feldspars phases, contributing to the overall K-reservoir of the soil.

Complexity of clay mineral formation during 120 000 years of soil development along the Franz Josef chronosequence, New Zealand

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Keywords: soil mineralogy; interstratifications; hydroxy intercalation; hydroxy interlayered minerals (HIM); weathering

Weathering of primary silicates to secondary clay minerals over time affects multiple soil functions such as the accumulation of organic matter and cationic nutrients. However, the extent of clay mineral formation and transformation as a function of soil development is only poorly understood. In the present study, the degree of weathering of sediments along a 120-kyrs soil formation gradient at the Franz Joseph glacier, New Zealand was investigated qualitatively. Clay mineralogical properties within soil profiles (topsoils and subsoils) were deduced from X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), and X-ray fluorescence data (XRF). Irrespective of the site age, mica (both, di- and trioctahedral) and chlorite (trioctahedral) were the dominating clay minerals. Upon weathering, a remarkable suite of transitional phases such as vermiculite and several interstratifications containing vermiculitic, smectitic, chloritic, and micaceous layers developed, resulting in a higher amount of expandable layers as detected by ethylene glycol solvation (EG) using oriented XRD specimens. The degree of weathering was correlated with soil pH and depletion of elements such as K, Ca, Na, Fe, and Al relative to Si, regarding both, soil depth and site age. IR spectroscopy results indicated traces of kaolinite as a weathering in all samples. However, XRD data showed higher contents of kaolinite, especially at the 120 kyrs site, indicting a slow formation via transitional phases. Our study emphasizes that long-term soil development causes complex clay mineral assemblages, both temporally and spatially. Linking this variability to soil functioning, however, warrants further research.

Experimental aluminization of vermiculite interlayers: An X-ray diffraction perspective on crystal chemistry and structural mechanisms

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Keywords: Hydroxy-interlayered smectite, Hydroxy-interlayered vermiculite,
Interlayer Al, Clay mineral aluminization, Acid soils

Natural aluminization of swelling clay minerals is ubiquitous in acidic soils leading to the formation of hydroxy-interlayered (HI) minerals. This process has drawn special attention over the last 4-5 decades owing to the negative impact on soil fertility of the induced reduction of cation exchange capacity. Combination of chemical analyses and of X-ray diffraction profile modeling on a series of experimentally self-aluminized samples aimed at an improved description of HI minerals and more especially of their interlayer crystal chemistry.

Both exchangeable alkali cations and hydroxy (Al, Fe) cations coexist within HI vermiculite interlayers. The latter form discontinuous gibbsite-like interlayer sheets with ~15% completeness, despite layer-to-layer distances similar to that of chlorite. From charge compensation considerations, the isolated hydroxy (Al, Fe) cation clusters bear ~1.5 positive charges per cation.

Analysis of X-ray diffraction data indicates that aluminization of initially swelling interlayers is a layer-by-layer process leading to mixed layers composed of randomly interstratified swelling and aluminized layers, all aluminized layers likely hosting a similar number of hydroxy (Al, Fe) cations along the aluminization process.

This model contradicts the widely accepted description of HI minerals as a solid solution between expandable 2:1 clay and aluminous chlorite end-members. As a consequence, the proportion of HI layers in the mixed layer is a robust estimate of aluminization progress and both the amount of extractible (Al, Fe) and the extent of CEC decrease are positively correlated to this essential parameter.

Dolerite weathering in soil environment: mineralogy and petrography (Central Siberia, Russia)

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Keywords: dolerite weathering, smectite(s), petrography outlooks

The studies in the Central Siberian Plateau with its flood basalt complex or traprocks provide information on weathering and pedogenesis on mafic materials in cold continental climates. In the key plots traprocks were represented by slightly weathered dolerite. The conversion of dolerite to clayish materials in soil environment was investigated using micro-morphological studies in thin sections and quantitative XRD analysis.

The studied samples of dolerite were sampled from the lithic contact in the soil profiles as well as from soil horizons. Besides plagioclases and pyroxenes forming a poikilitic structure, secondary products from dolerite weathering were identified, such as Fe-oxides and di- and trioctahedral smectite(s). The smectite(s) occurs in fine-crystalline, spherulitic aggregates with colloform, felty structures. Two groups of well-drained soils on dolerite were studied: "shallow with hard rock" and "deeper and mature with saprolite". In the fine size fractions of all profiles smectite(s) was identified. The main process resulting in the permanent release of smectite(s) into the soil profiles is in fact physical disintegration of coarse rock fragments due to extreme temperature amplitudes.

Profile distribution of smectite(s) in the soil groups is not the same: smectite is predominant in the whole profile of shallow soil and only in the bottom horizons of mature profile.. The *00l* peaks in the XRD patterns of oriented samples from the upper acidic horizons of mature profile are very low in intensity, which may indicate smectite transformation into an amorphous phase. According to the results of the Rietveld analysis of the XRD patterns of the powder samples, the *hk* peaks of smectite are still present, the decrease of total smectite content as well as the increase of the amorphous phase is rather insignificant. In addition to that in the upper horizons the conversion of smectite aggregates to b-fabric (plasmic fabric) [1] is pronounced.

On the bases of above, it has been concluded that recent pedogenesis effects dispersion of smectite, which is accompanied by conversion of smectite aggregates to b-fabric, not smectite transformation to amorphous phase.

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Change of the metal sorption properties of clay minerals due to laboratory and natural pedogenic alterations

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Keywords: wetting and drying, hydroxy interlayering, vermiculite, montmorillonite

Due to their beneficial properties, clay minerals are the most significant inorganic constituents of the soil. Compared to primary silicates, clay minerals are stable phases in surficial soil environments. However, they can change with the physico-chemical conditions, and they can be transformed into other clay mineral or dissolved and neoformed. Consequently, their properties are modified.

Adsorption of some heavy metals (Pb, Co, Cd) on the clay fraction of brown forest soils (Luvisols), and on a soil montmorillonite (Ca and K form) submitted to 140 wetting and drying (WD) cycles in the laboratory were investigated. The clay mineral characteristics and clay mineral transformation processes, as well as metal sorption were determined by XRD, TEM-EDS, FTIR and thermal analysis.

Layer charge modification of smectites, hydroxy-interlayering of vermiculite, chlorite vermiculitization, iron oxidation and precipitation of Fe-oxy-hydroxides, as well as potassium fixation and illitization are the observed clay mineral processes in the studied soil profiles. The soil smectite has heterogeneous layer charge distribution. Analyses of the individual smectite crystallites by TEM-EDS revealed that Co adsorption capacity correlates to the layer charge. Additionally, potassium content reduces metal uptake. Similar to that of copper, cobalt and cadmium adsorption is enhanced by the precipitation of thin iron oxide coating on the surface of the clay particles [1]. Hydroxy interlayering is a common clay mineral process in slightly acidic environment in the soils of temperate zone. Al-hydroxy interlayering have been found to decrease remarkably the Pb uptake of a soil vermiculite. Laboratory cyclic WD caused potassium fixation in K-smectite, and thus it decreased significantly the Pb adsorption capacity. The study has evidenced that various clay mineral transformation processes can influence the adsorption capacity of the soil for potentially toxic elements. This must be taken into consideration when retention of the heavy metals in the soil is predicted.

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Formation of NH_4-illite-like phase at the expense of dioctahedral vermiculite in soil environment – an experimental approach

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Keywords: dioctahedral vermiculite, NH_4 fixation, soil illitization, ammonium illite

The objective of the present study was to investigate the influence of NH_4^+ saturation on the structure of dioctahedral vermiculite (hereafter divermiculite). Because no divermiculite standard reference material was available, two natural divermiculite-rich soil clay samples were used in the study. The clays were saturated with NH_4^+ using different protocols simulating natural processes likely taking place in soils (Table 1.). The degree of NH_4^+ - fixation by the divermiculite was evaluated using X-ray diffraction, elemental N analysis, and infrared spectroscopy. All the treatments involving NH_4^+ saturation caused NH_4^+ fixation and irreversible collapse (i.e. contraction to ~10.3 Å) of at least a portion of the prior hydrated (vermiculitic) interlayers. Air-drying of the NH_4^+-saturated samples greatly enhanced the degree of the collapse. The results obtained did not provide a conclusion to the impact of the reaction time on the degree of irreversible collapse. The results clearly indicated that the collapse of dioctahedral vermiculite leading to the formation of NH_4-illite-like phase is likely to occur in soils. The formation of NH_4-illite-like phase by NH_4^+ fixation of vermiculitic interlayers needs to be taken into consideration in studies dealing with clay mineralogy of sedimentary basins.

Table 1. Sample symbols and treatments used in the experiments conducted.

Sample	treatment used
(1E)_Na	Na^+ saturation
(1E)_NH_4	NH_4^+ saturation
(1E)_NH_4_Na	NH_4^+ saturation + Na^+ saturation
(1E)_NH_4_D_Na	NH_4^+ saturation + air-drying + Na^+ saturation
(1E)_NH_4_T1_Na	NH_4^+ saturation + 2 months ageing + Na^+ saturation
(1E)_NH_4_T2_Na	NH_4^+ saturation + 4 months ageing + Na^+ saturation
(6E)_Na	Na^+ saturation
(6E)_NH_4	NH_4^+ saturation
(6E)_NH_4_Na	NH_4^+ saturation + Na^+ saturation
(6E)_NH_4_D_Na	NH_4^+ saturation + air-drying + Na^+ saturation
(6E)_NH_4_T1_Na	NH_4^+ saturation + 2 months ageing + Na^+ saturation
(6E)_NH_4_T2_Na	NH_4^+ saturation + 4 months ageing + Na^+ saturation

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The Late Viséan pedocomplex of Moscow basin (Russia): mineralogical and geochemical characterization

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Keywords: palaeosols, Mississippian, clay mineralogy, palustrine deposits, bog marl

During the Late Viséan (Mississippian) the studied area was situated in the inner part of a flat, vast and very shallow-water epeiric basin that has no modern analogues. Numerous pedogenically altered subaerial exposure surfaces within shallow marine carbonates attest to periodical sea-level fluctuations and climate change. Here we demonstrate the results of the multiproxy study of the complex disconformity at the Mikhailovian-Venevian boundary from Polotnaynyi Zavod quarry (Kaluga region, Russia).

The obtained data show that the discovered disconformity at the top of Mikhailovian known as “black rhizoidal limestone” [1] consists from three units (from the bottom to the top): rendzina (PS1), subaerial - subaqueous soil developed from a bog marl (PS2), and non-marine (palustrine) black “rhizoidal” limestone. The pedocomplex is embedded in marine limestone layers. The bottom PS1 is developed from heavy montmorillonitic clay (up to 65 % of clay fraction). The clay fraction of PS1 contains montmorillonite and kaolinite. The top horizon is richer in kaolinite and contains traces of goethite. Additionally, it is rich in OC (up to 2%) with abundant macroscopic and microscopic organic fragments, invertebrate faeces, as well as plant imprints. All of them are substituted by micritic carbonate. Abundant *Stigmaria* testify that soil was developed under lepidodendron vegetation. Inborn OC is aliphatic in nature and alkyl groups predominate. The whole profile is weakly carbonaceous, the top horizon. The upper PS2 developed from a bog marl is carbonaceous (63–94 % of $CaCO_3$). The clay content ranges 1–11 %. OC is < 0.5%. Inborn OC is aryls dominated (aromatic). Two types of well-preserved roots attest that PS2 was developed under different vegetation relative to the PS1. Clay fraction is kaolinite dominated with minor smectite and goethite. The top soil horizon contains less $CaCO_3$ and more clay relative to marl. Both PSs are characterized by enhanced values of PWI, CIA and CIA-K [see 2] geochemical indices, Ba/Sr values and Ga concentrations. The $\delta^{13}C$ isotopic composition of the carbonates ranges from -6.28‰ to -4.55‰ which is typical for secondary pedogenic carbonate. Results of the mean annual precipitation (MAP) and mean annual temperature (MAT) calculations are in the accordance with [2, 3] and show that the pedocomplex was developed under wet and warm climate (MAP ~ 1000 mm, MAT ~ 15°C).

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Comparing clay mineral diagenesis in interbedded sandstones and mudstones (Vienna basin, Austria)

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There is no consensus about the rate and style of clay mineral diagenesis in progressively buried sandstones v. interbedded mudstones. The diagenetic evolution of interbedded Miocene sandstones and mudstones from the Vienna Basin (Austria) has therefore been compared using core-based studies, petrography, X-ray diffraction and X-ray fluorescence. There was a common provenance for the coarse- and fine-grained sediments, and the primary depositional environment of the host sediment had no direct effect on illitization. The sandstones are mostly lithic arkoses dominated by framework grains of quartz, altered feldspars and carbonate rock fragments. Sandstone porosity has been reduced by quartz overgrowths and calcite cement; their pore-filling authigenic clay minerals consist of mixed-layer illite-smectite, illite, kaolinite and chlorite.

The overall mineralogy of mudstones is surprisingly similar to the sandstones. However, for a given depth, feldspars are more altered to kaolinite, and smectite illitization is more advanced in sandstones than in mudstones. In sandstones, smectite illitization progresses with depth; at 2150 m there is a transition from randomly interstratified to regular interstratified illite-smectite. The higher permeability of sandstones than in mudstones allowed faster movement of material and pore fluid necessary for illitization and feldspar alteration. The significance of this work is that it has shown that open-system diagenesis is important for some clay mineral diagenetic reactions in sandstones, while closed-system diagenesis seems to operate for clay mineral diagenesis in mudstones.

The problem of the Chalk's smectite exemplified by the Upper Jurassic and Upper Cretaceous olistoliths of marls from the Outer Carpathians (Poland)

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Keywords: chalk, smectite clay, olistoliths, Outer Carpathians, Upper Jurassic and Upper Cretaceous

Smectite-dominated clay assemblage characterizes the chalk deposits of Europe and the understanding of its origin and nature is of important scientific and economic significance. A combined standard and high-resolution petrographic methods (optical and FESEM), and XRD and thermal analysis approach is put forward for the investigation and understanding of smectite clay development in the olistoliths of chalk from the Outer Carpathians. The investigated Upper Jurassic marls of the Silesian Unit (marls from the Vendryně Formation) and Upper Cretaceous marls of the Skole Unit (Węgierka Marls) [1] [2] associated with the opening and reconstitution stage of the Carpathian basin.

The composition of clay determined by using of XRD correlate with the organisation of clay particles in these rocks revealed by FESEM. The olistoliths of Jurassic marls contain R1 ordered illite-smectite (R-1 I-S) that display lamellar arrangement, whilst those of Upper Cretaceous with randomly ordered high-smectitic illite-smectite (HS R0 I-S) are dominated by clay showing boxwork or rose-like texture.

It is suggested that smectite to illite evolution in the olistoliths of chalk is retarded to some extent due to limited mechanical compaction resulted from early micropores stiffening by calcite overgrowth cement.

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Provenance and palaeoenvironmental controls on the clay mineralogy of marine sediments from Aegean Sea, Greece

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Keywords: Clay minerals; sediment provenance; palaeoclimate; Aegean; Greece

Sediments from two deep-sea bottom cores in south Aegean (TI13 core) and NW Aegean (C40 core), Greece, were examined by quantitative mineralogical and geochemical analysis in order to further assess paleoclimatic changes in notherneastern Mediterranean. Both cores consist of calcareous muds with black organic rich horizons, and contain the sapropel sequence S1. The sediments are dominated by calcite, Mg-calcite, quartz, feldspars and clay minerals. Accessory serpentine, talc and hornblende indicate provenance from an ultrabasic component. Palygorskite was used to quantify the aeolian input. Comparison of the clay mineral abundances in the bulk samples determined by Autoquan software using Rietveld refinement and standardless profile fitting and the clay fractions determined according to [1], indicates that the bulk sediment is enriched in kaolinite and chlorite and depleted in smectite relative to the clay fraction, whereas illite is more evenly distributed in the bulk sample and the clay fraction. Moreover the well expressed negative relationship between illite and smectite observed in the clay fractions, which has been described in several Aegean cores in previous studies, does not exist in the bulk sediments of the two cores, suggesting different mode of enrichment of the two clay minerals.

Projection of the smectite content with phases not affected by weathering such as quartz, suggests at least 2 source areas for this mineral. Multiple provenance of smectite is in accordance with the observation of a smectite phase with low dehydroxylation temperature (~520 °C) and another phase with dehydroxylation temperature greater than 600 °C. The Nilotic influence in the mineralogical composition of the sediments is not as important as previously suggested and both the bulk and the clay mineralogy of the Aegean sediments is controlled mainly by input from the nearby landmass of Western Anatolia and eastern and northern Greece via small rivers. Moreover the fluctuation of the relative abundances of calcite and Mg-calcite and the values of Mg/Ca and Sr/Ca ratios in the forams of the sediments indicate characteristic drop of the sea level and cooler climate during the formation of the sapropels. The results of this study indicate that the semiquantitative approaches to determine clay mineralogy may lead to misleading conclusions. Moreover, they can be used to assess provenance and palaeoclimatic conditions in small basins based on clay minerals.

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Ediacaran clays of the East European Craton – a unique record of the paleoenvironment

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Keywords: Berthierine, clay minerals, East European Craton, Ediacaran, kaolinite

During the Ediacaran (635–542 Ma) the Earth's atmosphere and hydrosphere underwent major changes, attaining at the end of this period a composition that has remained relatively stable until today. Ediacaran changes in the Earth system broadly coincide with the emergence of complex, multi-cellular, megascopic forms of life. These observations have inspired intensive research of the Ediacaran rocks, to gain information on the Earth surface conditions during this period. The major difficulty of such studies is the diagenetic/metamorphic overprint that affected all well-known and widely studied Ediacaran profiles. The Ediacaran rocks cover a major portion of the East European Craton, outcropping in several localities and penetrated by shallow boreholes in many others. In the NW part of the craton, selected for this study, the Ediacaran rocks were not affected by major diagenetic alterations, as indicated by several lines of evidence. Over 1600 samples of Ediacaran rocks were collected from Russia, Estonia, Lithuania, Belarus, Poland and Ukraine and studied first by quantitative XRD to establish mineral composition. These preliminary results are reported here. The section begins with a series of tillites and fluvioglacial deposits (Vilchanskya Series) of unconstrained age, deposited over sandstones (Orshanskaya Series) and locally over dolomites (Lapickaya Series). Clay fraction of these continental glacial deposits: kaolinite, illite, illite-smectite and fine-grained hematite is identical to older Pinskaya Series, indicating the glacial transport from W. Kaolinite+hematite are clearly products of weathering older than the glacial period. The overlying Volynskaya Series, dated 560–570 Ma, contains basalt flows, tuffs, and tuffites. A pure dioctahedral smectite was identified in the bottom tuffites, indicating a smectite-type weathering in this period. The main body of basalts and tuffs contains zeolites, saponite, chlorite, mixed-layer chlorite-saponite and aluminoceladonite, interpreted as products of hydrothermal alteration. In the weathering profiles, developed on the top basalt flow, a transition from saponite or chlorite into dioctahedral smectite and then towards kaolinite+hematite was detected. The transition is complete if the exposure to weathering lasted sufficiently long. Such composition of the weathering crusts is indicative of a wet and hot climate. The weathering products are identical to Recent.

The Redkino and overlying Kotlin Series are sediments of a marine transgression. They contain abundant kaolinite and fine-grained hematite, implying that the nature of weathering did not change since the pre-Ediacaran times. In a broad range of sedimentary environments from fluvial to marine, hematite is reduced and kaolinite is altered into berthierine, which is indicative of a hot equatorial climate.

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Mineral nanotubes in the recent marine sediments from the southeastern Adriatic

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Keywords: clay-sized particles; mineral nanotubes; recent marine sediments, Adriatic sea

The mineral composition of recent marine clayey sediments from different sedimentological environments of the southeastern Adriatic was investigated. The main objective was to determine the structural and morphological properties of submicron-sized mineral particles that occur in the investigated sediments. The mineral particles were examined by X-ray diffraction (XRD), field-emission scanning electron microscopy (FESEM) and electron microprobe energy dispersive X-ray analyses (EDX). The results obtained for the first time identify the presence of unusual mineral forms, nanotubes, which have not been determined in modern sediments of the Adriatic (Fig. 1). The occurrence, origin and structural and morphological properties of these solids will be discussed.

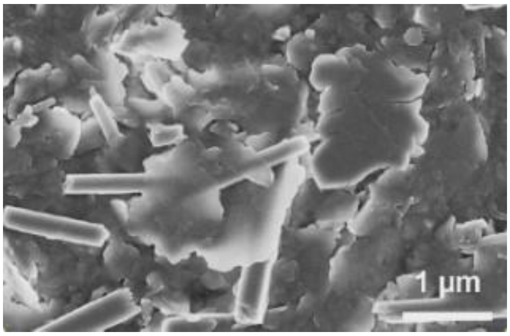

Fig. 1: FESEM photomicrograph of tubular mineral particles in size fraction containing particles with diameters <2 µm.

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Clay minerals from Mesozoic clastic reservoirs of the South Gabon Basin (West Africa) - diagenesis and impacts on regional geology

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Keywords: Gabon basin, illite-smectite, chlorite-smectite, berthierine, diagenesis

In sandstone reservoir rocks the role of clay minerals has been extensively studied in the last decades because clays readily occlude primary porosity, influence different geophysical parameters of host sandstones and react with drilling fluids, thus affecting various oil recovery practices [1]. The origin of clays in sandstones is complex and multifold, being either detrital or authigenic, formed through a series of diagenetic reactions [2].

In the area of South Gabon Basin in West Africa, several sandstones formations were formed during the opening of the South Atlantic. Two of the most prominent formations therein – Dentale and Gamba Fms. – were reported as most important hydrocarbon-bearing clastic onshore reservoirs in western Africa [3]. Their clay mineral paragenesis is seriously under-researched. In this contribution, we present the first results on the mineralogy and geochemistry of pore-filling and grain coating clays from both formations, discussing their diagenetic evolution and the significance they may have had on the regional geology reconstruction. A total of 30 and 44 samples originating from Gamba and Dentale Formations, respectively were analysed by XRD, SEM, QEMSCAN, and ICP-MS.

The studied sandstones showed to be dominated by anisopachous and discontinuous coatings or infills of mixed-layer illite-smectite (I-S), chlorite-smectite (C-S) and berthierine-chlorite (B-C). Such peculiar clay morphology, corroborated by the facies analyses [4], is characteristic for extrabasinal clays entrained into the sediment by clay infiltration, whereas the origin of B-C is linked to the diagenetic conversion of berthierine to tri-octahedral Fe-rich chlorite. Knowing that the composition of infiltrated clays has a decisive impact on the mesogenetic evolution pathways of porous clays, the burial depths of the cores analysed were chosen to conveniently match the transition of eodiagenesis to mesodiagenesis. This enabled to identify the primarily di- and tri-octahedral smectites that are, through a series of mixed-layer intermediates, transformed into illite or chlorite, respectively. In several horizons, however, higher clay abundances (~15–30 wt%) bear signs of pyroclastic material of a twofold geochemical character, conformant to the whole-rock trace-element geochemistry and diagenetic reactions, that led to the preferential formation of I-S and/or C-S. This offers a rare piece of evidence on the Cretaceous regional volcanic activity along the western African ridge at the time of the opening of the South Atlantic Ocean.

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Transition from regional to contact metamorphism in the area of Torres del Paine (Southern Chile) – insights from the clay mineralogy perspective

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Keywords: contact and regional metamorphism, illite-smectite, Torres del Paine

Clay minerals are used as metamorphic indicators of low-grade conditions due to their compositional variation and degree of ordering. The extent of chloritization and illitization is generally considered to be a function of temperature, which is related to burial depth, circulation of hydrothermal fluids, proximity of igneous bodies and/or deformation processes. The contact aureole surrounding the Torres del Paine intrusive complex (TPIC) is located in the Magallanes Basin at 51°S latitude. It exhibits excellent conditions to investigate the clay mineral reaction processes taking place during and after the emplacement of the intrusion. The thermal history observed in the Magallanes Basin is due to regional burial, deformation and contact metamorphism. Preliminary results dated the fold-and-thrust belt formation at around 60 Ma under regional anchizonal metamorphic conditions. The Miocene TPIC was emplaced into the Cretaceous Cerro Toro and Punta Barrosa formations between 12.59 and 12.43 Ma [1, 2, 3]. This study investigates the gradual change in clay mineralogy and rock fabric in relation to the distance to the TPIC in order to understand the thermal effects within the several 100 m wide contact aureole. A set of 20 samples were collected in profiles towards the contact aureole, as well as in selected spots surrounding the intrusion. The temperature conditions are estimated based on crystallinity indices, the maturity of organic material and the evolution of mineral paragenesis. Mineral identification and quantification is being done by XRD, SEM, and QEMSCAN. The initial regional metamorphic conditions, prior to the emplacement of the TPIC, are anchizonal with temperatures between 220 and 270°C. Contact metamorphic samples depict minimum temperatures of 330°C. The regional metamorphic anchizonal shale paragenesis consists of albite, chlorite and illite (dominant clay phases). Chlorite shows considerable chemical variations which can be assigned to the presence of a detrital high-T chamosite and an authigenic low-T clinochlore as well as mixed-layer chlorite (clinochlore) -smectite. Illite appears either as pure illite or mixed-layer illite (90%)/smectite. The gradual change to contact metamorphic samples is initiated by a pattern of decreasing expandability of illite and chlorite layers. Contact metamorphic chlorites and illites are characterized by small variations in their chemical composition due to the complete transformation/disappearance of interlayers and the chemical equilibration of detrital grains.

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The importance of illitic minerals in shale instability and in the unconventional hydrocarbon reservoirs of the USA

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Keywords: illite, shale, instability, porosity, permeability

Shale instability leads to serious operational problems with major economic consequences for the petroleum industry. Although shale instability may occur for many different reasons, it is generally accepted that the clay mineralogy of the shale formation is a primary causative factor. Currently, the principal cause of shale instability is considered to be volume expansion at the inter-lamellar level following osmotic swelling of Na-smectite, but such a mechanism cannot be considered as a universal causative mechanism because illitic and kaolinitic shales may also be unstable. This review considers alternative scenarios of shale instability relating particularly to illitic minerals. The influence of interacting factors that relate to shale clay mineralogy such as texture, structure and fabric are discussed, as are the pore size distribution and the nature of water in clays and shales and how these change with increasing depth of burial. From the literature it appears that the thickness of the diffuse double layer (DDL) of the aqueous solutions associated with the charged external surfaces of clay minerals is probably of the same order or even thicker than the sizes of a significant proportion of the pores found in shales. In these circumstances, overlap of the DDLs associated with exposed outer surfaces of clay minerals on opposing sides of slit-like micropores (<2 nm in diameter) and mesopores (2–50 nm in diameter) in a lithostatically compressed shale would bring about electrostatic repulsion and lead to increased pore/hydration pressure in illitic shales. In this scenario, the locus of action with respect to shale instability and its inhibition is moved from the interlamellar space of the smectitic clays to the charged external surfaces of the illitic shales bounding the walls of the slit-like pores.

In shales and sandstones, illitic material is usually described in terms of two different phases, namely illite *per se* and mixed-layer illite-smectite (I/S). Evidence is presented to show that it is often the case that only one illite phase exists and that in reality the mixed-layer I/S is simply very thin illite (< 5nm in thickness) in the early stages of its growth. Such material is of common occurrence in the unconventional hydrocarbon reservoirs of the USA. Clay mineralogy is an important factor in the exploitation of such reservoirs with regard to poro-perm properties as well as the mechanical properties relating to hydraulic fracturing.

Clay minerals on Mars: Global scale mineralogy and geologic context

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Keywords: Mars, hydrothermal, volcanic, nontronite, astrobiology

Mars is the planet most geologically similar to Earth. Like Earth, the crust of Mars is composed of igneous rocks that have been chemically and physically weathered, eroded, sorted and redistributed. However, unlike Earth, Mars lacks continents, plate tectonics, and long-lived oceans. Most of the Martian crust is seemingly composed of mafic igneous rock (both lavas and tephra) that has been modified by impact cratering.

Hydrothermal deposits, sedimentary rocks and soils within the Martian crust are generally Fe/Mg-rich, reflecting a basaltic protolith. Most of these deposits are ancient, dating to ~3.6-4.1 Ga. As Mars and Earth were likely similar early in their histories, the ancient, intact geologic record on Mars is older than that of Earth, and therefore likely contains clues to early geological, and potentially organic chemical processes that are simply not preserved on Earth.

A major discovery in the last ~12 years has been the detection of 1000 s of deposits of phyllosilicates on Mars using near-infrared (NIR) remote sensing data. The NIR data (λ= 1.3 µm) are sensitive to the crystal chemistry and hydration of the clays minerals, but lack key information about structure critical to interpretation of clay mineralogy. While it was long suspected that the Martian soil might contain Fe-rich smectitic clays, number of deposits and the diversity of mineralogy and geologic context of these clay mineral deposits have far exceeded expectations. Most of the clays detected remotely on Mars correspond to Fe-rich dioctahedral smectites and smectitic mixed layer clays. Less common are trioctahedral smectites and di-trioctahedral mixed-layer smectites. In addition, deposits of chlorite, serpentine, glauconite, and vermiculite have been detected. Most of these occur in deposits that were seemingly altered in the subsurface by hydrothermal processes and subsequently exhumed by erosion or meteor impact. Other deposits represent layered, lacustrine sediments or layered, airfall deposits – probably altered tephra.

While most clays so far detected on Mars are Fe-rich, aluminous deposits are also found. In fact, many of the layered deposits of Fe-rich smectites are overlaid by ~10s of metre-thick deposits of kaolinite- and montmorillonite-rich sediments or soils. Allophane is likely also present, but difficult to uniquely detect. The origin of these aluminous clays remains somewhat elusive. They might represent a highly weathered soil residue or they might represent altered tephra that was felsic/intermediate in composition.

The geologic record of Mars holds critical clues to the early Solar System processes not preserved on Earth. The clay minerals that occur there are clear indicators of the action of water early in Mars' history and therefore they point to locations where the crust of Mars contain habitable environments. Hydrothermal clay deposits on Mars may hold clues to the origin of life.

Early Mars – How wet and how warm?

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Keywords: infrared, interstratified clays, Mars, submarine hydrothermal sites

The largest proportion of clay detected on Mars using near-infrared remote sensing is Mg/Fe-rich and is hydrated, for which reason it is considered to consist mainly of smectite. There is large support for a hydrothermal origin of many of these clays because approximately half of their detection sites are within impact craters, indicating underground formation, and because hydrothermal activity is a likely explanation for the very thick clay layers observed (up to hundreds of m). These clays formed mainly during the Noachian period (4.1-3.7 Gy), when Mars contained more liquid water than presently, although how much is still debated.

Earth analogues for these types of clays are found in submarine hydrothermal sites. Mg/Fe-rich clays from 5 locations world-wide were sampled from collections. They were studied in detail with chemical, XRD, thermal and infrared methods. They are endmember nontronite and mixed-layer glauconite-nontronite, talc-nontronite and talc-saponite. Their crystal-chemical character is complex. Talc-nontronite specimens have nontronite domains in the octahedral sheets of talc layers. For the purely dioctahedral samples, thermal and infrared data have good linear correlations with chemical data. For clays with trioctahedral components these correlations are more complex or do not exist. These are important findings because clay identification on Mars is largely based on near-infrared remote sensing and our data point to new features to be considered for a more reliable interpretation of the mineralogy and chemistry of Martian clays.

Using our near-infrared data of the Earth analogues we catalogued the relative abundance of Mg/Fe-clays on Mars with respect to their FeO/MgO contents. We found that ~70% of the clays have FeO/MgO = 10-30, which indicates a substantial segregation between Fe and Mg during the alteration of the original basaltic rock with FeO/MgO ≤ 2. This fact implies the involvement of large volumes of water and/or oxidizing conditions in the formation of this large proportion of Martian Mg/Fe-clays. Further detailed investigation of the near-infrared data aims at a more unequivocal identification of clay mineralogy. Disordered, hydrated talc, mixed-layer talc-nontronite and glauconite-nontronite are hard to distinguish from saponite and nontronite in Martian spectra. Being able to do so would allow setting constraints for the temperature of clay formation or diagenesis.

The use of automated mineralogical analysis to complement oedometer and desintegraion tests to evaluate geometallurgical implications of laumontite altered rock

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Keywords: laumontite, andesite, geometallurgy, expansion pressure

The reversible hydration of leonhardite to laumontite and its concomitant expansion of the crystal lattice are known since the 1950s. Its deleterious effects on concrete stability, in particular in humid and saline environments have been documented by the cement industry and civil engineering publications. In Chile, laumontite bearing rocks are widespread associated with very low grade metamorphic or hydrothermally altered volcanic or subvolcanic rocks some of which host major ore deposits. This presentation combines a mineralogical study of a laumontite rich rock sequence by optical microscopy, semiquantitative X-ray diffraction, automated mineralogy and the monitoring of free and confined expansion by modified standard oedometer tests, as well as monitoring of rock disintegration in water and ethylene glycol. Automated mineralogical microanalysis allows the observation of laumontite distribution and its directionality in the rock, however, it is not possible to differentiate very fine grained groundmass laumontite from feldspar compositions, thus resulting in lower laumontite percentages when compared to semiquantitative X-ray diffractions. An initial challenge is the adjustment of the microchemical reference database with analyses of pure laumontite; here best large specimens for repeated microchemical analysis are obtained from vesicular fillings of basaltic rocks and not from pervasive altered andesites. Adequate monitoring of directionality may require scanning of multiple thin sections for one sample or core section thus increasing counting times and cost. For the studied rocks, semiquantitative X-ray diffraction proved to the most economic mineralogical analysis. To test expansion pressure, standard soil oedometer tests can be adapted for use with finely crushed rock aggregate. Due to the small size of the zeolite channels in laumontite, ethylene glycol exposure will not reveal the presence of this expandable phase; submerging the rock in water for several day will reveal the instability of the rock, in particular when overburden is added at the end of the experiment. It is recommended to include laumontite in the “mineral check list”, when expansion, long term humid stability are important in mineral processing or laumontite rock may be incorporated as aggregate in concrete that will be submerged or exposed to high humidity in processing instalations.

Preparation of cobalt hydroxides and their deposition on metal supports

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Keywords: cobalt hydroxides, cobalt oxides, supported catalysts, VOC total oxidation, nitrous oxide decomposition

Cobalt hydroxides and oxides are extensively explored for materials in energy storage and heterogeneous catalysis. We prepared Co-containing precursors by precipitation of cobalt nitrate in aqueous solutions using various precipitation agents and reaction conditions; the β-$Co(OH)_2$, Co^{II}-Co^{III} layered hydroxide, and basic cobalt carbonate were found in the obtained products. After heating at 500 °C, the Co_3O_4 spinel-like oxide was formed and the catalyst obtained from β-$Co(OH)_2$ precursor showed high catalytic activity in N_2O decomposition [1].

Amount of active components in catalysts can be reduced, when thin active layer is deposited on supporting material. We used the stainless steel sieve as the support and the cathodic reduction of cobalt nitrate in aqueous solutions was applied for cobalt hydroxides synthesis on the support surface. The product consisting of small platelet crystals contained crystalline phases with layered structure; the Co^{II}-Co^{III} layered hydroxide and β-$Co(OH)_2$ as an admixture were identified by XRD. Formation of large cobalt carbonate crystals on supports was observed during hydrothermal treatment of stainless steel sieves in solutions containing urea and cobalt nitrate. Combination of hydrothermal treatment and subsequent electrochemical reaction increased the amount of deposited precursors and improved adhesion of the Co_3O_4 oxide, formed after heating, to the support. The plasma sputtering of Co followed by its oxidation was used as an alternative method for obtaining cobalt oxides on stainless steel sieves. Cobalt was oxidized to Co_3O_4 and CoO during heating in air; the volume of deposited layers increased and formation of platelet crystals on the surface was observed. The sieves coated with cobalt oxides were also used for subsequent electrochemical deposition in order to increase amount of active component (Co) in the deposited layers. All prepared samples were tested as catalysts in the total oxidation of ethanol and decomposition of nitrous oxide.

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Use of molecular simulations in complex characterization of layered organo-inorganic hybrid materials

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Keywords: molecular simulations, layered structures, interactions

Molecular modelling calculations based on empirical force fileds can be used for structure characterization of a wide range of layered organo-inorganic hybrid materials. In combination with X-ray diffraction, FTIR spectroscopy and TG analysis they can provide a detailed view on the structure arrangement of the guests in the interlayer space and can explain the relationship between the structure and observed properties of investigated materials.

We report the results on strontium phenylphosphonate intercalated with 1,n diols. In this case the simulations showed how the shape of the host layers influences the arrangement of the guest molecules in the interlayer. From the structural point of view the intercalates can be divided into two subgroups: (i) intercalates with 1,2- to 1,4-diols and (ii) intercalates with 1,6- to 1,8-diols. The alkanediols of the first group are immersed in the free spaces among the benzene groups, their molecules adopt a horseshoe shape meaning cis conformation and are bonded by both of their OH groups to one host layer. The longer alkanediol chains of the second group allow anchoring to both neighboring layers of the host forming a kind of pillared structure in the interlayer space. The diol molecules are in this case bonded to the host layers by their OH groups to the oxygen atoms of the host layers and to water molecules present in the interlayer space through hydrogen bonds. The values of the basal spacing obtained from the experimental powder X-ray patterns are in a very good agreement with the basal spacing values calculated from the models. The molecular simulation of a 1,5-pentanediol intercalate, which we were not be able to synthesize, explained why this intercalate cannot be stable.

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Petrographical, mineralogical and chemical identification of natrolite group zeolites in amygdules of basaltic lavas

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Keywords: sequence of crystallization, natrolite, mesolite, scolecite, amygdaloidal

The types and order of crystallization of the zeolites was demonstrated by examining the mineral assemblage in amygdules from a basaltic flow in a shallow-marine environment. The compounds necessary for the formation of secondary minerals might have been derived from alteration of volcanic glass and Ca-rich pyroxenes in the host rock as well as from the associated marine sediments. From petrographical and chemical analyses, it can be suggested that the composition of the vesicle-filling solutions was suitable to precipitate first sodium-rich zeolite, followed by a progressive increase in Ca content and finally ended with a calcium-rich zeolite. The growth of the earliest phase starts around an unidentified nucleous is natrolite. It is followed by mesolite, which forms epitaxial overgrowths with natrolite (Fig. 1). Scolecite is the late phase of the crystallization sequence. The partial transformation of mesolite to natrolite which occur as rims of the mesolite cores can be differentiated on back-scattered electron image [1].

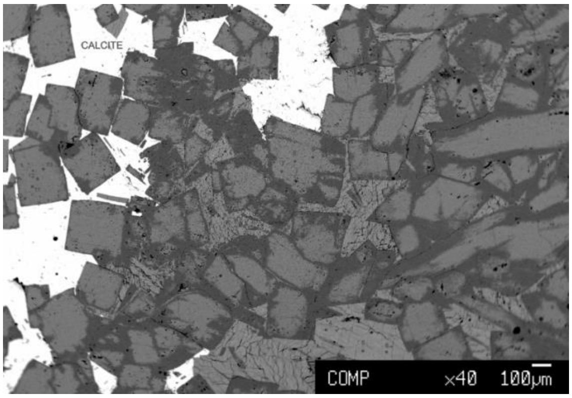

Fig. 1: Back-scattered electron (BSE) images of mesolite crystals replaced by natrolite surrounded by scolecite and calcite (Zone II)

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Polyelectrolyte-stabilized layered double hydroxide dispersions

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Keywords: layered double hydroxide, polyelectrolyte, colloidal stability, dynamic light scattering, surface coating

Layered double hydroxides (LDHs) have been widely used in sensing, catalysis and drug delivery. In the latter application, the colloidal stability of the carrier LDH is a critical issue, since aggregation of the particles leads to unsuccessful delivery of the target molecules. Therefore, we aimed to stabilize LDH dispersions with polyelectrolytes, such as biocompatible heparin and a random copolymer of acrylic acid and butyl acrylate [1].

In general, the negatively charged polyelectrolytes adsorbed strongly on the particle surfaces of opposite charge leading to charge neutralization and subsequent charge reversal at appropriate doses. Dynamic light scattering experiments revealed that colloidal stability is largely sensitive to the polyelectrolyte dose and the ionic strength. Unstable samples were observed near the charge neutralization point, however, the dispersions were highly stable when the particles were completely coated with the polyelectrolytes. For instance, the heparin-coating resulted in an enormous stabilization effect reflected in the significant shift towards higher ionic strengths in the critical coagulation concentration (CCC) values (Fig. 1). The bare LDH particles were unstable at low salt levels, while the polyelectrolyte-coating gave rise to highly stable dispersions, which are potential candidates as carriers in delivery processes even at high electrolyte concentrations, where the bare particles would rapidly aggregate. These results allow designing efficient delivery systems, in which aggregation of LDH nanocarriers can be tuned with biocompatible polyelectrolytes.

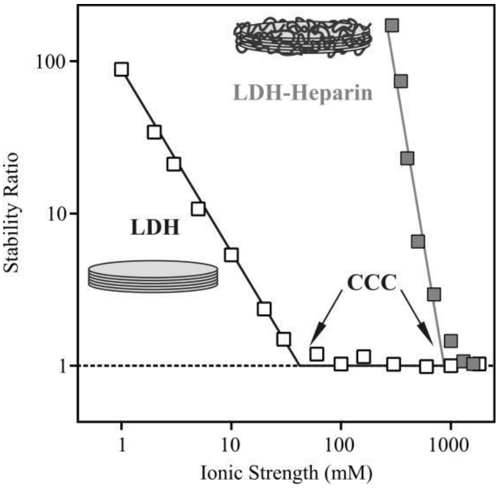

Fig. 1: Stability ratio of bare (empty symbols) and heparin-coated (filled symbols) LDH nanoparticles versus the ionic strength. Stability ratio close to unity indicates rapid particle aggregation, while higher values refer to more stable samples.

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Studying ancient ceramics: interplay between mineralogy, physics, chemistry and geology

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Keywords: Archaeoceramics, OM, XRD, EMPA

The relation between natural sciences (physics, chemistry, geology) and social sciences (archaeology) has a long history. It arises from the need for scientific data which may help to answer to general and particular questions which preoccupied, preoccupies and will ever preoccupy the minds when finding various ceramic artefacts at archaeological sites: From what kind of materials are they made of? How were these objects manufactured? Where are they from?

On the other hand, there is an obvious academic benefit from studying ceramics for mineralogists, not only for the archaeologists. For example, the complex ceramic mixture is an excellent field to study high-T pyrometamorphism. The initial inhomogeneous mixture of mudstone and tempering material transforms upon firing into a mosaic of micro-domains which are not in equilibrium but yet “coexist”, due to the short time of firing and rapid cooling.

The ceramic objects study needs an integrated approach, combining archaeological, mineralogical, petrographic, chemical and physical data. A wide range of analytical methods can be involved: polarized light optical microscopy (OM), X-Ray diffraction (XRD), electron microprobe (EMP), scanning electron microscopy (SEM), as well as Fourier transform infrared spectroscopy (FTIR), thermal analyses (TA), Raman spectroscopy and electron paramagnetic resonance (EPR). Each method provides a part of a final image.

For a provenance study, the knowledge of the geological and petrographic background of the area around the archaeological site combined with the mineralogy and petrography of the ceramics is mandatory. However, the geochemical data on major, minor, trace and RE elements may shed light not only on the geological sources but also on treatment procedures applied to raw materials, e.g., levigation, selection or mixing. Case studies on pottery sherds found at various prehistoric and historic sites illustrate the state of the art in archaeometric studies in Romania.

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Raw Material Sources of Halaf Period Ceramics from Domuztepe Mound, Kahramanmaraş-Southeast Turkey

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Keywords: pottery, Late Neolithic, Domuztepe, geoarchaeology, Turkey

Domuztepe Mound islocated at Kahramanmaraş area, Southwest Turkey, represents the Northwestern border of a unique material culture distribution commonly known as “Halaf culture” which had influenced vast regions of Northern Mesopotamia during the Later Neolithic time period (6000-5200 cal. B.C.). Halaf material culture is best known through its elaborately decorated ceramics which have long been speculated to originate from a center in Northern Iraq. Ceramics unearthed at Domuztepe has provided evidence that a single center in Northern Iraq may no longer be a viable explanation for the Halaf material culture distribution. Whereas an important portion of the ceramics and other material culture show close affinities with the material found in other parts of Northern Mesopotamia, they are also observed to be an integral part of independent traditions of local production. The aim of this study is to understand the local resource use of a group of archaeological ceramics recovered from the site of Domuztepe by using geoarchaeological and archaeometrical methods.

In this study the textural characteristics,mineralogical and chemical compositions of Halaf period ceramics and soil samples collected from potential clay sources for ceramic productionare analyzed by using petrographic and scanning electron microscopes,X-ray powder diffraction and inductively coupled plasma mass sprectrometric analysis. Cluster analysisis performed by using the mineralogicaland chemical data in order to group the ceramic samples and to relate them with the possible clay sources for provenance analysis.During the production of the ceramics at least three different types of clays consisting mainly of smectite, illite and chlorite minerals were utilized andthe soil samples also own similar clay mineralogical compositions indicating local raw material sources for ceramic production. The clustering of the chemical data indicatesmainly five different raw material compositions which is interpreted as different clay sources were preferred in aperiod of thousand years. Based on the textural analysis, weconcludethat during this period, a large portion of the produced ceramics were fired at temperatures less than 900 $^{\circ}$C.

Experiments on the mineralogical composition of low carbonate bearing common clays in the 500-800°C interval

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Keywords: amorphous matrix, experimental firing, Rietveld refinement

The term common clays here refers to the fine grained plastic materials frequently found in lowlands and river plains, suitable for pottery making. Their archaeological importance is significant, since these materials could be the primary source for burial, storage type or even some household pottery. The mineralogical composition obtained by firing of these clays is strictly determined by their carbonate content in raw state. While chemical analysis is most suitable to correlate ceramics and potential raw materials, mineralogical composition is needed to deduce firing temperature. Mineralogical data is also required to link especially Ca and Mg to mineral phases, ruling out the misinterpretation of bulk chemical data. A special firing range, in which chemical and mineralogical data interpretation might be problematic, is that between clay mineral dehydroxylation (500-600°C) and Ca +/- Mg +/- Al (alumino)silicate crystallization (generally <800-850°C). Even if firing temperatures for pottery are usually found to be >900°C, much lower values are indicated for the earlier mentioned burial and storage type vessels.

Low carbonate bearing clays were obtained from archaeological excavations on the Tisza river plain, near Miskolc and Szolnok. Both sites revealed large number of ceramic vessels from burial sites, most of which in very degraded state. Chemical analysis (XRF and ICP-MS) indicates that they were produced from local common clays, while mineralogy (XRD and polarized light optical microscopy) indicated a low firing temperature and possible rehydration. Thus, local common clays (illite and chlorite dominant clay fraction) were undertaken for laboratory firing experiments, on hand molded specimens. Thermal transformations were observed by thermal analysis to select firing temperatures (500, 560, 600, 720 and 800 °C), each batch subjected to XRD, polarized light microscopy and ATR-FTIR analysis.

Result indicate, that after clay mineral dehydroxylation (560-600 °C) an increase in amorphous fraction occurs (by XRD) shortly followed by carbonate calcination. Carbonate decomposition occurs via solid state reaction with clay mineral metaphases, resulting in X-ray amorphous “glassy” silicate phase. At >700°C calcite and dolomite content of 1-5 weight percent is totally decomposed, illite peaks are severely reduced in intensity, but still no newly formed phases are detected. Only above 800 °C melilite or clinopyroxene phases are developed. However, the changes in amorphous material type (XRD, ATR-FTIR) and nanocrystalline components identification by full powder pattern deconvolution (XRD) bears information for Ca and Mg content and their solid phase relations in the “glassy” and nanocrystalline silicate matrix. Also, materials formed in this thermal recrystallization gap are susceptible to rehydration and smectite formation, through time.

Ceramic "Sugar Jars" from Aveiro, Lisbon and Madeira regions (Portugal): composition, source of the raw materials and technological processes assessment

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Keywords: ancient ceramics, sugar jars, archeometrics

Recent archaeological underwater finds in Aveiro coastal lagoon (remains of a sunken vessel, dating from the XV/XVI century, loaded with a cargo of pottery) boosted the scientific interest on the characterization of the so-called "sugar jars". These sugar forms were conic ceramic jars having a hole at the bottom, being used specifically for the stage of the purge of the sugar cake. These pieces played a paramount role in sugar production cycle, being used for the maturation of the sugar, and since the 15th until the beginning of the 19th centuries, the old pottery centres from Aveiro and Lisbon regions, produced heavily these "formas de açúcar" ("sugar forms") which were exported to sugar production areas, at places as diverse as Madeira, Canaries, Cape Verde, Cuba and Brazil.

Other recent archaeological findings in Aveiro, Lisbon and Madeira are giving opportunities to characterize different typologies of production. The conservation and restoration intervention intended to prepare implies the knowledge of the present state of the support material, in this case terracotta. Possible local and regional clayey raw materials were also studied.

Our main goal is to obtain information allowing typological definition, group discrimination, raw materials characterization and provenance of the studied materials. Mineralogical analysis by x-ray powder diffraction was carried out on bulk samples. Chemical composition was assessed by X-Ray fluorescence and provided the major and trace elements chemical data.

Multivariate statistical methods were applied, in particular, cluster, principal components and discriminant analysis, the later being a statistical method that assigns samples to one or more of previously defined groups.

The obtained results of composition have given important information about the provenance of the studied materials, and also about their raw materials. Mineralogical and chemical data obtained in samples from Aveiro point to a local production, using the upper Cretaceous marly (dolomitic) clays (Maastrichian) and clayey sands as main raw materials. Ceramics from Barreiro (Lisbon) are in general more silicated and less carbonated, composition close to the Tagus Miocene Basin clays. The higher iron content of Aveiro clays favours the glazing of ceramic paste at lower temperatures, giving them better mechanical resistance values which can justify "their best quality", as referred to in ancient documents.

Furthermore, the analysis showed that the chemical composition of ceramic vessels found in Machico city (Madeira), where sugar production was very important on XV and XVI centuries, is closer to the chemical composition of Aveiro clays, which can indicate the place of production of those ceramics.

Archaeometric study on Turkish ceramic water pipe from Rudas Bath, Budapest, Hungary

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Keywords: Turkish bath, ceramic pipes, XRD

From the Turkish occupation in historical Hungary (1541-1686) five Turkish baths more or less whole survived, and one of them is part of the Rudas Bath. The "yeşil direkli ilica" (green pillar bath) was built by Sokollu Mustafa Pasha who governed Buda from 1566 to 1578. During the latest renovation works started in 2004 one part of the original ceramic segmented pipeline was revealed, which transported the thermal water from the spring to the bath and was built inside the wall.

The ceramic material was analyzed X-ray fluorescence spectrometry (XRF), X-ray powder diffraction (XRD), polarized light microscopy (PLM) in thin section and scanning electron microscopy with energy dispersive spectrometry (SEM+EDS).

The investigated material is very fine grained, with lamellar, stratified fabric, the orientation of muscovite lamellae indicating layer by layer molding on a tubular shape. According to XRD and PLM, the following mineral components could be identified: quartz (SiO_2), mullite ($Al_{4.59}Si_{1.41}O_{9.7}$), anatase ($\alpha$-$TiO_2$), muscovite ($KAl_2(AlSi_3O_{10})(OH)_2$), microcline ($KAlSi_3O_8$), maghemite ($\gamma$-$Fe_2O_3$) and thaumasite ($Ca_3(SO_4)[Si(OH)_6](CO_3)\cdot 12H_2O$). Amorphous material is present in 24-26 weight percent, possibly dominated by SiO_2. Among crystalline components quartz is by far dominant, over 50 weight percent, while mullite is only 8-10 weight percent. All the other components are <3 weight percent. Presence of trace amounts of rutile might by hidden by microcline peaks.

This mineral assemblage indicates the use of kaolin as plastic – binding matrix, on a quartz rich powder, possibly washed sand, thus the muscovite and microcline content. However, part of microcline was possibly formed during firing, from a low amount illite component. Firing exceeded 1000 °C, but the mineral assemblage bears some inconsistence, since anatase should irreversibly be transformed to rutile >600ºC. Similarly, the lack of cristobalite, as a regular product of kaolinite decomposition, is a sign for diverging from regular kaolin based ceramics. The dissimilarities could be related to chemical altering effects by the thermal waters, for which the pipes were designed. Precipitation of thaumasite is related to this process, and could lead to critobalite and glassy matrix solubilisation, by which process also the Ti release and anatase precipitation would be possible.

Tuning clay properties for new development in sustainable building materials

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Human activities seriously threaten the environment but it is also deleterious on the economy, as the cost of environmental catastrophes could be as high as 20% of the world GDP in 2050. The building industry is one of the human activity with the largest environmental impact with 40 % of total energy consumption, 40% of waste produced and 40% of the CO2 released and concrete is the construction material used in the larger volume. The cement which is the active binding element of the concrete could account for 10% of total anthropogenic CO_2 emissions in the near future. Thus there is an urgent need for more environmentally-friendly, economic, durable and higher performing cement materials. The available elements in the earth's crust restrict the options for substitute cementitious materials. Ideally, the composition of this new building material needs to be closer to the composition of the Earth. Clays for instance are readily available around the world at an affordable price and have high but largely underused potentials. This research explore potential use of clay in construction. Depending on the local socio-technical context, we show that clay can provide a grounded material allowing low capital investment or low technical requirement when needed as well as high technical specificity for high strength or aggressive environment.

Performance characteristics of concrete with metakaolin sand important for building practice

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Keywords: metakaolin, pozzolanic reactivity, concrete

This paper deals with the investigation of technically important properties of concrete prepared with metakaolin sand substituting 10 wt. % of the ordinary Portland cement CEM I (PC). Metakaolin sand (MKS) was prepared from kaolin sand from the deposit Vyšný Petrovec by calcination at 650 °C for 2 hours. MKS contains 49.8 wt. % of metakaolin. Frattini test was applied for the estimation of the pozzolanic reactivity. The pozzolanic reactivity of MKS is comparable with traditional natural and industrial pozzolans (Fig. 1). MKS is reflected as high-efficient pozzolan when partially substituting the PC.

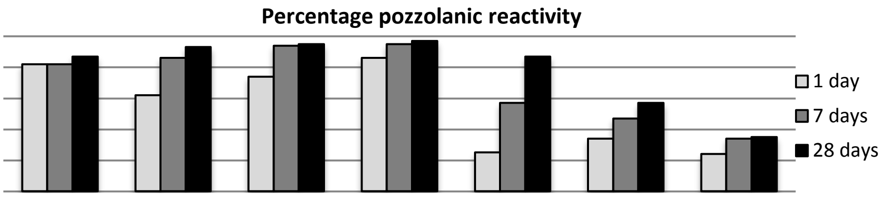

Fig. 1: Percentage comparison of pozzolanic reactivities

Technically important properties of concrete prepared with 10 wt. % of MKS (C-MKS) were compared with reference concrete (C-REF) made from 100 wt. % of PC. Concretes were prepared with constant water to cement ratio w/c = 0.35 and with constant content of superplasticizer. On the fresh concretes rheological tests were performed and hardened concretes were tested for compressive strength, depth of water penetration, suction capacity, dynamic and Young's modulus of elasticity, volume changes, frost resistance and resistance to water and defrosting chemicals. Table 1 shows mechanical properties of both concretes after 28 days curing.

Table 1: Mechanical properties of concretes after 28 days curing

Concrete	Compressive strength [MPa]	Depth of water penetration [mm]	Suction capacity [mm]	Modulus of elasticity	
				Dynamic [GPa]	Young's [GPa]
C-REF	54,9	38	3.1	56.1	37.6
C-MKS	66,5	27	2.7	55.2	39.1

The findings indicate MKS from Vyšný Petrovec as perspective pozzolan for use in building practice by the same way as traditional supplementary cementitious materials e.g. diatomite, natural zeolite, fly ash and blast furnace slag, respectively.

Properties of metakaolin-based geopolymers with addition of Portuguese diatomites

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Keywords: diatomite, metakaolin, geopolymers

Geopolymers, a class of largely amorphous aluminosilicate binder materials, have been studied extensively over the past several decades [1]. During this investigation, Portuguese diatomites were studied to prepare new metakaolin-based geopolymer formulations thought sodium alkaline activation. The materials collected from Rio Maior and Amieira, used as additive (5 to 20 wt. %), can provide a good low cost alternative as silica source due to their amorphous composition. These diatomite deposits, abundant in Pliocene outcrops, proved a good potential in a wide range of applications, especially in construction materials; such as concrete [2] and asphalt [3]. Compared to those already studied and/or being used diatomite, Rio Maior and Amieira products have shown similar mineralogical and geochemical properties (SiO_2:83-86%, Al_2O_3:6-8%, Fe_2O_3: 1-2%, lost on ignition 5-6%, traces: CaO, Na_2O, MgO, P_2O_5, SO_3, K_2O, TiO_2, Zr, MnO. The effect of diatomite addition in metakaolin-based geopolymers was evaluated by X-ray diffraction (XRD) and scanning electron microscopy (SEM) in order to understand the variation in the amorphous phase composition and the influence in the cemented microstructure.

Due to their high reactivity with alkaline solution, the metakaolin/diatomite confectioned geopolymers exhibited suitable compressive strength values (4.5 MPa) just after a curing period of 7 days.

Moreover, in order to promote the use of local resources and minimize exportation costs, a kaolin bulk sample (Portugal) was also used in this study. Mixed with diatomite and calcined at 550 °C, the obtained slurries helped to obtain better compact microstructure and good technological properties (compressive strength superior to 5 MPa after 7 days of curing).

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Multitracer (HTO, $^{36}Cl^-$, $^{85}Sr^{2+}$) diffusion in compacted natural and reduced charged dioctahedral smectites

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Keywords: dioctahedral smectite, RCM, layer charge, particle size, diffusion

Diffusion processes of contaminants through geotechnical barriers in context of waste repositories have been thoroughly studied using references smectites, illites or clay rocks. Surface properties of clays are known to influence the diffusion behaviour of anions by anion exclusion [1] and cations by surface enhanced diffusion [2]. This study aims to contribute to the understanding of the influence of layer charge and particle size diversity of smectites on diffusion behaviour. Four Na-saturated dioctahedral smectites of the montmorillonite-beidellite series and their related Na-saturated reduced charged materials (RCM) were selected [3]. The <0.2 μm materials varied both in layer charge and lateral dimension. Through- and out-diffusion of the tracers HTO, $^{36}Cl^-$ and $^{85}Sr^{2+}$ were performed in compacted materials at $\rho_d = 1700$ kg m^{-3} using static-filter diffusion cells [4]. Diffusion experiments were modelled using COMSOL Multiphysic® according to the Fick's laws to determine the best-fit parameters values for the effective diffusion coefficients (D_e) and the rock capacity factors (α). For the reactive species, α is defined by a retardation distribution factor (R_d) in addition to the diffusion-accessible porosity factor used for the unreactive species. Concerning the natural dioctahedral smectites, no obvious influence either of the layer charge or of the particle size was observed on the HTO diffusion. However for the $^{36}Cl^-$ diffusion, the material with the larger particle size showed significantly lower D_e and α values. D_e values for $^{36}Cl^-$ diffusion were 10 times higher for RCM than for the natural smectites. The reduced surface charge density leads to a decrease of the extent of the diffuse double layer and a concomitant increase of interparticle porosity. The evaluation of data for the $^{85}Sr^{2+}$ diffusion, in which the layer charge is expected to play a major role, is currently in progress. The $^{85}Sr^{2+}$ diffusion results will be discussed considering the influence of the surface charge of the materials and the diffusion contribution in both interlayer and interparticle pores.

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Ion exchange reactions and boiling in the second parcel of the alternative buffer material test (ABM-II) in Äspö, Sweden

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Keywords: CEC; exchangeable cation population; bentonite buffer

Bentonite barriers for high level radioactive waste (HLRW) sealing were tested in many real- and up-scale deposition tests in crystalline rock. Only few experiments use more than one bentonite. In the “alternative buffer material, ABM” tests conducted by SKB, Sweden, nine different bentonites and two marine clays were used. The chemical and mineralogical composition was investigated before and after a heating (and wetting) period.

Large differences of the exchangeable cation populations of the bentonites were observed for the first package (ABM-I) after 28 months at maximum temperatures of 135 °C [1] along with mineralogical changes mainly at the contact between the buffer and the hot canister [2,3]. Similar processes were expected for the second parcel (ABM-II). Changes were reported elsewhere for blocks #2, #4-#6 from the lower part [4]. The authors observed an increase in exchangeable Ca, and a decrease in Na, Mg, and K whereas the cation exchange capacity (CEC) did not change.

In the present study the CEC and the exchangeable cation distribution of all blocks are considered. Again an almost complete reorganization of the exchangeable cation populations of the bentonites of the whole parcel was observed. Interestingly, a significant variability of trends was observed exceeding the differences reported for ABM-I where only minor variability along horizontal profiles was observed. In contrast, in ABM-II a decrease of the exchangeable Ca values towards the rock side was observed for some blocks and almost all blocks showed a small decrease of the exchangeable Mg values towards the rock side. The most significant difference was the presence of halite in the upper part of the parcel which occurred together with a strong disintegration of some buffer blocks indicating boiling. This difference may have been possible because in ABM-II the bentonites were water saturated before the heaters were switched on which may have favoured the observed processes.

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Heat transfer investigations carried out on brick based wall

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Keywords: solid brick, heat transfer, aerogel, thermal conductivity

These days, the thermal insulation of existing and new buildings is one of the most important actions for reducing the energy loss of buildings and to reduce the emission of green house gases. The Directive of the Energy Performance of Buildings defines the energy performance of a building as the energy needed to meet the energy demand associated with the 'typical use' of the building. One of the novel insulations used for additional insulation is the silica aerogel.

This paper examines the thermal properties of aerogel and fired clay brick as individual and in-built materials. A brick is building material used to make walls, pavements and other elements in masonry construction. Traditionally, the term brick referred to a unit composed of clay, but it is now used to denote any rectangular units laid in mortar. A brick can be composed of clay-bearing soil, sand and lime, or concrete materials. Bricks are produced in numerous classes, types, materials, and sizes which vary with region and time period, and are produced in bulk quantities. Two basic categories of bricks are fired and non-fired bricks.

Aerogels are nanoporous lightweight materials, were discovered more than 70 years ago. In these years their applications are truly spread over. In this article measurement results and theoretical backgrounds about the thermal properties of silica aerogel are presented. At first, effective thermal conductivity measurement results of individual clay brick and aerogel layers, moreover their combinations achieved by a Holometrix type Heat Flow Meter will be presented. Then thermal transmittance measurements carried out on a 0.015 m Plaster/0.25 cm Brick/0.015 m Plaster wall covered with 0.013 m thick aerogel insulation will be presented as well. [1-5] As a result, comparison of the thermal conductivity values reached by the different methods will be introduced.

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Compression behaviour of natural and remoulded clay

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Keywords: Cyclic consolidation, structured clay, sensitive clay

In the present study undisturbed and remoulded clay samples from Norway (Onsøy clay) are subjected to monotonic and cyclic loadings of different load amplitude. The stress-strain behaviour is studied regarding the material response due to structure. Structure includes fabric and bonding, where fabric is the arrangement of the soil particles and bonding is the particle contact, which is not of a frictional nature [1]. In parallel, a study on fabric is performed using SEM and μ-CT.

The material is characterized as marine clayey sediment with moderate sensitivity.

Cyclic tests are carried out under one-dimensional compression conditions in a newly designed oedometer cell. The drainage takes places on the top, while pore water pressure evolution is measured on the bottom of the specimen.

Reconstitution is conducted in accordance with Burland [2]. Therefore, the material is mixed with a water content exceeding the liquid limit and dried to the natural water content afterwards. Since the salinity of the pore water affects the compression behaviour, the salt content is kept constant during remoulding. The yield stress - which belongs to the stress maximum bearable by the bonding - was ascertained in one-dimensional static compression tests.

The settlements obtained in the cyclic tests are significantly smaller for the undisturbed samples particular beneath the yield stress. After exceeding the yield stress the values are more converging for the natural and the remoulded material. Significantly faster pore water dissipation is observed in the natural samples, even after exceeding the yield stress. The settlement during loading and unloading is analysed regarding plastic and elastic deformations. It is found that the stiff pre-yield behaviour of the natural samples is due to an elastic response of the structure. The SEM micrographs (Fig.1) confirm the aforementioned mechanical behaviour that is governed by the structure.

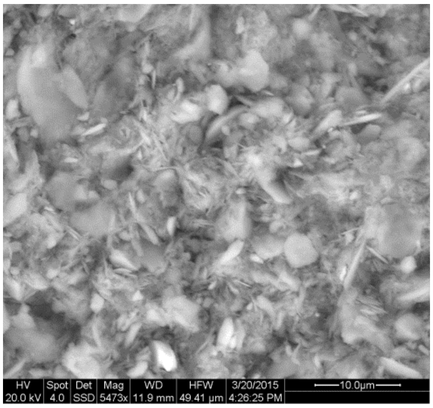

Fig. 1: SEM micrograph of the clay

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Enhanced delivery of chemical agents for soil improvement applications – treatment by guanidinium salt solutions

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Keywords: soil improvement, guanidinium, permeability, chemically enhanced drainage, stabilization of landslides

The modification of the soil mechanical properties of clays by applying appropriate chemical agents has been actively used for soil improvement, in particular for increasing soil strength and decreasing its compressibility. Efficiency of chemical soil improvement technologies heavily depends on their ability to deliver agents to the problematic soil areas via fluid transport in porous media. Sometimes the soil improvement resulting from chemical reactions has a side effect of decreasing soil permeability, slowing down and even halting further delivery of agents. An acute need in practical methods capable of avoiding or, ideally, reversing these side effects inspires a search for chemicals that can increase soil permeability and enhance both their own transport and the transport of other soil improving agents by “opening” of the soil pores beforehand.

The concept of enhanced delivery of chemicals for soil improvement applications based on clay treatment by guanidinium salt solutions was explored [1]. This treatment causes significant increase in shear strength and decrease in swelling potential of clayey soils. Furthermore, it increases their permeability by an order of magnitude and maintains this increase under high confining stresses, thus enhancing its own and other agents’ delivery. The underlying mechanism on the level of the surface chemistry is a cation exchange reaction leading to interlayer fixation [2] and aggregation of small clay minerals to stable larger silt-sized particles, thus providing a system of open pores. The resulting changes in soil fabric and structure were characterized based on observations on the pore and particle scale using different lab techniques. A simple analytical hydro-chemical model was developed to describe the process of enhanced delivery. The model could be successfully validated against both experimental data from soil samples subjected to the flow of guanidinium solution and a more sophisticated numerical analysis. Potential applications of this chemically enhanced drainage technique to stabilization of creeping landslides will be demonstrated.

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Effect of bentonite admixture on setting and reaction process of metakaolin-cement blends

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Keywords: bentonite, calorimetry, metakaolin, supplementary cementing materials, ultrasonic measurements

This study focuses on the potential use of bentonite as natural mineral admixture in cement mortars or concretes to improve certain properties, like workability and water retention of fresh blends.

In contrast to metakaolin, the pozzolanic effect (reaction with $Ca(OH)_2$) of raw bentonite is low. Metakaolin is a well-known pozzolanic material that is commonly applied to substitute parts of cement. Metakaolin accelerates the setting of the cement pastes and thus impair their workability [1, 2, 3].

The impact of bentonite admixture on setting and reaction process of metakaolin-cement blends was investigated. Ordinary Portland cement (CEM I 52.5 N) was substituted by 5–50 wt% of metakaolin (MetaStar 501). Raw bentonite (Calcigel, in Na- or Ca-form) was added to the mixtures in amounts of 5–30 wt%. The ratio water/solid was adjusted to the same initial slump (pure cement with w/c = 0.4) by increasing the amount of water. Setting and reaction process have been studied by means of calorimetry, ultrasonic measurements and penetration tests.

In case of metakaolin-cement blends, an acceleration of the hydration process could be observed with increasing amount of metakaolin. The final setting time decreased from 9 hours (pure cement) to 5 hours (blended with 50 wt% metakaolin).

It was expected that Na-bentonite admixture could provide retarding effects. This is because of the released calcium that can be bonded by the bentonite to prevent the early formation of calcium aluminate hydrate (C-A-H) phases [4]. However, admixtures of 5–10 wt% Na-bentonite showed small retarding effects on metakaolin-cement blends containing 10–30 wt% metakaolin. An admixture of 10 wt% Na-bentonite increased the final setting time of one hour if the cement was blended with 40 wt% metakaolin. In case of Ca-bentonite, no retarding effect could be found. A loss of stability of the resulting binders has been observed if higher amounts of bentonite (up to 30 wt%) were added to the mixtures. That means the retarding effort of bentonite admixture is limited by the interdependence of the three components (bentonite, metakaolin, cement). More effective plasticizers will be needed in order to increase the setting retardation remarkably. By all means, the here studied bentonite can be applied as a filler to improve the density of the hardened binders based on metakaolin-cement blends.

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Development of raw material concepts based on non-swelling clays for geotechnical application

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Keywords: kaolinitic clay, non-swelling behaviour

In geotechnical application for sealing of landfills, drilling fluids or injections bentonitic raw materials are wide-spread and dominating. Reasons are their important characteristics as the swelling behaviour and their thixotropic properties. In face of this, shrinkage and less stability towards salts and cements in aqueous solutions and brines cause risks for some application. For these cases, the use of non-swelling, kaolinitic clays is preferred, but often still unknown. The advantages of this type of raw materials are discussed for two cases.

Surface sealings of landfills require a much higher friction angle than bottom sealings and must be unsusceptible to exsiccation and sun cracks. Therefore, kaolinitic clays that are much less prone to shrinkage are preferred. A successful example is the covering of the landfill Sigmundskron near Bozen/Bolzano, Northern Italy. This landfill, in addition, is characterized by the leakage of landfill gas of elevated temperatures, why the resistance of the raw materials to crack formation had to be extremely high. At the end, a mixture of sand (40 wt%), different sizes of gravel (50 wt%) and kaolinitic, non-swelling clay (10 wt%) was used.

Another field of application are injection grouts. Important features of non-swelling clays are their positive influence to viscosity and flowability, especially as function of time. Whereas the settling rate of kaolinitic and bentonitic clay suspensions with concentrations of 3 wt% and 5 wt% were nearly the same, the rheologic yield points differ significantly. Whereas the bentonite starts with a high viscosity (above 4.000 Pas) and then shows a rapid decrease in viscosity, the kaolin starts with a lower viscosity (300 Pas) and is therefore much easier to inject. Interestingly, already after 40 s the viscosities of both reached almost the same value (about 1 Pas) and fulfil the requirement as suspending agent.

Another important difference is the development of the viscosity depending on longer times. Whereas the kaolinitic suspension shows nearly same viscosity compared to the 40 s value even after 1800 s (1.2 Pas) the bentonite suspension increases up to 3.5 Pas at the same time. This effect of a lower viscosity of the kaolin in combination with a good performance in stabilization that fulfils the given requirements allows injections on longer distances over a long time and the filling of distal located cracks.

Future works are dealing with application as ready-mix concrete, light-weight concrete and extruded mortar systems containing kaolinitic clay.

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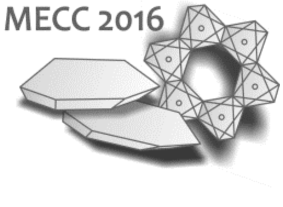
POSTER PRESENTATIONS



Molecular dynamics simulations of azobenzene intercalates in smectites

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Keywords: azobenzene, photoresponse, smectite, molecular dynamics

Photoactive compounds show response to radiation of specified energy. The most common photoactive compound – azobenzene changes its conformation from *trans* to *cis* isomer upon UV radiation. The possibility of transferring the unique properties of such a molecular switch into an inorganic structure is very attractive and was investigated in numerous papers [1]. Clay minerals were frequently applied as the host structures for which the basal spacing can be controlled with UV light. The molecular dynamics (MD) simulations were conducted to explain the physical and chemical basis of this phenomenon for intercalated smectites. All the MD simulations were performed for SWy-1 montmorillonite intercalated with hexadecyltrimethylammonium bromide in amount equal to CEC. The number of co-intercalated azobenzene (AZ) molecules was calculated from elemental analysis. Simulations involved the use of CLAYFF force field [2] and GAFF [3].

In the first set of simulations taking into account different initial starting structures, constant temperature and pressure MD simulations (NPT) showed no difference in basal spacing between AZ isomers. In the second set of simulations, photoisomerization was conducted during simulation for constant temperature and volume (NVT) systems. Sheets of smectite were ended with (100) edges according to recent results of [4]. The photoisomerization reaction was following the procedure described by [5] with a few AZ molecules changing conformation every 15 ps. A slight decrease of basal spacing was observed for cis→trans and trans→cis reactions, which was due to ejection of small number of AZ molecules from the interlayer space. No difference in basal spacings of cis- and trans- final structures was observed. In the third set of simulations, energy of water molecules adsorption on smectite with C16 and AZ was calculated for different hydration levels. It was found that this energy is more negative, if trans- isomer is presented in the interlayer space. This effect can explain experimentally observable reversible variation of the basal spacing, which is of about 2 Å.

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On stability of montmorillonites intercalated with tetrabutylphosphonium and tetrabutylammonium cations – computational study

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Keywords: DFT, molecular dynamic, montmorillonite, tetrabutylphosphonium, tetrabutylammonium

Modification of clay minerals by organic cations is a subject of great interest in recent period because of the possibility to develop new materials with the specific properties for new technological applications (e.g. polymer-clay nanocomposites, active sorbents, storage of radioactive waste, pigment preparation, fireproof coats, etc.). Especially montmorillonite (Mnt) is a suitable candidate for modification because of its easy swelling and ability to replace exchangeable cations. Knowledge on the structure and properties of organoclays is essential for their applications. Prepared organo-montmorillonites are often characterized by different physicochemical, spectroscopic, and microscopic methods. In spite of the intense experimental research of the organoclays, some important questions remain open or experimental data have not been completely interpreted yet because of the complex structure of the studied organoclay materials. In such situation molecular simulations can effectively complement experimental data.

This work is focused on the prediction of the stability of tetrabutylammonium (TBA) and tetrabutylphosphonium (TBP) cations in the Mnt interlayer space by using molecular simulations. Density functional theory (DFT) method in solid state and molecular dynamics implemented in VASP program [1] were employed in the calculations. The structural models were constructed on the base of the available experimental structural data and organoclay models used in previous simulations. Preliminary calculations showed that the TBP cation is more stable in the interlayer space of montmorillonite than TBA cation.

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New model of ethylene glycol layers intercalated in smectites for XRD modelling

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Keywords: ethylene glycol, smectite, XRD modelling

The model of ethylene glycol (EG) intercalate implemented in programs used for XRD modelling of clay minerals is based on two papers: for 1 layer it is [1] and for 2 layers it is [2]. The paper [1] presents only distribution of EG in vermiculite interlayer and do not give information on the temperature coefficients (B) of these atoms. The paper [2] provides structure along with temperature coefficients and states that it is essential to assume increased values of B=11 Å^2 for EG molecules. Surprisingly, these values for water and Ca^{2+} atoms were left unmodified: 1.68 Å^2. This assumption is not confirmed by recent works describing distribution of water atoms in the interlayer. Therefore to the aim of the studies was to provide new adjustable model of one and two EG layers model that is based on results of molecular dynamics (MD) simulations.

The range of EG content in the simulated structure was set in between 0.6 and 2.0 with step of 0.2 phuc, while for H_2O in between 0.0 and 1.2 with step of 0.3 phuc. For all the simulations, average atomic density profiles along the z direction were calculated. Subsets corresponding to certain basal spacing were chosen as representative for one- and two-layer complexes. The electronic density profiles of EG, H_2O and Ca^{2+} ions were fitted with Gaussian functions. The aim was to minimize the number of functions and achieve maximally simple but yet flexible model of interlayer structure. The received models show significant differences comparing to model that are based on [1] and [2]. The position of atoms in the interlayer space is generally different. It was also possible to determine relationship between position of the atoms and the basal spacing. For some atoms also relationship between basal spacing and ratio of gaussian distributions were found. The thermal factors are generally larger and Ca^{2+} ions can exist both in inner-sphere and outer sphere complexes and its ratio can be optimized. All the relationships were implemented in structure file used in BGMN program.

The new model shows larger flexibility than original models and generally it is possible to receive slightly better matching between experimental and theoretical diffractograms. The limitation of the new model is connected with the fact that scattering factors of water and EG molecules have very similar dependence on 2 theta angle and that there is quite similar distribution of water and EG molecules in the interlayer space. Therefore, during minimizing procedure EG and H_2O molecules in the interlayer space are not treated fully separately.

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Development of molecular cluster models for nano-kaolinite from crystalline structures

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Keywords: exfoliated kaolinite, molecular cluster models, quantum chemical calculations, morphological changes, vibrational spectra

Molecular engineering is an emerging field at the interface of fundamental basic science, engineering applications and new technology development. An important aspect of these efforts is the use of realistic theoretical models that are treated at experimentally validated level of theory. These virtual chemical models have the utility of rationalizing experimental observations, directing experimental work, and generating experimentally testable hypotheses.

Kaolinite with the simplest 1:1 layered composition, but with challenging clay reactivity, provides an exciting scientific opportunity to link the worlds of materials and molecules. Intercalation, exchange intercalation and exfoliation processes allow for a stepwise and controlled modification of structural periodicity, formation of organic/inorganic hybrid materials and with the elimination of the crystalline order creating molecular nano-clays. As molecular properties emerge, these processes increase the industrial value of clay materials in parallel with the possibility for surface modifications

We have developed computational modelling strategies on the basis of coordination chemical principles for describing the structure and reactivity of molecular nano-kaolinite. Virtual chemical models have now reached the level of sophistication that they can reproduce morphology and spectroscopic features. We are discovering new structural and energetic relationships that can provide direct feedback to experimental work for designing clay-derived material with tailored chemical and physical properties. The poster will demonstrate an automated molecular cluster building algorithm for any "generations" of nano-kaolinite structures, the interaction of these surfaces with water, dehydroxylation steps due to mechano-chemical activations. The computational results give excellent agreement with vibrational spectroscopic spectra and differential scanning calorimetric and gravimetric thermal analyses [1-4].

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The layer charge of smectites probed by molecular aggregation of a rhodamine dye

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Keywords: rhodamine 123, reaction kinetics, UV-Vis spectroscopy, chemometrics, metachromasy

The interaction between cationic organic dyes and colloids of clay minerals leads to dye molecular aggregation and significant changes in dye spectral properties. Numerous studies have reported the effect of smectite layer charge. The main objective of this work was a detailed characterization of the course of molecular aggregation of rhodamine 123 in the colloids of a series of smectites (two montmorillonites, two laponites and one saponite). For this purpose, molecular aggregation kinetics was measured by combining of UV–Vis spectroscopy with a stopped–flow rapid mixing device. The spectral data were analysed by chemometric methods: Principal component analysis (PCA) and multivariate curve resolution–alternating least squares (MCR). Non–linear regression analysis of the calculated concentration profiles of dye monomers and aggregates (obtained by MCR) led to the construction of reaction kinetics models.

PCA identified two main species, adsorbed monomers and oblique J–aggregates. There was no significant effect of smectite properties on the positions of the H– and J–bands of the aggregates. Small variations in the structure of the aggregates were indicated by slight differences in the ratio between the intensities of the bands. It is supposed that the formation of dye aggregates starts immediately after adsorption is finished. The analysis of the concentration profiles indicated that the formation of dye aggregates can be described by two kinetically independent reactions leading to the model of two parallel processes, both of the 1st–order reaction kinetics. The half-life was in the order of a few s, but was not significantly affected by the layer charge. On the other hand, the number of dye cations taking part in the reaction significantly increased with the layer charge. The charge density likely affects a number of catalytically active surface sites. The reaction mechanism model of dye molecular aggregation can be implemented in the method applied for probing the surface properties of smectites as well as of other layered nanomaterials.

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Near infrared study of the hydration properties of industrial silicate materials

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Keywords: near-infrared spectroscopy, montmorillonite, perlite, water adsorption and desorption

The potential of a near-infrared (NIR) spectroscopy to follow the hydration properties of montmorillonites (Mt) and perlites (Pl) has been introduced. These raw materials belong to the group of silicate minerals however their structure, chemical composition and properties differ significantly. Economically interesting deposits of both materials occur also in Slovakia therefore detailed studies of their properties have received a great deal of attention not only due to their industrial potential but also from the scientific point of view. The objective of this study was to compare the hydration properties of the montmorillonite (Jelšový Potok, Slovakia) saturated with different exchangeable cations and raw perlites obtained from different parts of deposit Lehôtka pod Brehmi (Slovakia). The interaction of water with Mt and Pl was investigated mainly by modern methods of NIR spectroscopy, supplemented with traditional gravimetric and thermal analysis. The extent of hydration was followed by NIR UpDRIFT accessory enabling the measurements of the samples directly in closed glass vials and dehydration by special NIR DRIFT temperate cell susceptible to in-situ measurement of the spectra in a temperature range 25-800°C. The combination band of water molecules $(\nu+\delta)_{H2O}$ near 5250 cm^{-1} was used to characterize the hydration properties of the samples. This region is free from the other silicates bands and can be used to provide information on the strength of H-bonds and water content in hydrated samples. The area of this band reflects the quantity of adsorbed water. The Mt samples were hydrated at 52 % relative humidity (RH) for 48 hours while 2 weeks at 100 % RH was chosen for Pl samples. Both, NIR spectra and gravimetric analysis showed the evident effect of the exchangeable cations on the hydration of montmorillonite. The water content increased in order $K^+ < Na^+ < Ca^{2+} < Mg^{2+}$ in dependence on the hydration energy of the cations. The highest amount of water was found for Mg-form (13.1 mass %) and the lowest for K-form (7.9 mass %). Completely different behavior was observed for Pl samples, which proved very poor hydration ability. The maximal amount of adsorbed water was only 3.3 mass %. Quite a diverse behavior of Pl and Mt samples was observed also upon their dehydration. While for Mt samples the area of the $(\nu+\sigma)_{H2O}$ band gradually fell down up to 300°C, for Pl samples only negligible decrease was found. Similar trends of water loss demonstrated also thermal analysis confirming that the NIR spectra can be used for estimation of water content in both types of materials.

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High-temperature and quantitative XRD study of typical Westerwald clays (Germany)

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Keywords: Westerwald, XRD, QPA, HTXRD

The Westerwald is one of the largest and oldest clay mining area of Germany. Those deposits were formed during the Eocene and Oligocene as a result of the weathering, erosion and redeposition of Devonian rocks. During the Miocene, intense volcanic activities led to a large basalt cover, protecting the clays from the erosion. The fine fraction is mainly composed of kaolinite and illite, with the possible presence of interstratified I-S. Other minerals such as quartz, feldspars, hematite, goethite or anatase are present in variable concentrations.

Four typical Westerwald clays were chosen for this study: kaolinite-rich clay, kaolinite-illite clay, a red and a yellow firing clays. The first goal is to perform quantitative XRD using two different methods and to compare them: reference intensity ratio (RIR) and Rietveld (using Topas and BGMN). The second goal is the study of those samples using high-temperature XRD (HTXRD). The samples were heated up to 1250°C and a XRD pattern was obtained *in situ* every 100°C. The results show the temperatures of vitrification and formation of mullite and cristobalite varying from one sample to another, which is mainly linked to their flux concentration.

Dielectric properties of synthetic ZnO nanoparticles in THz region

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Keywords: dielectric properties, nanoparticles, hydrothermal synthesis, THz-TDS, Far-Infrared

Increased demand for materials with catalytic and photocatalytic properties, intended for the production of precision sensors, solar cells, detoxification facilities, drugs, and many other applications, require the preparation of new materials with low cost and appropriate parameters. One possible way for a wide range use of inorganic/inorganic hybrid materials based on layered silicates, is combination of wide band-gap semiconductor with suitable optical transparency in the UV-VIS spectrum [1]. Recently, as reasonable alternative with optical and thermoelectric behaviour were investigated ZnO nanoparticles prepared by hydrothermal syntheses. This way of preparation offer simple-controllable conditions to achieve good homogeneity in specific shape and size during growth of ZnO nanoparticles. Dielectric properties of single components and hybrids prepared from these are important material parameters describing the behaviour in the electric field. For this purpose can be used the advantage of THz spectroscopy, which measures the direct change of intensity of electric field caused by interaction with investigated material. This can be described by frequency dependent complex refractive index $\tilde{n}_S = n_S - i\kappa_S$ where n_S is the real part of the refractive index and κ_S is the complex absorption index. Frequency dependent dielectric properties can be calculated from single measurements of transmission data. The aim of our work was the characterization of ZnO nanoparticles having different morphology on their dielectric properties to exhibit differences and simulates their packing density on the resulting THz spectrum. The application of such well-characterised ZnO nanoparticles bearing hybrid materials can find utilization in a various industrial sectors, such as gas sensors with high resolution and noise limits reduction or for thermal solar cells in photocatalytic reactors [2].

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Hybrid layered silicates and their study using THz time-domain spectroscopy

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Keywords: smectites, layered silicates, cation exchange, terahertz time domain spectroscopy, Far-Infrared

Our investigation focused on smectites including synthetic Hectorite (SH, Clariant International Ltd. Germany) and Laponite (SL, Sumecton SA, Kunimine Industries Co., Ltd. Japan) and natural Montmorillonite (MMT, SCa-3, CMS SCR, Otay San Diego County, California, USA). The main differences among these samples can be found in their chemical composition, cation-exchange capacity, and particle morphology. These layered silicates are used by industry, especially in hybrid-material manufacturing, and they are designated for different target applications, such as drug carriers, ceramics, and sub-micro filters or mediums that gradually release/ exchange ions or remedies in biochemistry, molecular biology, and analytical chemistry. One of the most important parameters affecting their colloidal properties and particle swelling in an aqueous environment is their cation-exchange capacity. Different cations located in the interlayer gallery of these layered minerals can be easily exchanged for their organic counterparts by an ion-exchange reaction. The modification of the interlayer space can be detected by spectroscopic method and monitored by the changes in far-infrared region. This region corresponds to the THz spectrum and can be monitored by novel Terahertz time domain spectroscopy using femtosecond lasers. Modified clay nanoparticles show specific absorption and phase shift between the transmitted terahertz wave and coherently received terahertz signal, which enables not only rich spectral analysis in the region from 3.33 to 100 cm^{-1} (3.0 to 0.1 mm) but also the determination of frequency-dependent dielectric properties. As this technique directly determines the absorption coefficient of the studied material, the aim of this work is to investigate the dependence of the spectral response in the THz region, with respect to cation-exchange capacity and the presence of absorbing species in the interlayer galleries of Hectorite, Laponite and Montmorillonite [1, 2].

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Thermal alteration of Fe-Mg chlorites

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Keywords: chlorite, dehydroxylation, oxidation, dehydrogenation, infrared spectroscopy, thermogravimetry

Thermal decomposition of trioctahedral chlorites from a common Mg-Fe-series involves dehydroxylation, oxidation, and dehydrogenation. The actual mechanism and order of the reactions, however, is still poorly understood. X-ray diffractometry, in situ alteration by diffuse reflectance infrared fourier transform spectroscopy (DRIFT), thermogravimetry (TG), and Mössbauer spectroscopy were applied to study the structural transformations of several natural Fe, Mg- trioctahedral chlorites. Thermal transformation of the studied specimens covers a broad range of temperatures, from 350 to 850°C, and depends on (i) the quantity and position of ferrous iron, (ii) the crystalochemical composition of the octahedral sheets, and (iii) oxygen availability during the reaction. The complex alteration process involves partially overlapping reactions of the inner octahedral sheet (in the 2:1 layer) and the interlayer octahedral sheet [1].

Thermo-DRIFT experiments were performed at 25 to 860°C in a nitrogen and dry air atmosphere. The OH group stretching bands were identified for the inner OH of the octahedral sheet in the 2:1 layer and the OH interlayer groups (brucite-like sheet). The application of a highly precise thermogravimetric analysis allowed accurate tracking the dehydroxylation-related mass loss for both octahedral sheets of chlorite.

In Mg-chlorites (27–34 % mol Mg, 6–19 % mol Fe), dehydroxylation of the interlayer octahedral sheet and the 2:1 layer occurs separately, at low and at high temperatures, respectively. The reactions manifest in TG as two mass-loss events corresponding to the gradual decrease of DRIFT bands and are related to the interlayer OH groups followed by the intensity loss of the bands coming from the inner octahedral group.

In Fe-chlorites (4–9 % mol Mg, 42–45 % mol Fe), TG-measured mass loss under pure nitrogen gas flow is lower than the theoretical mass loss calculated from the conventional dehydroxylation reaction. The extent of the mass-loss difference correlates linearly with Fe^{2+} content in chlorite. This is interpreted as resulting from dehydrogenation of the octahedral sheet that triggers oxidation of Fe^{2+} to Fe^{3+} even, in oxygen-free conditions, and decreases the quantity of OH groups available for dehydroxylation. Under oxidizing conditions, the Fe-chlorites reveal even lower mass loss upon dehydroxylation, due to intense dehydrogenation in the course of heating in air. In Fe-chlorites, the low-temperature effect of the thermal dehydroxylation of the interlayer octahedral sheet is not clearly separated from the expected effect of high-temperature dehydroxylation of the 2:1 layer.

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The surface properties of rehydrated metakaolinites

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Keywords: metakaolinite, rehydration, adsorption, specific surface area

This work is focused on the effect of different temperatures on the rehydration process, surface and physical properties of a kaolinite-based rehydrated metakaolinite. Rehydration of metakaolinite were studied from 150 to 250°C under autogenous pressures. A natural kaolinite was calcined to metakaolinite and then rehydrated at different temperatures to a highly porous kaolinite. The influence of different temperatures (within the range 150 to 250 °C) was studied systematically by means of Fourier transform infrared spectroscopy (FTIR), Scanning electron microscopy (SEM) and X-ray diffraction (XRD). 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 Brunauer-Emmet-Teller method (BET) surface area, the micropore volume was derived by the t-plot method and the pore size distribution by the Barret-Joyner-Halenda method (BJH) and Density Function Theory method (DFT). The results showed the existence of an optimum temperature at which the rehydrated metakaolinite provided a high specific surface area and high amount crystalline phase- kaolinite. 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}. From the IR spectra of samples treated at 175ºC the characteristic kaolinite bands have been developed. The Al - OH stretching (3800 - 3500 cm^{-1}) and bending modes (940 and 910 cm^{-1}), along with $Al-O_6$ stretching, were useful for the monitoring of kaolinite rehydroxylation. In our study the intensities of the $Al-O_6$ stretching band at 523 cm^{-1} were used as a check of the rehydration process. Since the tetrahedral deformation of the Si-O-Si band near 460 cm^{-1} did not shift significantly throughout the rehydration process, it can 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 area S_{BET} of raw kaolinite increased more than three times.

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The structural and the magnetic properties of quaternary sediment clay minerals

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Keywords: X-ray, Mössbauer spectroscopy, clay, minerals structure, magnetic properties

Within this research we study the 10-thousand-year-old Quaternary sediments of the region near Krasnoyarsk. The samples were studied using X-ray and Mössbauer spectroscopy methods.

The particles have different shapes and sizes, from 10 μm to 207 μm. The powder contains elongated grains, irregularly shaped grains sized comparably in all dimensions, and granular masses formed by micron particles of powder on top of the larger grains. Semiquantitative analysis of the composition of the powder showed the presence of elements such as Al, Si, Mg, Fe, Ca, K, Na, and O. In addition, X-ray analysis detected albite ($NaAlSi_3O_8$, Ankerite ($Ca[Fe^{2+},Mg](CO_3)_2$), Orthoclase ($(K[Al, Fe])Si_2O_8$) in the non-magnetic fraction.

The value of the alternating magnetic field, which reduces twice as much the residual magnetization, is 1280 A/m, and the coercive force is 2400 A/m. The magnetic field determining the transition of the magnetization vector from its connection with the crystal lattice to the connection with the external field has a value of 1600 A/m.

The three fractions, namely strong magnetic (Fe_3O_4 – 87,3 %, Fe_2O_3 – 0,7 %), soft-magnetic (Fe_2O_3 – 21,7 %), and non-magnetic (FeO – 53,1 %, FeOOH–46,9 %) were extracted by the magnetic separation method to determine of the minerals, which are magnetization carriers. In the strong-magnetic fraction, the main iron-containing mineral is magnetite, while hematite is probably localized on the surface of magnetite grains. The isomer shifts Δ and the quadrupole splitting δ indicate different local surroundings for emitting and absorbing nuclei and different valences of iron ions. The carriers of the magnetization of soft-magnetic fractions are hematite grains. The Δ and δ values indicate strong non-stoichiometry of wüstite. The fractions of FeOOH and FeO do not contribute to the residual magnetization.

It is possible to observe the increase in the saturation magnetization within the temperature range 20–250 °C, followed by a dramatic decrease in the temperature range 250–300 °C, and its increase again in the range 300–350 °C. Using X-ray analysis, abite, ankerite, orthoclase were also detected in the non-magnetic mineral fraction.

The above-mentioned results show the complex research in geology, while Mössbauer spectroscopy is helpful to identify magnetic minerals in complex compounds. Such iron-containing natural minerals provide information about the stability of the residual magnetization in geological time scales.

Intercalation and retention of carbon dioxide in a smectite clay promoted by interlayer cations

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Keywords: CO_2, smectites, intercalation, retention, X-ray diffraction

A good material for CO_2 capture should possess some specific properties including (i) a large effective surface area with good adsorption capacity, (ii) selectivity for CO_2, (iii) regeneration capacity with minimum energy input, allowing reutilization of the material for CO_2 adsorption, and (iv) low cost and high environmental friendliness. Smectite clays are layered nanoporous materials that may be good candidates in this context. Here we report experiments which show that gaseous CO_2 intercalates into the interlayer nano-space of smectite clay (synthetic fluorohectorite) at conditions close to ambient. The rate of intercalation, as well as the retention ability of CO_2 was found to be strongly dependent on the type of the interlayer cation, which in the present case is Li^+, Na^+ or Ni^{2+}. Interestingly, we observe that the smectite Li-fluorohectorite is able to retain CO_2 up to a temperature of 35°C at ambient pressure, and that the captured CO_2 can be released by heating above this temperature. Our estimates indicate that smectite clays, even with the standard cations analyzed here, can capture an amount of CO_2 comparable to other materials studied in this context. X-ray diffraction measurements were performed on an in-house (NTNU, Trondheim) and at synchrotron source (I911-4 beamline of MAXIV, Lund). Pressure composition temperature (pcT) isotherms were measured in a calibrated in-house built (IFE, Kjeller) volumetric Sieverts-type apparatus in order to obtain information on CO_2 adsorption.

Coupled FTIR and gravimetric studies of water on clay minerals

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Keywords: attenuated total reflectance, QCM, relative humidity, water sorption

In recent years advances in modeling of XRD patterns with respect to heterogeneous hydration state predicted the co-existence of 0W, 1W and 2W hydration states of the interlayers [1]. However, to get a direct statement concerning the water bindings in the clay mineral structure, further analysis methods such as infrared (IR) spectroscopy need to be used. Here, the interaction of water with Na^+-exchanged 2:1 phyllosilicates was investigated using attenuated total reflectance (ATR) - FTIR coupled with a quartz crystal microbalance (QCM). Both are connected to a mass-flow gas controller, where different relative humidity (r.h.) settings can be adjusted. The experiment was designed to collect IR spectroscopic and H_2O sorption data simultaneously [2, 3]. The advance of coupling ATR-FTIR with QCM is to quantify the water content and measure their FTIR spectra in-situ. The internal reflection element (IRE) used in the cell is a trapezoidal-shaped ZnSe crystal [4]. Several 2:1 layer silicates comprising smectites of different layer charge between 0.2 to 0.6 per formula unit and charge location (octahedral vs. tetrahedral charge), a vermiculite and a very fine grained illite sample were studied. The purpose of this study is to investigate the influence of the intrinsic structural heterogeneity of the silicate layers on hydration properties using ATR-FTIR with emphasis on the structural clay mineral and sorbed water bands.

Initial results have shown that different hydration states of the interlayers can be detected from the bending mode of water δ (H-O-H). The shifting of δ (H-O-H) seems to be well related to the decrease of interlayer space upon dewatering the sample.

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Arrangement of alkylammonium surfactants intercalated in montmorillonite as studied by IR spectroscopy

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Keywords: organo-montmorillonite, conformation, infrared spectroscopy

Infrared (IR) spectroscopy is one of the most often used methods for characterization of organoclays. These inorganic/organic hybrid materials found application in various technological areas such as adsorbents of organic pollutants, reinforcing fillers for plastics, or host structures for direct intercalation of polymers. The behaviour and properties of organoclays strongly depend on the structure and molecular environment of the intercalated surfactants, most often alkylammonium cations. Detailed information on the arrangement of organic cations in clay mineral interlayers provides also IR spectroscopy. The positions of the absorption bands related to the stretching vibrations of methylene groups (νCH_2) present in the mid-IR (MIR) spectra were found to be very sensitive to the degree of ordering of carbon chains. In addition to MIR, near-IR (NIR) spectroscopy also offers useful information on organoclays structure. As the overtone (2ν) modes of CH_2 groups are directly related to the CH_2 stretching vibrations, their positions should also reflect the modification of the alkyl chain arrangements. The objective of this paper was to compare the competence of different sample preparation techniques, and MIR *vs* NIR regions to follow the changes in the alkyl chain arrangement within the montmorillonite interlayers. The samples were prepared from a Na-saturated <2 μm fraction of bentonite Jelšový Potok (JP, Slovakia) and trimethylalkylammonium (C_N-TMA^+) cations with increasing length of alkyl chain from C6 to C18. The KBr pressed disk, attenuated total reflection (ATR), and diffused reflection (DRIFT) techniques were applied for MIR region, DRIFT was used for NIR. The MIR spectra of C_6-TMA-JP showed the asymmetric ($\nu_{as}CH_2$) and symmetric (ν_sCH_2) stretching bands at 2928-2930 cm^{-1} and 2860-2863 cm^{-1}, respectively, while for C_{18}-TMA-JP the bands were found at 2922-2928 cm^{-1} and 2847-2852 cm^{-1}. A gradual shift towards lower wavenumber with increasing alkyl chain length confirmed a transition from disordered (*gauche*) to more ordered (*all-trans*) structures of the surfactants. The comparison of the sample preparation techniques indicated that the KBr pellets are more suitable to study the conformational ordering than ATR or DRIFT. The NIR spectra of organo-montmorillonites showed complex band in the 6100-5600 cm^{-1} region related to $2\nu CH$ vibrations of CH_3 and CH_2 groups. The position of the most intense component related to $2\nu_{as}CH_2$ was shifted from 5811 cm^{-1} for C_6-TMA-JP to 5784 cm^{-1} for C_{18}-TMA-JP confirming the creation of more ordered structure of surfactants with the increasing alkyl chain length. The magnitude of the $2\nu_{as}CH_2$ shift was clearly higher than observed in the MIR region for CH_2 stretching modes which benefits the utilization of the NIR spectroscopy for probing the conformation of alkyl chains. These findings are of high importance for the preparation of organoclays with proper surfactants and for the investigation of the microstructure of the resulting organoclays using suitable techniques.

Absorption studies of sub- and supercritical CO_2 in smectite clays

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Keywords: SANS, DLS, high pressure, CO_2 absorption, smectites

The Small Angle Neutron Spectroscopy (SANS), pressure-composition-Temperature (pcT) techniques and a high pressure/temperature cell (SPM25) have been employed to study CO_2 absorption in two different smectite clay types, Na-fluorohectorite and Laponite. In addition, nanoporous Vycor glass and aerogel, with well-defined pore sizes, were used as reference materials. The latter two materials display different behaviors in contact with *sub*- and *super-critical* CO_2, a two-phase system (Vycor) where CO_2 shows bulk behavior inside the matrix, and a "three-phase" system (aerogel), where there is an additional region of CO_2 with higher than bulk density close to the pores surfaces. Two different clay types, Na-fluorohectorite and Laponite, were subsequently investigated. Both samples presented a two-phase behavior, regardless of whether the clay samples were hydrated or not, thus not showing excess CO_2 adsorption close to the surfaces, even up to pressures above 150 bar. We also investigated the layer stacking or Li-fluorohectorite (organically modified) upon CO_2-loading, and found that there was a continuous increase in layer distance up to a value of 80 bar. This increase of the interlayer distance is a strong indication of CO_2 intercalation between the clay layers for this material. Dynamic Light Spectroscopy (DLS), on the other hand, allows obtaining absolute measurements of several parameters of interest, like molecular weight, radius of gyration, translational diffusion constant and so on. We studied clay materials in different pressure and temperature conditions, including sub-critical and supercritical state of CO_2 to obtain mean size of the clay particles. Pressure composition temperature (pcT) isotherms were measured in a calibrated in-house built (IFE, Kjeller) volumetric Sieverts-type apparatus in order to obtain information on CO_2 adsorption.

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Photo-Fenton catalytic activity of green synthesized β-FeOOH/kaolinite

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Keywords: green synthesis, coffee extract, β-FeOOH/kaolinite, photo-fenton, Methylene blue

This study focuses on the green synthesis β-FeOOH on kaolinite support and its use in the methylene blue removal from an aqueous solution.

For the green synthesis, coffee extract was mixed with $FeCl_3$ solution and kaolinite in order to obtain stable iron nanoparticles supported kaolinite; β-FeOOH/kaolinite.

The removal of methylene blue from aqueous solution was performed photo-Fenton process involving the use peroxide H_2O_2 and UV light. A series of batch experiments were conducted in order to determine the discoloration rate.

The first experiment, in presence of catalyst β-FeOOH single phase, demonstrated that by increasing the quantity of the akaganeite the removal rate also increases. After 300 minutes, total discoloration (100%) was achieved with just 5mg of catalyst.

The second trial was done using the same amount of β-FeOOH/kaolinite and the results illustrated that at a lower concentrations (bellow 10ppm) better removal values were obtained (95% after 300 min).

Sorption of carbon dioxide on Ti-, Zr- and [Ti,Zr]-pillared montmorillonites

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Keywords: CO2 sorption, pillared montmorillonites, thermal analysis

Pillared clays are large surface area micro/mesoporous materials which find application as adsorbents, catalysts or catalyst carriers. Recently, we have shown that excellent catalysts for the combustion of toxic chlorinated organic compounds present in waste industrial gases can be designed using Ti, Zr or [Ti,Zr]-pillared montmorillonites as supports for the active phase [1,2]. In the present study we decided to check whether this series of pillared montmorillonites is capable of binding carbon dioxide. Sorption studies were carried out in a Paar reactor (USA), and the amount and manner of CO_2 attachment were estimated by thermal analysis (DTA, TG, DTG, QMS), using Netzsch STA 449 F3 Jupiter apparatus. The tests were performed with a flow of CO_2 at atmospheric pressure and at a pressure of 50 atm of CO_2. The effect of pre-drying of pillared montmorillonite sorbent on the efficiency of carbon dioxide sorption was studied as well. It was found that the investigated pillared montmorillonites bind different amounts of CO_2 per mass unit. [Ti,Zr]-PILC was the best sorbent of CO_2 in normal conditions, Ti-PILC a little worse, while the least of CO_2 was bound by Zr-PILC. Drying of the samples for 4 hours at 300°C resulted in partial removal of water, but despite emptying of pore network, a decrease of carbon dioxide sorption was observed. However, the binding of CO_2 adsorbed on pre-dried samples was stronger as compared to the unpretreated samples, as evidenced by the shift of the CO_2 emission curve towards higher temperatures. In CO_2 adsorption tests carried out at elevated pressure, for all samples the amount of bound CO_2 increased in relation to the result obtained under normal conditions. The highest increase was observed for Ti-PILC sample, smaller for [Ti, Zr]-PILC, the smallest for Zr-PILC. It was also observed that desorption of CO_2 was correlated with the departure of water at the same temperature. This points to the participation of adsorbed water in binding of carbon dioxide in the pore system of pillared montmorillonites. Superposition of thermal effects associated with the removal of water and carbon dioxide during the samples heating makes the precise estimate of the amount of CO_2 sorbed by pillared montmorillonites difficult.

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Structural differences of kaolinite and montmorillonite co-intercalated with ammonium salts and azobenzene

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Keywords: azobenzene, intercalation, kaolinite, montmorillonite, photoresponse

Intercalation of layered silicates with azobenzene is performed in order to obtain a photoactive material controlled remotely with UV radiation. Upon UV radiation azobenzene isomerizes from *trans* to *cis* form, which is associated with a change of the molecules dimensions. This reaction may occur within the interlayer space of a layered material and then it influences the structure of the host component.

A Na-montmorillonite from Wyoming deposit, USA (SWy) and kaolinite from Maria III deposit, Poland (M) in a methoxy-form (MM) were used as host materials. The minerals were pre-intercalated with a series of trimethylalkylammonium (C_n) and benzyldimethylakylammonium (BC_n) cations, where n is the number of carbon atoms in the alkyl chain, equal to 12, 14 and 16. Afterwards the azobenzene (AZ) was incorporated into the obtained intercalates in a closed teflon vessel at 120°C for 24 h using a weight ratio of AZ/pre-intercalate equal to 0.2.

The d_{001} basal spacing for the pure SWy increased from 11.9 Å to 16.4 Å, 18.2 Å and 20.5 Å for SWy–C_{12}, –C_{14} and –C_{16} samples, respectively, and the samples with BC_n ions showed larger d_{001} by an average of 1.5 Å. This range of d_{001} values suggests formation of a bilayer of intercalated molecules. In the case of kaolinite, the basal spacing of MM sample (8.7 Å) increased after salts intercalation up to: 40.3 Å (C_{12}), 35.1 Å (C_{14}), 46.9 Å (C_{16}) and 30.0 Å (BC_{12}), two maxima – 39.4 and 32.0 Å (BC_{14}), 41.9 Å (BC_{16}). The peaks were not well definied and broad, moreover the d values did not correlate with the length of alkyl chain as opposed to smectite. However the large d_{001} values indicated that the C_n and BC_n molecules were tilted with respect to the kaolinite layers in contrast to smecite intercalates. It is suggested that the OCH_3 groups attached to the octahedral sheet of MM sample were a driving force for the tilted arrangement of intercalated molecules.

The co-intercalation of AZ caused further increase of the basal spacing. In case of SWy–BC_{14}, –BC_{16} and –C_{16} samples the XRD patterns were well resolved and showed distinct peaks at 32.0 Å, 35.9 Å and 36.9 Å, respectively, with accompanying 2nd and 3rd order reflections. The XRD patterns of the other samples were less resolved, with two or more broadened peaks, suggesting a mixed layer structure of obtained material. For the kaolinite the presence of AZ shifted the basal reflection of BC_n pre-intercalates to ~50 Å. The AZ intercalation induced ordering in the arrangement of molecules as several low-angle diffraction peaks were replaced by one symmetric peak. This could be attributed to π-π interactions between rings of BC_n salts and AZ. Such ordering was not observed when AZ was co-intercalated with C_n salts.

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The effect of experimental factors on alkali activation of halloysite

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Keywords: halloysite, alkali activation, nanotubes

Halloysite is a layered aluminum silicate, belonging to the kaolin group minerals. The minerals naturally exhibits a nanotubular morphology which is unique in mineral world. In this work, the influence of alkali concentration, reaction temperature and time on halloysite structure was investigated. The halloysite from Dunino deposit, located in the southwest Poland was investigated. In all experiments 100 ml of aqueous NaOH solution and 4 g of halloysite were mixed. The experiments, testing the alkali concentration, were carried out for 0.01 to 5 mol NaOH/L concentration range at room temperature. The influence of reaction temperature was determined in 50-90°C temperature range for 1 mol/L NaOH and 24 h time. In the case of time factor studies the suspension aliquots were collected after 0.5; 1, 2; 5; 8 and 24 h. The materials were characterized using XRD, FTIR and N_2 adsorption/desorption. The IR results indicated, that the treatment with NaOH in the range of 0,01-5 mol/L at room temperature did not affect the structure of halloysite. However, the temperature above 60°C caused alterations in halloysite structure. The changes of bands relative intensities, attributed to different vibration modes of inner surface and inner hydroxyls (3700-3600 cm^{-1}) were noticed. The IR spectra also revealed increase of intensity and broadening of bands associated to stretching and bending vibrations of absorbed water, 3430 cm^{-1} and 1647 cm^{-1} respectively. Additionally, high temperature caused structural changes within the aluminosilicate framework of halloysite. This was atested by the frequency shift and broadening of bands at 1033 cm^{-1}, 1008 cm^{-1} and 540 cm^{-1}, assigned to Si-O-Si vibrations. The decrease of bands intensity at 936 cm^{-1} and 914 cm^{-1}, confirmed alteration and/or removal of Al-O-H groups. These bands become more evident with the temperature increase. The XRD results confirmed the presence of hydrated sodium carbonates and sodium aluminum carbonate silicate as a products of halloysite alteration. Furthermore, peaks attributed to sodium aluminum silicate, were observed. The time factor studies revealed that the alteration of mineral structure with NaOH was not rapid but occurred gradually as the above described changes in the IR spectra became more evident with time. Moreover, this observation was also confirmed in the XRD results. The peaks associated with additional crystalline phases appeared after 5 h of treatment at 80°C and 90°C. The textural analysis revealed that the alkali activation caused the decrease of surface area and total porosity. In addition, the pore size distribution showed that the pore diameter of ~18 nm corresponding to the diameter of halloysite lumen, decreased with the increase of temperature. These results suggested that the precipitation of dissolution products occurred inside the halloysite nanotubes.

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Alternative organo-clays as a sorbent for removal of pharmaceuticals from the aqueous phase

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Keywords: sorption, clay minerals, ionic liquids, pharmaceuticals

Diclofenac is a commonly used non-steroidal anti-inflammatory pharmaceutical which passes easily trough WWTPs [1]; it is supposed to be persistent and have many adverse and toxic effects [2-3]. Therefore it is mandatory to remove this drug from wastewater streams, which will soon be required by law [4].

There are several methods used for the treatment of such contaminated waters: microbial degradation, chemical oxidation or incineration. However, the most frequently used technology is adsorption, applying a variety of sorbents. Although activated carbon is widely used, its production and regeneration are costly, making research into alternative adsorbents such as clay minerals a high priority. Clay minerals are source of low cost and widely available materials, however they are hydrophilic compounds therefore not suitable for removal of polar organic pollutants. To use clays as effective sorbents, their surface must be modified, which is usually achieved by introducing cationic surfactants to the clay mineral surfaces,. One of the potential surface modifiers are ionic liquids (IL), which exhibit surfactant-like behaviour on clay mineral surfaces. However, few studies have successfully demonstrated that IL-modified clay minerals can be used to efficiently remove pharmaceuticals from the aqueous phase.

To assess the sorption of diclofenac onto ionic liquid-modified sepiolite and nontronite, a batch equilibrium method was used. We used the ionic liquid 1-methyl-3-octyl-imidazolium chloride [OMIM][Cl] as surface modifier, one of the most applied and studied imidazolium derivatives. Results of the individual experiments were compared to ascertain the significance of clay surface modification by various concentration of IL on the adsorption of pharmaceutical diclofenac from the aqueous phase.

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Organically modified clay sorbents for p-nitrophenol removal from aqueous solutions

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Keywords: surfactant modified clay, p-nitrophenol, sorption, water treatment

Organically modified clays have attracted a great interest due to their wide application in industry and environmental protection as sorbents for organic pollutants in water, soil and air [1]. p-Nitrophenol is considered as common environmental contaminant found particularly in the effluents from pesticides, pharmaceuticals, petrochemicals, plastic, paper and other industries [2].

The aim of the study was to prepare organically modified clays using five different surfactants and to evaluate the removal efficiency of p-nitrophenol through batch sorption studies.

In this study, natural smectite dominated clay from deposit Saltiski (Lithuania) and synthetic montmorillonite *Montmorillonite K 10* purchased from Sigma-Aldrich (Germany) were modified by different nonionic (4-methylmorpholine N-oxide, dimethyldodecylamine N-oxide) and cationic (dodecylamine, benzyltrimethyl ammonium chloride, dodecyltrimethyl ammonium chloride) surfactants. Organic modification was based on exchanging the interlayer cations and by adding different surfactants in various concentrations.

Obtained modified clay materials were characterized by powder X-ray diffraction (PXRD), Brunauer-Emmett-Teller surface area analysis (BET method), Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM). The sorption of p-nitrophenol was investigated under various environmental conditions - e.g., pH, adsorbent dosage, contact time and temperature.

This study is of great importance for understanding the structure, properties and potential applications of organically modified clays, especially for water treatment.

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Unique photoactive nanocomposites based on rhodamine 6G/polymer/montmorillonite hybrid systems

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Keywords: montmorillonite, polymer, organic dye, adsorption, dye aggregation

Encapsulation of photoactive molecules, such as organic laser dyes into the gallery of various inorganic layered nanomaterials, which are modified by conjugated polymers can potentially find applications in various areas such as optoelectronics, photonics, bio-imaging, bio-sensing, and nanomedicine [1]. This study focused on the preparation of unique fluorescence hybrid inorganic-organic nanomaterials.

Addition of polymers to smectites results in the formation of nanocomposites where the smectite particles are well dispersed in a polymeric phase. Organo-montmorillonite (MMT) complexes [polydiallyldimethyl(PDDA)-Kunipia F] with various loadings of polycation were modified with a laser dye Rhodamine 6G (R6G) to obtain photofunctional hybrid materials for monitoring of dye – polymer – MMT nanocomposite interactions. The polymer-MMT´s were prepared in a colloidal state via ion-exchange reaction. The content of polycation (PDDA) in suspensions varied from 20 mg to 1000 mg per 1 g of Kunipia F (KF) MMT. Dramatic changes were observed in the structure of PPDA-MMT containing 200–300 mg of polymer per 1 g of KF, which was the saturation point of the polycation for this system. The crucial problem to be solved in preparation of hybrid inorganic–organic systems with good photoluminescence properties is the elimination of H-aggregate formation, which is known to be an efficient quencher of fluorescence from other species [2]. H-aggregates can be removed using suitable reaction conditions during the preparation of hybrid systems and also by using an appropriate chemical premodifier in the silicate precursors. The loading of polycation significantly influences the spectral characteristics of intercalated fluorescent dye. The fluorescence spectra confirmed that only a small amount of R6G cations are sufficient to render hybrid systems photoactive. The presence of polycations enhanced the fluorescence ability and no fluorescence quenching was observed. Therefore, the PDDA molecules significantly improve the photophysical behavior of the dye adsorbed on MMT and contribute to a suppression of a molecular aggregation. These PDDA/MMT nanocomposite systems are novel and have not been studied before in order to prepare highly fluorescence hybrid systems [3]. The PDDA molecules were able to suppress the formation of non-luminescence H-aggregates and to enhance the overall luminescence properties.

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Effect of chitosan on the crystallisation of brushite

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Keywords: composites, brushite, chitosan, crystallization

The deacetylated chitin derivative, chitosan is of considerable scientific and practical interest due to its multifunctional molecular structure, presence of free amino groups, bactericidal properties [1] and biocompatibility. It is appropriate to immobilize various compounds [2].

The purpose of the work was to synthesize brushite in the presence of chitosan and to analyze the properties of the manufactured composites.

Brushite was prepared from an aqueous solution by reaction (1). The concentration of the initial reagents was 50 mmol/L, pH = 5.50 ± 0.05 and the synthesis time was 72 hours. The masses of the chitosan additives were 0.0100 g (sample 1), 0.0400 g (sample 2) and 0.0800 g (sample 3).

$Ca(NO_3)_2 + (NH_4)_2HPO_4 + 2H_2O \rightarrow CaHPO_4 \cdot 2H_2O\downarrow + 2NH_4NO_3$ (1)

The X-ray analysis of the samples indicates that the resulting phase under these conditions is brushite which belongs to the monoclinic system. The phase composition in the presence of chitosan does not change. The Fourier transform infrared spectroscopy (FTIR 1202) shows that all the samples contain chitosan. As the chitosan mass increases, the crystallites formed in the initial solution grow in size: sample 1 is 4.0 μm, sample 2 is 4.8 μm and sample 3 is 11.8 μm (Fig. 1).

Fig. 1: Optical microscopy of precipitation: a- sample 1, b – sample 2, c – sample 3

The specific surface area is 5 m^2/g (BET). According to the data obtained through TGA, (T = 298–873 K) the greatest mass loss occurs in the range of 473–673 K. Chitosan starts to destruct at a temperature of 473 K. The samples change in color: sample 1 is beige, sample 2 is pink and sample 3 is dirty pink. At a temperature of 673 K, the color changes more rapidly. At a temperature of 873 K, chitosan is removed from samples 1 and 2, and sample 3 is carbonized.

Thus, chitosan is found to affect the crystallization of brushite in the $Ca(NO_3)_2$ - $(NH_4)_2HPO_4$ system. Micro-sized composites of the brushite-chitosan system are produced. The composition and thermal stability of the composites are studied.

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9,10-dihydroxy-octadecylammonium: a structurally unique class of clay intercalable surfactant

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Keywords: organoclay, surfactant, conformer, MAS NMR

The intercalation of montmorillonite with a broad range of organic cationic surfactants, with the aim of preparing inorganic additives for polymers, has attracted wide attention from academic and industrial researchers because polymer-clay nanocomposites frequently exhibit unexpected properties arising from the synergy of their components.

The structurally unique surfactant 9,10-dihydroxy-octadecyltrimethylammonium iodide (OH-ODTMA), prepared by a two-step synthesis from commercially available oleylamine, was successfully intercalated into montmorillonite. In addition, oleyl trimethyl ammonium cation (OLEYL-TMA), the precursor of the aforementioned novel surfactant, as well as the commercially available and widely used octadecyltrimethylammonium (ODTMA) cation were also intercalated into montmorillonite. The resulting organoclays were characterized in detail by various physicochemical techniques to understand the effect of alkyl chain functionalization on surfactant properties and arrangement in montmorillonite interlayers. The XRD showed a definite intercalated structure for all three surfactants, manifesting a pseudo-trilayer arrangement. The combination of IR and MAS NMR spectroscopy allowed investigation of the effect of unique surfactant functionalization on the structural features at the nanometer level of composites consisting of the organic surfactant and inorganic montmorillonite.

Infrared spectroscopy, based on the shift of the stretching and overtone CH_2 bands, showed that the gauche conformation was extensively adopted by the novel structurally unique surfactant OH-ODTMA, while the well-known ODTMA cation mostly adopted the more ordered trans configuration.

The ^{13}C MAS NMR spectra revealed that the surfactant ODTMA was arranged in a more orderly fashion within clay interlayers than OLEYL-TMA and novel OH-ODTMA, as confirmed by the calculation of the ratio of *gauche* : *trans* conformers after deconvolution of NMR signals 30 and 33 ppm.

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Enrichment and organophilisation of smectite saturated clays

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Keywords: smectite, purification, coagulation, organoclays, SWy-2

Smectites are widely used in a range of applications because of their high cation exchange capacity, swelling capacity, high surface areas, and consequential strong adsorption and absorption capacities [1]. In a case of smectite saturated Triassic clays from the Baltic region a certain fractionation is required to enrich the smectite and to remove other unwanted matrix minerals, especially feldspar, carbonates and quartz. The mentioned inorganic impurities decrease the sorption properties and quality of the Baltic clay materials.

Increase of application of smectites in the manufacture of advanced materials (including organoclays) raises the need for purification and enrichment. Various regular methods can be used to purify the smectite saturated clay samples. The most common method for obtaining purified clay minerals is fractionation by sedimentation after the removal of oxides, hydroxides and organic matters [2]. A simple, fast procedure of purification and concentration of smectite is proposed [3]. The method is based on dispersing smectite saturated clay in a sodium phosphate aqueous medium followed by concentration of smectite by coagulation using water soluble organic coagulant (KOHIDRAC). KOHIDRAC is a product of condensation of acetone with hydrazine dihydrochloride. This procedure results in feldspar and carbonate free smectite samples. Amounts of quartz are also decreased by several factors in finished samples.

Clay-organic derivatives have found application as rheological control agents in lubricants, drilling fluids, greases, oils, paints and even antibacterial materials and coatings. A critical factor of organoclay synthesis is time consumption, also complicated procedures sometimes involve the use of organic solvents. A new one-step approach for obtaining organoclays from smectite clays (raw, enriched and SWy-2) has been investigated. The method is based on intercalation of organic compounds into air-dried smectite clay samples by solid-state reaction without the use of organic solvents [4]. The mechano-chemical process for clay-organic derivatives significantly minimizes time and energy consumption, providing high yields of organoclay at the same time.

Enriched and organophilised clay samples are characterized by X-ray powder diffraction, FTIR spectroscopy, differential thermal analysis and thermogravimetry. Sorption capacity of treated materials is established by methylene blue method.

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Preparation and structural characterization of organoclay based on zwitterionic surfactant: A comparative study

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Keywords: organoclay, zwitterionic surfactant, SWy-2, XRD, FTIR

Zwitterionic surfactants (ZS) are received increasing attention from industrial and scientific fields [1], due to their excellent water solubility, insensitivity to temperature, good biodegradability, efficient production, low costs, and a synergistic effect with a wide variety of ionic and nonionic surfactants [2]. Up to now, many ZS have been synthesized [3] and the increasing demand for this kind of surfactant has already enabled them to achieve well above average growth. In previous studies we have shown that the type of organic surfactant used can significantly influence the structural characteristics and adsorptive behavior of organoclays (OC) [4]. In this respect, ZS containing both positively charged (quaternary ammonium) and negatively charged (carboxylic, sulfonate, or sulfate group) functional groups, might significantly improve the adsorption capacity of OC. Today there are studies of ZS interaction with clay [5]. However, the behavior of ZS intercalated into the interlayer of clay has not yet been clarified, which is important to understand the modification mechanism. Our research involves a series of zwitterionic surfactant-modified montmorillonites (ZSWy) synthesis using Na-montmorillonite (SWy-2) and five zwitterionic surfactants – lauryl-myristyl betaine, cocamidopropyl betaine, oleyl aminepropyl betaine, hydroxyethyl alkyl imidazole, and aminoethyl imidazoline. Modification has been carried out by ion-exchange reaction. These ZSWys were characterized by X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy, specific surface area (SSA) and contact angle measurement. The characterization results demonstrate that the basal spacings of the ZSWys are proportional to the surfactant concentration and the alkyl chain length. FTIR spectroscopy confirms the ZS incorporation into the interlayer and the occurrence of a new peak assigned to the stretching vibration of C-H in the alkyl chain of ZSWys. The SSA of clay samples is determined by adsorption of Ar gas at −196.15 °C. The results suggest that adsorbed ZS may adopt a variety of conformations in the interlayer and external surfaces of clay minerals. The use of the contact angle as the measure of wettability has proved to be a useful method for assessing the hydrophobicity of organoclays. Imidazoline surfactant adsorbed on the surface of SWy-2 gives the most hydrophobic surface.

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The effect of the organic cation central atom on the thermal stability of organo-montmorillonites

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Keywords: thermal analysis, infrared spectroscopy, alkylammonium, alkylphosphonium, acid treatment

Thermal stability of natural and acid-treated organo-montmorillonites was investigated by means of thermogravimetric analysis (TA) coupled with infrared spectrometer for analysis of evolved gasses, and by in-situ measurement of near-IR spectra using a special heatable IR accessory. Montmorillonite (Cheto, SAz-1) was intercalated with tetrabutylammonium (Bu_4N^+) and tetrabutylphosphonium (Bu_4P^+) cations. Samples were treated with 6 M HCl at 80°C for 12 h and solid reaction products were characterized in detail.

The TG/DTG profiles showed pronounced mass loss due to decomposition of organic cations. While Bu_4N-S showed onset temperature of organic cation decomposition near 200°C, Bu_4P-S began to decompose at significantly higher temperature, above 300°C. Upon organic phase evolution the absorption bands related to the C–H vibrations of gaseous products (aliphatic hydrocarbons) appeared in the infrared spectra. The temperature at which the highest intensity of the C–H bands was observed was consistent with the temperature of maximal rate of surfactant decomposition detected from DTG lines. Acid treatment caused a partial decomposition of the montmorillonite layered structure. The mass loss attributed to the organic cation decomposition dropped down below 50% of its initial value due to leaching of organic phase upon treatment. However, the temperature of the maximal rate of decomposition was higher compared to acid untreated samples indicating that only more strongly held organic cations survived harsh condition of acid treatment and remained attached to the perturbed layered structure.

Complementary information on organo-montmorillonites stability was obtained by the near IR spectra measured under gradually increasing temperature. The intensity of the first C–H overtones band started to decrease due to organic cation release at lower temperature for Bu_4N-S than for Bu_4P-S. The spectra of acid treated samples showed also the first overtone of the Si–OH units. The intensity of this band increased significantly with increasing temperature. Si–OH groups remained present in the structure even after heating for 500°C.

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Vermiculite and montmorillonite interaction with sulfur at melt adsorption

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Keywords: vermiculite, montmorillonite, sulfur, intercalation, carbon

Clay minerals and especially 2:1 phyllosilicates are attracting various fields of application due to their friendly nature for modification. Traditionally interlayer space or silicate layer surface is modified with organic molecules or inorganic cations and functional chemical groups, for upgrading the properties of clays for further utilization e.g. in composites.

In the field of electrochemical application such as capacitors [1] and batteries [2], layered phyllosilicates are gaining interest, hence there is possibility to store cation into interlayer space at charging and discharging cycle. An interesting material for the matrix of cathodes is sulfur with addition of carbons.

Organophilized vermiculite and montmorillonite were used as 5wt. % nanofiller in S matrix to interact with orthorhombic stacking of S_8. Heating up the mixture the sulfur melting and polymerizing processes are taking place. Heat treatment of mixtre up to 300°C was applied to encourage S for mobility. Processes as sulfur melt adsorption with following vapor melt infusion was observed during modification of clays. The structural changes were studied using X-ray diffraction and spectroscopy methods. Morphology was observed using scanning electron microscopy and light microscopy.

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Benzalkonium chloride adsorption surface sites on two raw montmorillonites and their organo-clay

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Keywords: benzalkonium chloride, montmorillonite, nano-montmorillonites, surface sites

Benzalkonium chloride (BAC) is a cationic surfactant with bactericidal and fungicidal properties and relatively low toxicity to human beings. These properties allow it to be used as an active ingredient in pharmaceutical or cosmetic formulations, public health areas, food and feed areas as well as wood preservatives. The addition of cationic surfactant exchanged montmorillonites (Mt) (denoted nano-Mt) to certain polymers allowed to improve mechanical properties [1] and transfer the surfactant bactericidal activity [2] to the final product. The aim of this work was to evaluate the surface adsorption sites involved when BAC was used to obtain nano-Mt. To attain this objective BAC (C_0= 0.01 and 1.25 mM), was adsorbed on two raw Mt (commercial Cloisite, M_{Cloi} and Argentine raw Mt, M_{Cas}) and a nano-Mt ($M_{Cas\text{-}ODTMA}$ and $M_{Cloi\text{-}30B}$ exchanged 100 % CEC with octadecyltrimethyl-ammonium bromide and methyl, tallow, bis-2-hydroxyethyl ammonium chloride, respectively). The products were characterized by XRD and Zeta potential (ζ) measurements, to study inner and outer surfaces, respectively.

BAC adsorption at the nano-Mt interlayer space increased the basal space from 1.9 to 2.0 nm indicating a surfactant rearrangement. In the cases of M_{Cloi} and M_{Cas}, BAC adsorption increased the basal space in two steps: from 1.1 to 1.4 and to 1.75 nm, as BAC concentration increased from 0.01 to 0.1 mM. This phenomenon is assigned to monolayer to bilayer BAC arrangement in the interlayer. The ζ curves vs pH indicated a decrease of negative surface charge only with higher concentration of BAC (C_0= 1.25 mM) for raw Mt. In the case of nano-Mt a gradual increase of positive surface charge was found as BAC concentration increased. Particularly, for raw Mt with adsorbed BAC, an edge isoelectric point (IEP) at pH 4 was found. This value is similar to others IEP reported with different cations [3]. Indicating that for raw Mts, interlayer sites were preferred for BAC adsorption, whereas up to attain a certain BAC concentration the outer surface sites were also occupied. For, nano-Mt samples BAC adsorption mainly occurred at the outer surface, due to interlayer space already occupied by the respective surfactants.

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Organo-clays as supports for immobilization of ruthenium nanoparticles

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Keywords: organo-clays, Ru nanoparticles, immobilization

The work aimed at design, synthesis and study of novel nanostructures involving the use of polymer polycation modified clays as supports for immobilization and stabilization of metal nanoparticles confined in the interlayer space.

Organo-modified clay mineral samples were prepared by delamination of the natural smectite - Jelšowy Potok (JP) or synthetic Laponite RD® (Lap), and subsequent intercalation of the organic cationic polymer species with high charge density (polydiallyldimethylammonium chloride - PDDACl) mixed with $RuCl_3$ in the amount corresponding to 2 Ru wt.% with respect to the clay component. Two weight ratios of clays to polymer JP/Lap:PDDACl (1:0.05 and 1:0.25) were used. The polymer-free Ru-JP and Ru-Lap were prepared as references. The resulting Ru^{3+}-containing organic clay derivatives were reduced with $NaBH_4$ to obtain metallic particles distributed in the organo-clay supports.

The amount of PDDACl influenced the interlayer spaces of the clays. XRD analysis showed an increase of the d_{001} basal spacing in the PDDA-JP_1:0.05 and PDDA-Lap_1:0.05 samples (1.50 nm) compared to the natural clay mineral (1.25 nm), indicating intercalation of polycations between the layers of smectite. Introduction of higher amount of polycations to the clay mineral suspension (1:0.25) resulted in a slight increase of the interlayer expansion (1.60 nm). Co-introduction of PDDA and Ru cations, followed by reduction with $NaBH_4$, results in materials whose interlayer spacing differs both from that characteristic of the organoclay counterparts without metallic ruthenium, and from the one observed in metallic Ru-containing unmodified clay.

SEM-EDS and XRF analyses confirmed the presence of Ru in the structure of modified clays. The physico-chemical properties of organo-clay/Ru composites are discussed in terms of possible polymer-clay-Ru particle interaction. The materials were tested for their catalytic properties in the reaction of 2-butanone hydrogenation.

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Characterization and adsorption behaviour of a saponite from Patagonia Argentina

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Keywords: clay mineral, sorption, heavy metals

Ferromagnesian trioctahedral smectites with Mg^{2+} and Fe^{2+} as the predominant octahedral cations are wide-spread in nature, especially as the main authigenic clay minerals produced by the alteration of oceanic and continental basalts and other basic volcanic material. Ferromagnesian smectites appear as members of a complete Mg/Fe solid solution series:

$Mg_3(Si_{4-x}Al_x)O_{10}(OH)_2M^+_x$ --- $Fe_3^{2+}(Si_{4-x}Al_x)O_{10}(OH)_2M^+_x$

where the layer charge x is assumed to be 0.6 or less and M^+ represents cations related to permanent charge [1].

The high specific surface area, chemical and mechanical stability, layered structure, high cation exchange capacity, etc., have made these clays excellent adsorbent materials. In addition, the presence of both Brönsted and Lewis types of acidity boosts the adsorptive capacities. On the other hand, heavy metals have become prominent pollutants these days due to their toxic and lethal effects. Adsorption at the metal ion-mineral interface is often utilized as a very effective way for scavenging undesirable metal ions from an aqueous phase and clays play the role of a natural scavenger by filtering out pollutants.

The aim of the present work was to characterize a new sample of saponite from Colan-Conué, Province of Río Negro, Patagonia Argentina. Saponite was characterized by chemical analysis [Total Fusion, Cation Exchange Capacity (CIC), Specific Surface Area (SSA)]; X-ray diffraction (XRD) using a Geiger Flex Rigaku D Max III-C, and Infrared Spectroscopy (IR) using a Nicolet FTIR spectrometer model Nexus 470.

Adsorption of Zn^{2+} and Cd^{2+} (from aqueous solutions $1.5x10^{-3}$ $mol.L^{-1}$) as a function of pH and ionic strength (I) were studied. Zn^{2+}, Cd^{2+}, Mg^{2+}, Fe^{2+} and Na^+ amounts in the suspensions were determined by Atomic Absorption Spectrometry (EEA). The adsorbed amounts were calculated by the difference before and after adsorption process. Adsorption behaviour was similar for Zn^{2+} and Cd^{2+}. An important influence of ionic strength was noted: at I = 0.001 the amount of hydrolysable ion was at least two times greater than I = 0.1. In addition, at I = 0.001, a relationship between adsorbed/released ions ($Zn^{2+}/Cd^{2+}{}_{ads}/Na^+{}_{rel}$) was established showing that part of the adsorption occurs at permanent charge surface sites. At I = 0.1 a release of surface H^+ was observed, and the adsorption process was strongly dependent on pH of the medium with enhanced adsorption as the pH turned from acidic to alkaline side. No Mg^{2+} release from octahedral sheet was observed. The adsorption data gave good fits with Langmuir isotherm.

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Montmorillonite as nanocarrier of first-line tuberculostatic drugs

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Keywords: montmorillonite, isoniazid, etambuthol, modified drug delivery

Montmorillonite (MT) is a phyllosilicate clay, with a multilayered structure of Si/Al oxide in multilayer stacks [1]. Isoniazid (INH) and Etambuthol hydrochloride (ETB) are two first-line antimycobacterial agents for the therapy of tuberculosis (TB), which lacks of patient-compliance [2]. The aim of this work was the use of MT to obtain a modified drug delivery system able to improve patient compliance in the pharmacological therapy of TB.

A known amount of pharmaceutical-grade MT (Veegum HS®) was dispersed in ethanol solutions of INH and ETB with a drug to clay ratio 1:1 w/w. Combinations of the two drugs were also proved with a ratio 1:1:1 w/w. After 24 hours of magnetic stirring, the solvent was evaporated (Rotavapor®, Buchi model RII). The residue was dried at room temperature and characterized by Differential Scanning Calorimetry (DSC) to assess drug loading into the clay mineral. The DSC analysis of the samples was performed at 10ºC/min in the 30-300 ºC temperature range (DSC Mettler FP800, Mettler-Toledo GMBH, CH).

Fig. 1 shows the DSC curves of the raw materials (INH, ETB, MT) and the interaction products (MT-ETB; MT-INH; MT-ETB-INH). Melting points of the free drugs were 202ºC and 173ºC for ETB and INH respectively. Moreover, the enthalpy of transition (ΔH) were 126 J/g for ETB; 169 J/g for INH; 34,2 J/g for MT-ETB; 39,3 for MT-INH and 43,8 J/g for the ternary mixture MT-ETB-INH. On the basis of these results, it can be assumed that both ETB and INH have been successfully loaded in the mineral clay.

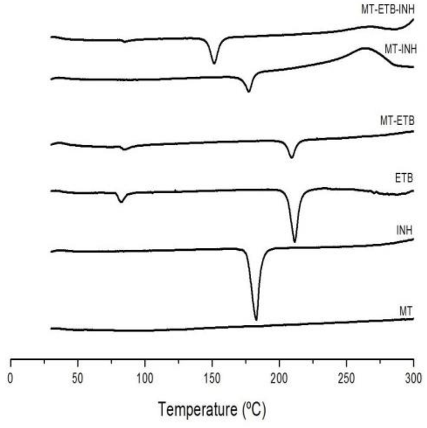

Fig. 1. DSC curves of the samples studied

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Palygorskite as isoniazid and etambuthol hydrochloride nanocarrier

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Keywords: palygorskite; tuberculosis; nanocarrier; modified drug delivery

The development of effective modified drug delivery systems for tuberculosis (TB) treatment is a global health priority [1]. Clay minerals play a crucial role in modulating drug delivery through various mechanisms and with different purposes [2]. Among them, Pharmasorb Colloidal (PC) is an activated attapulgite clay designed for use in pharmaceutical and cosmetic application [3].

A known amount of PC was dispersed in ethanol solution of INH and ETB with a drug to clay ratio 1:1 w/w. Combinations of the two drugs were also proved with a ratio 1:1:1. The preparation was left under magnetic stirring for 24 hours, and then the solvent was evaporated (Rotavapor®, Buchi model RII). The dry residue was characterized by Differential Scanning Calorimetry (DSC) to evaluate drug loading into the clay mineral. This thermal analysis was carried out at 10ºC/min in the 30-300 ºC temperature range (DSC Mettler FP800, Mettler-Toledo GMBH, CH).

Fig. 1 shows the DSC curves of the primal matters (INH, ETB, PC) and the interaction products (PC-ETB; PC-INH; PC-ETB-INH). Melting points of the free drugs were 202ºC and 173ºC for ETB and INH respectively. In addition, the enthalpy of transition (ΔH) were 126 J/g for ETB; 169 J/g for INH; 28,9 J/g for PC-ETB; 72,9 J/g for PC-INH and 11,5 J/g for the ternary mixture PC-ETB-INH. This results confirm the successfully loading of the drugs on the clay.

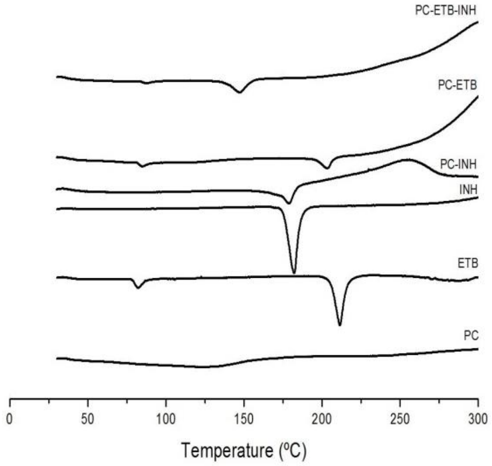

Fig. 1. DSC curves of the samples studied

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Healing clays from longroiva (ne portugal): technological properties and quality assessment

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Keywords: peloids, pelotherapy,geomaterials

Pelotherapy is a therapy with peloids that is used worldwide, either in thermal centers or in situ. They are commonly applied for the treatment of arthro-rheumatic and skin diseases. Peloids are the product of the mixture of a solid phase (muds/clays) and a liquid phase accomplished after undergoing a maturation stage.

Portugal is very rich in thermal spas and is developing pelotherapy and dermocosmetic products based on healing minerals, with particular emphasis on clay minerals and other clayey geomaterials.

In the Longroiva region (NE Portugal) occurs Cenozoic green-withish arkoses (middle Eocene to Oligocene), representing proximal sediments of very low gradient drainage. These arkoses are very rich in K-feldspars and plagioclases, the later very weathered; locally, clay-rich levels occur, commonly controlled by subvertical N-S faults.

Mineralogical and geochemical compositions of these clayey levels were assessed by XRD and XRF; structural formulas were computed from SEM-EDAX data. Some samples are very rich in Kaolinite, others in Smectite, Illite being always present.

Several technological properties, such as grain size distribution, specific surface area, pH, cation exchange capacity, exchangeable cations, adsorption, plasticity, viscosity, abrasivity, specific heat and cooling rate were also assessed. Studied samples show in general good results, adequated to be used as healing minerals for mud treatments (pelotherapy) but just those more Smectite rich and also more rich in clay fraction are adequate for dermocosmetic production. Heavy metals and other Potential Harmful Elements (PHE) contents are, in general, low.

Quality assessment show that they need to be submitted to artificial ageing (maturation) procedures aiming to improve some properties namely plasticity, cooling rate and abrasivity.

Pb(II) adsorption by natural and modified bentonite

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Keywords: bentonite, iron oxide, adsorption, lead

The work deals with the study of adsorption properties of natural clay bentonite (B) as adsorbent of lead cations. To enhance its adsorption capacity, the coating of bentonite surface by iron oxide particles, in two selected weight ratios (2:1 and 4:1), was used [1, 2]. The samples were denoted as BM1 (2:1) and BM2 (4:1). The changes of the surface parameters after the modification were studied by the low temperature nitrogen adsorption. The increase of the value of specific surface area was observed after the modification for both samples, higher was obtained for the BM2 sample, from 39 to 80 m^2 g^{-1}. The porosity also changed, both modified samples showed broader distribution in the range of mesopores. The structural properties of sorbents were analysed by the X-ray diffraction method and Mössbauer spectroscopy. The morphology was studied by the scanning electron microscope. The nonhomogenous distribution of maghemite particles on the bentonite surface was observed. The maghemite particles were of spherical shape creating agglomerates.

The Pb(II) adsorption experiments were conducted in the plastic tubes placed in the rotary shaker. The different conditions, such as pH of the model solutions, contact time and initial metal ion concentration was studied. To compare the influence of initial metal ion concentration on the adsorption capacity of sorbents, the experiments were conducted in concentration range 10 - 500 mg Pb(II) L^{-1}, pH 5 and sorbent dose 1 g L^{-1}. The results were processed by the Langmuir adsorption isotherm. The calculated values of maximum adsorption capacity were 96 mg Pb(II) g^{-1}, 86 and 91 mg Pb(II) g^{-1} for natural bentonite, BM1 and BM2, respectively. Higher adsorption rates of modified sorbents were observed for lower initial metal ion concentrations, what should be interesting for the treatment of contaminated water.

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Comparison of surface properties of clays and waste brick dust in terms of fixation of toxic ions

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Keywords: toxic ions, clays, waste brick dust, adsorption parameters

Toxic metals (Cd, Zn, Pb), toxic oxyanions (As, Sb, Cr) and radioactive ions (U, Cs) belongs to the most toxic inorganic contaminants with the risk to human health. It is very important to prevent the contamination spreading, therefore many studies have been focused on the investigation of new remediation techniques using the adsorption for fixing toxic ions to suitable materials [1].

Natural and Fe (Al, Mn)-modified clays are considered to be suitable materials for the fixation of toxic ions due to their physico-chemical and surface properties, low cost and easy availability [2,3,4]. However, the attention is now focused on waste ceramic materials, especially the brick dust waste. They illustrate similar properties with clays, but compared to clays the main component of brick dust is quartz. Previousd study [5] indicated that the brick dust waste could be also an efficient sorbent of toxic ions, but additional research is necessary.

In this work 2 samples of clays and 2 samples of brick dust waste were analyzed using XRD, XRF and IR spectroscopy to compare their structure, composition and surface characteristics. The adsorption properties was indicated the presenceof cationic (Pb2+, Cd2+), anionic (AsV, SbV) and radioactive (UVI) contaminants, which were analyzed by AAS, HG-AFS, UV-VIS spectrophotometry and ICP-OES, respectively. The effect of studied sorbents was evaluated according to the type and amount of adsorbed ion and physico-chemical properties of the contaminated aqueous environment.

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Characterization of clay fraction in dust particles and sediments with SEM/EDX

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Keywords: heavy metals, atmospheric deposition, sediments, urban area, scanning electron microscopy

The aim of this work was study and characterization of clay fraction in dust particles and sediments with SEM/EDX. Atmospheric deposition is a significant source of many toxic pollutants and their major input into the surface and other components of environment. Košice is the second largest city in Slovakia - mixture of dust particles originates from the urban area. The paper deals with the study and characterization of particles size and shape, their origin and chemical composition of particles. The samples were analyzed from 8 sampling sites in Kosice and the surrounding area and were collected during the winter and summer season. The scanning electron microscope (SEM) is able to provide morphological observations and elementary composition measurements for bulk, single dust particles and sediments. Various sharp fracture particles, ashes, prismatic particles, spherical particles were observed in the studied samples. The dust particles were composed of aluminosilicates containing higher contents of Si, Fe, Al, Mg and K.

Branches of the Hornád and Hnilec Rivers drained these former mining areas and flow into the water reservoir Ružín. The mining activities and the metal content present in the soil in the mining areas monitored for a long time influenced the quality of the bottom sediments in the reservoir. The bottom sediments are comprised of sand, slit and clay fractions. The content of heavy metals in the clay fraction is a very good indicator of environmental pollution. The bottom sediments are contaminated by trace and semi-trace metals, Hg, Cu, Zn, Cd, Cr, Pb, Ni, Sb and As, which accumulated in the reservoir for a long time. The interaction between the clay fraction and contaminants was studied.

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Modified vermiculites and their sorption for ranitidine from aqueous solutions

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Keywords: vermiculite, modified clay mineral, ranitidine, adsorption

Emerging pollutants like pharmaceutical compounds have recently become an environmental concern because of the large number of different organic compounds that may be present in the environment [1]. The traditional systems for the removal of organic pollutants from water adopt an adsorption using activated carbon. New adsorbents materials derived from clay minerals have attracted attention because they are abundant, low-cost materials, environmentally compatible and show unlimited potential [2]. This work focused on use of modified vermiculites as adsorbents for ranitidine. Ranitidine, as other anti-secretory drugs, effectively inhibits basal and stimulated gastric acid secretion which leads to a sustained rise in intragastric pH. Approximately 70% of the systemically available ranitidine is excreted in unchanged form into the urine [3]. An environmental consequence is its conversion to N-Nitrosodimethylamine (NDMA), which is a carcinogen [4]. In this work sodium and leached vermiculites were silylated with chloropropyltrimethoxysilane and were subsequently reacted with the alkyldiamines ethylene-(en), 1,4-butyl-(but) and 1,6-hexyldiamines (hex). The solids were characterized by elemental analysis of chlorine, carbon and nitrogen, infrared spectroscopy, X-ray diffraction and adsorption/desorption nitrogen measurements. The organofunctionazed solids were applied for the adsorption of the ranitidine from aqueous solution. The adsorption kinetics (500 mg L^{-1}, pH 5.5) were fitted to the pseudo-second order model. The adsorption equilibrium was reached within 280 min, Adsorption isotherms were tested with the Langmuir and Freundlich isotherm models. The best fit was found with the Freundich model, indicating that physisorption may be the limiting step in the adsorption process. The maximum adsorption capacity was approximately 80 mg g^{-1} which demonstrates the good performance of the organofunctionalized vermiculites.

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Chitosan-montmorillonite beads for anionic dye removal

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Keywords: montmorillonite, chitosan-montmorillonite beads, dye, adsorption

In recent years, the presence of dyes in water is a serious environmental problem due their carcinogenic and mutagenic effects on aquatic life and also on human life [1]. Dyes generally have a synthetic origin and a complex molecular structure which ensures physico-chemical, thermal and optical stability due the presence of aromatic groups [2]. Therefore, the removal of dyes from waste effluents is necessary and adsorption has been shown to be one of the most applicable technologies [3]. In this work, a series of chitosan and chitosan/KSF-montmorillonite beads (1-25% w/w) were prepared by mixing the biopolymer and the clay mineral in presence of sodium tripolyphosphate (TPP) as crosslinker agent. The synthesized biocomposites were characterized by CHN elemental analysis, X-Ray diffraction, Fourier transform infrared, ^{13}C nuclear magnetic resonance, thermogravimetry, scanning electron microscopy and transmission electron microscopy and measurements of point of zero charge (pHpzc). The results suggested that hybrid materials were properly obtained and also their properties were improved compared to the pristine chitosan and montmorillonite (MMT). Further, the beads were evaluated in the adsorption of an anionic dye (Remazol brilliant blue R) under batch operations at different experimental conditions: pH of medium (1-8), contact time (0-660 min) and the dye concentration (100 to 1600 mg L^{-1}). Kinetic and equilibrium sorption parameters were evaluated using pseudo- first and pseudo-second rate equations and Langmuir and Freundlich models. The results were very promising where the maximum dye sorption was 310 mg g^{-1} at pH 3.0 for 25% chitosan/MMT beads and suggested that the sorbents can be applied for removing anionic dyes from wastewater. The dye sorption on chitosan/MMT beads interface was better compared with conventional adsorbents.

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Silicon substituted hydroxyapatite structure, morphology and properties

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Keywords: hydroxyapatite, silicate groups, model physiological solution

Materials based on hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$ (HA) are analogs of the mineral component of the bone tissue and considered as those most promising to be applied in bone defect replacement. The main method of controlling the characteristics of HA consists in the chemical modification of calcium orthophosphates. Since silicon is known to have a binding role in the physiological processes of bone and cartilage tissue growth and restructuring, the development of different methods of synthesis of silicon substituted hydroxyapatite (SiHA) comprises an urgent physical-chemical problem [1]. To achieve a fuller physiological response of the organism on recovery of the damaged bone tissue, the hydroxyapatite chemical modification must be done in solutions similar to a human organism's physiological fluids. Application of model electrolytic systems whose content is identical to that of biological fluids comprises a promising way of composite biomaterial fabrication. For this purpose, the composition of the human extracellular fluid model solution was developed (Simulated Body Fluid (SBF)). This solution can be used in synthesis of calcium phosphates and evaluation of their biological activity [2]. Information on the possibility of obtaining SiHA in the above system is currently not available. The objective of the present work was to establish the possibility of producing hydroxyapatite from a model solution of the extracellular fluid solution modified by silicate ions.

The formation of SiHA in the model solution of a composition corresponding to the system $CaCl_2$–$MgCl_2$–K_2HPO_4–$NaHCO_3$– Na_2SO_4–$NaCl$–Na_2SiO_3 (TES) and that of the human extracellular fluid has been established by means of the methods of chemical and XRD analysis, IR Fourier spectroscopy, and optical microscopy. It was revealed that variation of the initial concentration of the silicon containing reagents (0.5–5.0%) in the extracellular fluid solution resulted in the increase of the silicate ions concentration in the obtained precipitates, which yields the aggregation of the crystalline particles. No significant differences in the structure of the formed solid phases depending on different types of containing reagents have been established. The results of all analyses corroborate the substitution of phosphate groups by silicate ones in the apatite structure upon the addition of silicate ions. It has been demonstrated that the fabricated modified apatites crystallize in the nanocrystalline form and approach physiological parameters: in perspective, this results in the increase of the resorption degree and the solubility and bioactivity of the obtained SiHA capable of integrating with the bone tissue.

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Collagen of the bone matrix - properties and characteristics

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Keywords: collagen, bone matrix, hydroxylapatite, paramagnetic radicals

Despite the considerable amount of research devoted to the study of bone matrix, diagnosis and correction of such states is among the social problems. So far, there has been no consensus on the changes in the organic composition of bone tissue which occurs with age or as a result of various diseases.

Thermal analysis was used to analyze the content and energy of transformation processes of the bone tissue components in the temperature range of 25–1000°C. The transformation of the organic component proceeds at the temperatures: from 200 to 430°C when low and high molecular weight organic substances are removed, in particular, non-collagenous proteins of molecular weight lower than that of collagen (in association with structural water, II), and from 430 to 600°C when collagen is disorganized (III). At 25–200°C, the adsorbed water is lost (I). At temperatures above 700°C, carbon dioxide is released from the mineral bone component due to the transition of non-stoichiometric carbonate hydroxylapatite to stoichiometric hydroxyapatite. Next, we investigated the nature of the paramagnetic thermo-chemical radical ion of the organic component. In thermal annealing of powder samples of the bone tissue at temperatures above 200°C, a single signal "R-centers" of the organic component ($g = 2.0047 \pm 0.0005$, $\Delta H= 5.81 \pm 1.06$ G) can be recorded in the ESR spectra. It is shown that the temperature range of the radical ion stability fully coincides with the temperature range for the organic component decomposition (burning in air) of the bone tissue equal to 200–600°C, where 200–430°C corresponds to the degradation temperature range of high molecular weight organic substances with a molecular weight lower than that of collagen ; and 430–600°C is the temperature range for thermal transformation of the high molecular weight component, i.e. collagen (II). It is found that in thermal decomposition of substances whose composition is unordered, compared to collagen (I), a larger number of paramagnetic radicals formed at 200–430°C with spin-spin, dipole-dipole and other interaction types stronger than those for the collagen component (II). Micro-interactions between radical ions of the modified collagen fibrils are not distinct that can be attributed to close packing caused by redistribution of the load on the bone. In the course of bone arthrosis, the molecular weight of the organic content is observed to be less than that of collagen. Close packing of the deformed collagen fibers is one of the causes for the increased hardness of "arthritic" bones.

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Analysis of smectite as anticancer drugs carrier: simulation, synthesis, characterization and controlled release study of cisplatin and mitomycin

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Keywords: smectite, cancer, modified drug release, cisplatin, mitomycin

Currently, the development of innovative drug delivery systems with controlled release is one of the main tasks of biomedical profile aimed at overcoming an unfavorable situation in oncology. For the treatment of malignant tumors more than 50 remedies are used in clinical practice today [1]. However different in chemical structure and the mechanism of action, they have a common drawback, which is due to their short-lived period of stay in an organ, tissue, cell target [2]. The Increase of activity and prolongation of action of anticancer drugs is possible on the basis of their targeted delivery and controlled release in the nidus of cancer process. For this purpose, a number of methods is proposed so far, including the use of hydrogels [3], polymers and micelles [4], magnetic nanoparticles [5] as carriers of anticancer drugs. Despite demonstrated efficacy, the existing types of carriers have several disadvantages and limitations related in particular to their poor solubility, rapid degradation, presence of side effects on organism. Clay minerals have advantage over above mentioned delivery systems due to their inherent biocompatibility, low cytotoxicity and the ability of a researcher to control a wide range of surface properties. The use of clay minerals as anticancer drugs carriers can be an effective alternative to the existing conventional approaches to cancer therapy, and in solving the problem of the prolongation of drug effect and reduces the risk of side effects.

The purpose of the present research is to analyze possibilities and limitations of the use of smectite as sustained release delivery vehicle for cisplatin and mitomycin. More specifically, smectite-cisplatin and smectite-mitomycin anticancer complexes are prepared so that drug molecules are intercalated between the clay layers. The characterization of clay–drug intercalates has been done using X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), thermal gravimetric analysis (TGA). In vitro drug loading and release study has been carried out using UV-visible spectrophotometry. The drug release has been investigated under conditions simulating the sequential pH, concentration and temperature changes that occur during the in vivo process. Density functional theory (DFT) and molecular dynamics (MD) methods have been used to study theoretically the loading/releasing of anticancer drugs in smectite clay and to determine the conditions of these processes. This study has exposed that smectite not only plays a role as a carrier matrix for drug, but also facilitate significant modification of release.

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Characterization of bentonites for pharmaceutical application in Korea

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Keywords: bentonites, pharmaceutical, mineralogy, heavy metals, Korean Pharmacopoeia

Korea Institute of Geoscience and Mineral Resources(KIGAM) recently implemented a program to assess the potentiality and utilization of domestic clay minerals for food and drug industries. The primarily targeting clay mineral is the bentonite for the pharmaceutical application in the preliminary stage of research. Bentonites and zeolites are widely distributed in the Tertiary volcanic complex in the Gampo area, east-southern part of the Korean peninsula. It is assumed that bentonite mineralization is structurally and locally controlled by the adjacent fault system.

Geological modelling of bentonites-bearing tuffaceous rock units was done for the identification of field occurrence of bentonite deposits. Specifically, heavy metal contents(including Pb and As) by ICP-MS, pH, microbial limit, particle size distribution, fineness of powder, loss on drying, gel formation, swelling power were analysed for the characterization of bentonites in the pharmaceutical applications test which is described in the Korean Pharmacopoeia [1]. The mineral components of bentonitic tuffs from the study area are Ca-montmorillonite, quartz, opal-CT, anorthoclase, cristobalite and so on revealed by x-ray diffraction analysis, FT-IR and electron microscopic observations. It is notable that opal-CT is associated in most of bentonite ores in this area, whereas commercial bentonites for gastrointestinal drugs have no or trace amounts of opal-CT. Therefore it is needed to purify the bentonites using ultrasonic dispersion and ultra-fine particle separation for the gastrointestinal system usage.

The authors present preliminary results of field survey for the understanding geologic structure and high quality bentonite mineralization. Mineralogical and geochemical characterization results of bentonites ores and purified bentonites are also to be presented for the application of pharmaceutical usage.

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Mineral carbonation process using ca type vermiculite

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Keywords: cationic exchange, CO_2, $CaCO_3$, XRD, SEM

Increasing carbon dioxide concentration due to anthropogenic emission is emerging as a serious problem leading to global warming. One way to reduce CO_2 emission into the atmosphere is to sequestrate CO_2 by storing it permanently either under geologic media like sedimentary basins or as mineral carbonates [1].

Especially, mineral carbonation has recently been much focused on because gaseous CO_2 can be converted into chemically stable carbonate minerals with a spontaneous and exothermic reaction. The carbonation process is often designed by mimicking a natural weathering reaction between CO_2 and silicate minerals containing alkaline earth metals

Here, we attempt to mineralize gaseous CO_2 into calcium carbonates at different reaction temperatures by supplying calcium ions from vermiculites using the cationic exchange method. The characteristics of calcium carbonate powders were investigated by X-ray diffraction (XRD) and scanning electron microscopy (SEM).

We were able to successively mineralize gaseous CO_2 into calcium carbonate polymorphs (calcite and vaterite) by supplying calcium ions from vermiculite using the cationic exchange reaction. This new method is expected to advance the economic efficiency of the mineral carbonation process for CO_2 sequestration.

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The origin of industrial fluorine emission of a Hungarian brick factory

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Keywords: fluorine, emission, brick industry, Kiscell Clay

Due to its health hazard, the fluoride emission of certain industrial activities (e.g. aluminium processing, brick and ceramic industry) is regulated, the current allowed emission limit in several European countries is 10 mg/m^3 HF.

We studied a brickyard where, unlike in other Hungarian brick works, fluoride emission had been above the threshold limit before a fluorine absorber unit was installed years ago. Our previous results (Ringer et al., in prep.) excluded all types of raw and technological materials, except of the locally quarried clay (Oligocene Kiscell Clay Formation) itself as the source of fluorine.

The aim of our current study is to determine whether the high fluorine emission is caused by specific technological or local geological factors.

The determination of fluoride content was made using ion-selective electrode technique. In order to study the release of fluorine from the clay firing tests were carried out. During these tests we took into account the following factors: the firing temperature and time, the heating rate and the calcite content [1; 2].

There were no data on fluorine content published for Kiscell Clay Formation. In order to provide data for comparison we studied clay samples also from other known outcrops of that formation located in a distance of ten-hundred km from the originally studied factory.

Our data indicate that local geological factors (e.g. volcanic activity during the deposition of clay) may result in a special geochemical overprint of the Kiscell Clay used.

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Laboratory bioextraction of Fe and Si from clay and diatom rich samples by lake baikal assemblages

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Keywords: clay, diatom, iron, bacteria, bioleaching

The differentiation of smectite species in Lake Baikal is formed through biotransformation of smectite after extraction of Fe and through bioformation of amorphous aluminosilicate phases and vivianite during diatom dissolution by psychrophilic bacteria in the cold bottom/pore water. These aluminosilicate phases could be the nucleus for clay minerals neoformation. Symbiosis of bacteria and diatoms living in sediment/water interface are dependent on the abundance of organic carbon and silicic acid, supplied by seasonal biochemical weathering of silicate minerals and input of organic carbon from rivers, and catchment by vegetation and frustules of diatoms [1]. It could stimulate activity of psychrophilic bacteria in extraction of Fe and Si from sediments of Lake Baikal during the past. The objective of the laboratory test was to investigate Fe and Si mobilization from the sediment during the different temperature promoted by the glucose additions. The cultures were incubated under static conditions at 4 °C or 18±2 °C for a total of 105 days. Experimental bacterial extraction of Fe and Si from sediment at 4 ºC showed a possibility of clay biotransformation and neoformation in sediment/water interface of Lake Baikal. Iron was more sensitive than Si during extraction of the solution by bacteria depending on temperature and organic matter presence.

In clay rich sample, the highest total Fe concentration was 14.96 μmol Fe/g and 42.92 μmol Fe/g at 4 ºC and 18 ºC respectively, during 105 days of bioleaching. Natural control of clay rich sample, without addition of bacteria and glucose, contained 0.927 μmol Fe/g of the highest total Fe concentration at 4º C.

In diatom rich sample, the highest total Fe concentration was 4.2 μmol Fe/g and 14.32 μmol Fe/g at 4 ºC and 18 ºC respectively, during 105 days of bioleaching. Natural control of diatom rich sample, without addition of bacteria and glucose, contained 2.02 μmol Fe/g of the highest total Fe concentration at 4 ºC because of the destruction of the organic matrix which protects diatom frustules.

X-ray analyses and light microscopy showed the formation of amorphous aluminosilicate mineral phases that was connected with the high production of exopolysaccharides during biodestruction of diatoms. At the end of incubation time, crystals of vivianite were also detected.

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Study of peat-clay-mineral medicinal water systems for use in balneotherapy

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Keywords: peat, peloids, balneotherapy, semisolid dosage forms, rheological properties

Peloids are natural medicinal products of semisolid consistency, resulting from the interposition of organic (peats) or inorganic (muds) solids in medicinal mineral water [1]. Both types of peloids are administered topically as local applications (muds) or baths (muds and peats), for the treatment or prevention of certain pathologies. The presence of special clay minerals in muds produce systems with rheological properties that allow local application.

With these premises, a peat, supplied by the company "Turbera del Agia" (Padul, Granada, Spain) (TS) and a pharmaceutical grade clay (Pharmasorb colloidal©, (P)) were mixed in different proportions with mineral medicinal water from the thermal spring of Graena (Granada, Spain) and the resultant rheological properties were determined. The relative solid/liquid ratio was maintained to 25/75 w/w.

TS was mainly composed of organic materials with a minor proportion (<5% w/w) of minerals, including gypsum, mica and quartz (Fig. 1). P was mainly composed of palygorskite (>90 % w/w) [2]. The systems showed typical non-Newtonian viscoplastic flow curves with apparent viscosity and thyxotropy values increasing with relative clay concentration (Table I). Accordingly, samples TS-P3 and TS-P4 showed apparent viscosities adequate for local topical application.

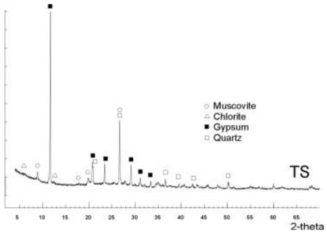

Fig. 1: XRD pattern of peat.

Table I: Apparent viscosities values (250 s^{-1}, 25ºC) of the suspensions (mean values ± s.d., n=6).

Sample	% TS	% P	Viscosity (Pa s)
TS-P1	20	5	0.006 ± 0.0018
TS-P2	15	10	0.027 ± 0.0012
TS-P3	10	15	0.058 ± 0.0005
TS-P4	5	20	0.069 ± 0.0010

Acknowledgements: This study was supported by the Andalusian grants RNM-1897 and CTS-946.

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Molecular modeling of praziquantel-montmorillonite interaction

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Keywords: montmorillonite, praziquantel, modelling, spectroscopic properties

Veegum HS® is a pharmaceutical grade montmorillonite. This solid is a natural clay mineral which has a laminar structure with one octahedral sheet and two tetrahedral sheets. Between both layers there is an interlayer space, where organic molecules are able to be adsorbed [1]. Because of that, these clay minerals are important and common excipients in pharmaceutical products [2]. Clay minerals, like montmorillonite, can modify drug bioavailability, solubility or drug release [3]. Praziquantel (PZQ), (RS)-2-(cyclohexylcarbonyl)-1,2,3,6,7,11b-hexahydro-4H-pyrazino[2,1a] isoquinolin-4-one, is the drug of choice for an extended parasitic disease, Schistosomiasis. PZQ has low water solubility and its preparation is a racemic mixture, whose R-enantiomer is the only compound which possesses antihelmintic activity. As a result, it is important to know his spectroscopic and other chemical-physical properties and to improve its bioavailability. The aim of this work was carrying out a theoretical-experimental study of adsorption of PZQ in the interlayer of montmorillonite. The molecular and crystal structure of enantiomers and racemic mixtures of PZQ and phyllosilicate were modeled with atomistic calculations based on empirical interatomic potentials and quantum-mechanic methods explaining the experimental behavior and infrared frequencies were reproduced interpreting and assigning new bands of PZQ.

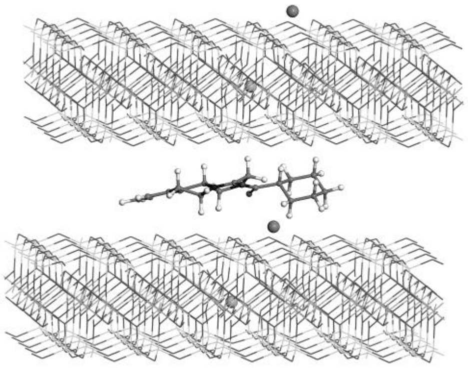
Fig.: Optimized molecular structure of PZQ intercalated in montmorillonite.

Acknowledgements: This study was supported by the Andalusian grants RNM-1897 and CTS-946.

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Development of colored geopolymers using Maya Blue-based pigments

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Keywords: geopolymers, sepiolite, Maya Blue pigments, dyes, UV stability

Geopolymers are inorganic amorphous silicon-based polymers materials of increasing scientific and industrial interest especially for engineering applications. Diverse types of clay minerals are currently explored as source in the production of such materials which are prepared at very high pH media. For certain applications it would be interesting to produce colored geopolymers, however the direct incorporation of organic dyes was not easy as they may become degraded under the extreme basic conditions used during the synthesis. In this communication, we will report a new approach that uses the concept of ancient Maya Blue pigment to encapsulate diverse organic dyes in the structural tunnels of the fibrous clay to be protected once incorporate as a pigment during the geopolymer formation. Sepiolite is relatively stable in basic media and dyes such as methylene blue (MB) and methyl red (MR) present a convenient size to be adsorbed in the clay inside its structural nanopores. In this way, when the geopolymer is formed the encapsulated organic dye is preserved and the final products show colors that made fade a little with the evolution of the polymerization reaction but remain still persistent with time once the reaction ends. The resulting colored geopolymers are highly stable to treatments with hydrogen peroxide, UV irradiation or in acid conditions. This preliminary study [1] is a first example that may open way to other approaches for functionalizing inorganic binder materials with organic elements sensitive to thermal treatments used in conventional ceramic processing.

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Influence of humic acid and bacteria on sorption properties of quartz sand

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Keywords: quartz sand, bacteria, humic acid, copper, sorption

In the present work, the abilities of quartz sand to remove Cu(II) ions from the aqueous solutions were studied. Addition of humic acid and bacteria were investigated to enhance the sorption properties of quartz sand sample. The effect of initial metal ion concentration on adsorption of copper ions was also investigated. When humic acid adsorbed onto the surface of microbes, can have an important effects on bacterial activity [1]. Addition of humic acid and bacteria increased the sorption capacity of quartz sand. All experiments were carried out by batch adsorption technique at concentration range 10 - 50 mg Cu/l. Bacterial suspension was prepared with the concentration of bacteria 2 g/l (wet weight). The Langmuir linearized model was applied to interpret the experimental data, see fig.1(part b).

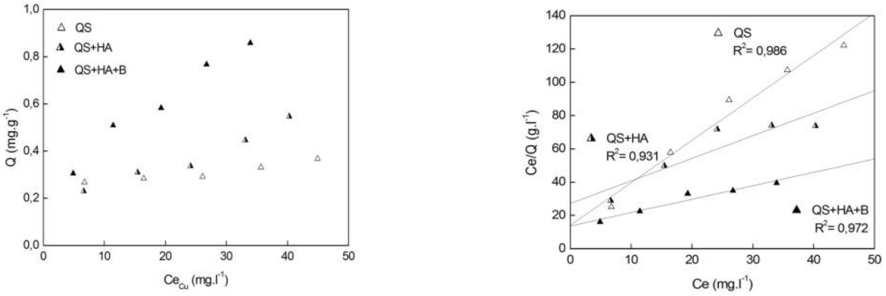

Fig. 1

a.) Effect of initial ion concentration on Cu(II) adsorption

b.) The Linearized Langmuir model on Cu(II) adsorption

The adsorption of copper on samples increased with the increasing initial copper ion concentration especially for quartz sand with addition both humic acid and bacteria, but the equilibrium was not established at this concentration range, see fig.1(part a). Based on calculated values of sorption capacities it can be concluded that quartz sand samples were effective in Cu(II) ions removal in this order: quartz sand < quartz sand + humic acid < quartz sand + humic acid + bacteria. We can conclude that addition of humic acid and bacteria increased the sorption capacity of quartz sand. Additional adsorption experiments are needed to evaluate the influence of humic acid and bacteria onto sorption properties of quartz sand at higher concentration range and moreover the possibility of using this material in column studies.

Acknowledgements: This work was supported by the project VEGA 2/0049/15.

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The effects of short-time interaction of potassium- and sodium chloride with Na-montmorillonite and illite-smectite mixed-layered clay minerals

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Keywords: Na-montmorillonite, illite-smectite, electrolytes, mineralogical changes

Potassium and sodium electrolytes have found a wide use in petroleum engineering as inhibitive components of water-based drilling fluids. Their role is to reduce the extent of borehole erosion associated with the swelling and dispersion of smectites as a result of natural cation exchange. These drilling fluids can penetrate into the rock especially in case of porous sandstone. When coming in contact with cuttings the penetration is more likely. The question was what types of changes are induced in clay minerals by these drilling fluids, and when the analyses of those clays are performed in laboratory the identified clays are the ones present in the formation or the ones which are modified by cation exchange or phase transformations.

Oriented samples were prepared on glass slide and measured by X-ray powder diffraction (XRPD) in air-dried state, after ethylene-glycol solvation and after heating at at 550 °C. In order to identify the changes induced by contact of NaCl and KCl in clay minerals, mixtures of Na-montmorillonite (SWy-2) and illite-smectite (ISCz-1) with 5 and 10 wt% of analytical grade of KCl and NaCl were prepared at room temperature. To approach the temperature conditions at depth where smectite persists, another series of oriented samples with similar mixtures of clays were made in two steps: a) the dry samples were mixed with deionized water and kept for four hours at 100 °C in an open pot; b) the dried heat-treated samples were mixed with deionized water for preparation of oriented slides.

The X-ray powder diffraction data indicate a systematic migration toward lower *d*-values of the *d*(001) of Na-montmorillonite in air-dried state, suggesting a slight decrease in expandability in contact with NaCl and a more intense decrease with KCl mixtures. The heat-treated NaCl mixtures showed no shift and the *d*(001) shift of KCl mixtures was also smaller than in the unheated ones. A decrease of the 001 intensity was also observed with increased effect in KCl mixtures. After glycolation in the mixtures with 10 % NaCl and 10% KCl a slight shift toward lower values of *d*(001) was observed whilst in the 100°C treated glycolated samples a migration toward higher *d*-values was present. These results imply that the monovalent cations affect the swelling pattern of Na-montmorillonite and these changes may be linked to surface charge changes and interlayer cation incorporation. Illite-smectite 001 reflection was also affected by addition of NaCl and KCl and the 003 reflection was suppressed. The effect of KCl was more pronounced in these samples too.

The results indicate slight mineralogical changes during interaction with electrolyte fluids, but the main clay types identification is no longer affected in the given range of analytical conditions however special care must be taken in defining the smectite content in illite-smectite mixed-layered clays.

The concept of uncompactable porosity

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Keywords: bentonites, porosity, dry density, uncompactable pores

Compacted bentonites are used for sealing purposes. To characterize the swelling potential of bentonites, dry density – swelling pressure relations are often presented. Kaufhold et al. [1], however, showed a significant variation of published dry density – swelling pressure relations. These differences could at least partly be explained by the “concept of uncompactable porosity”. In 2013 Kaufhold et al. [2] compared the results of compaction on the resulting dry density of 38 different bentonites. The reasons for the differences were depending on water content, CEC, and porosity. In this context meso- and microporosity was found to play a special role because these two types of pores are uncompactable [3] – at least in short term laboratory applications. Kaufhold et al. [4] found a decrease of the pore peak maximum with increasing thermal maturity of potential German gas shales. Millions of years combined with enormous compaction are obviously able to further reduce the average distance of clay particles but that does not apply to laboratory or technical conditions. The 38 bentonites applied significantly differed with respect to their primary porosity (i.e. before compaction [5]). Bentonites are commonly dominated by micro- and macroporosity, but a few bentonites with significant mesoporosity were found as well. This became important again as the swelling pressure of the same bentonites was tested. For these tests the dry density had to be similar to be able to compare the bentonites. However, those samples with either meso- and microporosity needed much heavier load to reach the same dry density as other bentonites. This can be explained by the “concept of uncompactable porosity”: Samples with uncompactable porosity have a more heterogenous density distribution after compaction. The uncompactable pores are low density regions but all samples had the same total dry density. To reach this dry density, materials with uncompactable pores need to have areas with larger density to compensate for the low density uncompactable pores. In these areas particles are closer to each other than in the other samples. They, therefore, can exert a larger swelling pressure when hydrated as compared to those samples with low uncompactable porosity. In conclusion, the different portion of uncompactable porosity in different bentonites can explain differences of properties which are commonly related to the dry density.

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Ball clays of company kaolin AD, Bulgaria for ceramic applications

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Keywords: ball clay, ceramics, characterization, technological properties, Kaolin AD

This study is focused on the mineralogical, chemical, physical and technological properties of several ceramic clays (two Bulgarian types and two Serbian types) produced by company Kaolin AD, Bulgaria. The X-ray powder diffraction patterns are performed to analyze the clay and non-clay minerals and the X-ray fluorescence method is used for elemental analysis. The data collected from these techniques show that the clay minerals are kaolinite, hydromicas/micas, smectite and chlorite and the non-clays minerals consist mainly of quartz and feldspars. The results from the chemical analysis of the clay samples show that the most important components are SiO_2 (59.0-66.4 %) and Al_2O_3 (21.0-28.8 %), since they have a conclusive influence on the refractoriness and strength of the final product. Kaolin AD clays are typically ball clays ($SiO_2/Al_2O_3 = 1.8\text{-}3.1$) with different content of Fe_2O_3 (1.62-5.07 %). They are defined as medium to high plastic clays with different ranges of sintering temperatures, which makes them suitable for the production of various kinds of materials in the ceramic industry.

Iron minerals removal from quartz sands by microbial leaching

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Keywords: quartz sands, bioleaching, iron removal, heterotrophic bacteria

Quartz sands is the most important non – metallic raw material that is used as the ingredient in glass, foundry casting, ceramics, filters, plastic and many other applications and the purification of quartz sands is extremely important for many industries.

Microbiological leaching of silicate industrial minerals is a conversion of undesirable insoluble iron minerals into a soluble form by metabolic activities or products of microorganisms. These microorganisms need carbon as an energy source, which involves biological metabolism such as fermentation; the products of organic acids act on the dissolution of insoluble iron oxides which is accelerated by chelation accompanied with iron enzymatic reduction [1].

Naturally occurring quartz sands contains oxide iron minerals as coatings on grains or impregnations in the quartz particles with different intensity. The extent of iron coatings removal from quartz sands depended on way and conditions of bioleaching. The composition of medium, pH, and concentration of oxygen, presence of active bacterial species, granularity and bounds of iron minerals as well as the mineralogical composition of the quartz sands are the important factors which effect process of bioleaching.

2 months bioleaching (2.BL) removed 32.5 % Fe_2O_3 from industrially washed quartz sands (CH2) because iron concentration CH2 before of bioleaching was 0.34 % Fe_2O_3 and after bioleaching 0.23% Fe_2O_3. The first magnetic separation (1.MS) decreased up to 68% Fe_2O_3 from CH2 and the second magnetic separation (2.MS) decreased up to 82% Fe_2O_3 and quartz sands contains 0.06% Fe_2O_3 after combination of bioleaching and magnetic separation (Fig.1).

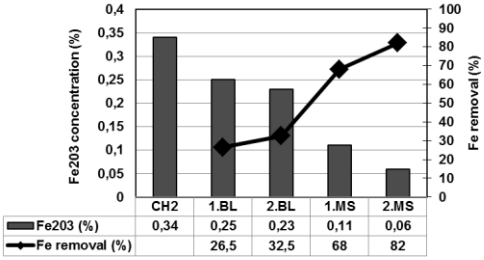

Fig. 1: The progress of iron concentration and iron removal after 1 month bioleaching (1.BL), 2 months bioleaching (2.BL), first laboratory magnetic separation (1.MS) and second laboratory magnetic separation (2.MS) in CH2 sample.

Acknowledgements: This work was supported by PROJECTO CORFO I+D Cod. 13IDL2-23505 and by VEGA Agency under the contract No. 2/0049/15.

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Clay bound water measurements for oil- and -gas bearing shales

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Key words**:** CBW, water sorption isotherms, shale

Ineffective porosity in shales is predominantly controlled by the amount of clay minerals and associated clay bound water (CBW). Depending on the ambient conditions, the quantity of water adsorbed on clay surfaces varies from one to three water layer equivalents [1]. In this study we try to estimate a range of CBW using water sorption measurements performed on sample sets differing by clay minerals and organic matter content and thermal maturation.

To estimate the range of CBW, isometric rock chips (~3g), were pre-dried at 200˚C (16 h) and equilibrated at ~40% RH (CBW_{min}) for 48h and heated once again to 200˚C (25 min) to obtained a mass of adsorbed water. The same procedure was applied for ~80% RH (CBW_{max}). In order to validate the assumption of CBW_{min} and CBW_{max}, water sorption isotherms on powdered samples were also obtained.

The quantity of adsorbed water in samples equilibrated at 40% and 80% RH show good correspondence with water sorption isotherms (WSIs), determined on the same sample depth equivalents. WSIs were used to calculate the critical RH value at which a statistical single water layer (1W) and double water layer (2W) adsorption is achieved [2]. A calculation based on WSIs showed that 1W was complete at the RH range of 20-30% while 2W equivalent - at RH 50-60%. The assumed CBW_{min} conditions (40% RH) ranged in-between 1W and 2W layers. All WSI showed a rapid mass gain at an RH of 76% to84 % demonstrating that RH ~80% defines reasonably assumed arbitrary boundary between an adsorption-dominated system and a capillary condensation-dominated system.

The results of CBWs were combined with porosity values from Dual Liquid Porosimetry technique [3] to show the contribution of ineffective porosity in total porosity. For samples with low porosity values and substantial content of expandability clay mineral, CBW can constitute almost 100% of total porosity. The results demonstrated that equilibration of chip samples at 40% and 80% RH yields a simple approximate solution for the evaluation of the CBWs which can be representative for formation conditions characterized by different water saturation.

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Surface interaction sites of Ni adsorption on montmorillonite

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Keywords: heavy metal cation, nickel, montmorillonite, surface sites, adsorption

Clay minerals, due to its low cost, high cation exchange and ubiquitous presence in most soils, have been widely used as geological barrier to immobilize metal cations, arising from industrial or domestic waste. Particularly, for Ni^{2+} adsorption on raw montmorillonite (Mt) the interlayer sites were assigned as the main surface adsorption sites involved in the Ca-montmorillonite (from pH 5 and 6.4) [1] and two types of complexes were found for raw Mt: bidentate variable charge surface hydroxyl sites and bidentate permanent charge exchange sites [2].

The aim of this study was to analyze the pH and solid/liquid relation influence in the Ni^{2+} adsorption on Mt and evaluate the surface sites involved trough analysis of inner and outer surface Mt. To attain this objective a raw Argentine Mt was utilized as adsorbent (isoelectric point at pH = 2.7), with Ni C_o = 50 ppm (from $NiSO_4$ solution), pH analyzed were 2, 4 and 6, and solid/liquid relations = 1, 2 and 3 mg/ml. XRD analysis were utilized to determine the Ni entrance in the inner surface (interlayer) and zeta (ζ) potential measurements to evaluate the outer surface interactions.

The Ni adsorption increased from 7 to 24 mg/g with pH increase from 2 to 6 and decreased to 57 and 38 % respect of maximum adsorption at pH 2 and pH 6, respectively with the increase of solid/liquid relations from 1 to 3. The Ni^{2+} interlayer entrance was favored at pH = 2, by displacing the raw Na, with a 001 reflection peak area relation Ni/Na = 12.75, while for pH 6 the same relation decrease to 1.86.

Similar shape and values of ζ potential curves were found for Mt and Ni^{2+} adsorbed on Mt at pH = 2 samples. Whilst the decrease on negative surface charge of Ni^{2+} adsorbed on Mt at pH = 6 respects to raw Mt sample was indicative of the Ni adsorption on the outer surface by interaction with the variable charge (or edge) surface hydroxyl sites.

Those results indicated an important interaction of Ni^{2+}, and replacement of Na^+ raw cations, with the inner or permanent charge exchange sites at pH = 2, while a more important Ni^{2+} interaction with the outer or variable charge surface hydroxyl sites happened at pH = 6.

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Clay-size fraction separation by coagulation from sodium tripolyphosphate stabilized illite clay dispersion

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Keywords: illite clay, coagulation, purification

Illites are the most common and abundant clay minerals on earth. In Latvia, clays are mainly used for different kinds of building ceramics and cement, as well as decorative uses, art, and household ceramics production. This is mainly due to the fact that illite clay minerals in nature are always mixed with other minerals such as quartz, carbonates, hematite, etc. These impurities, directly reduce the commercial value and range of application of illite clays. Therefore, purified clay minerals might find a new innovative and perspective scope of application such as polymer nanocomposites.

Clay-size fraction separation method [1] is based on dispersing illite clays in sodium tripolyphosphate solution, non-clay particles sedimentation and clay-size fraction coagulation with acetone azine hydrochloride (coagulant is obtained by reacting acetone with hydrazine dihydrochloride). Using this method it is impossible to get rid of the iron oxides. Therefore, iron oxides were reduced by the dithionite-citrate system buffered with sodium bicarbonate.

In these studies Devonian clay samples were used from Kuprava deposit in Latvia. The most efficient dispersing of clay particles in polyphosphate solution were obtained if the clay samples were left to swell for 24 hours, and then treated in an ultrasonic bath. It is also commercially not efficient to repeat clay-size fraction separation from the same clay sample, because, in the first separation, it is possible to separate 57% of clay minerals from the total mass of the clay, but in the other five separations together only 9%. The proposed method allows to get rid of calcite, dolomite minerals impurities and significantly reduce the quartz content in the sample. The cation exchange capacity (CEC) of the clay samples determined by methylene blue method increased from 13 meq/100g for raw illite clay to 28 meq/100g for the illite clay-size fraction.

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Clay mineralogy in some agricultural soils from southwestern Pampean region, Argentina

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Keywords: soil clay minerals, loess, weathering

The parent material of Pampean soils is constituted by loess and loess-like deposits. According to the traditional model, the origin of these sediments is found in the Andes and in northern Patagonia. These materials are considered mineralogically homogeneous, especially in the clay fraction composition: illite is dominant and in many instances the only clay mineral. Mineralogical differences between zonal soils are considered to be of pedological origin due to clay neoformation and illuviation. Following a different approach diverse evidences point out the existence of different soil parent materials, and suggest that the area has been influenced by different sources of sediments [1]. Both approaches contribute to clarify the origin and composition of Pampean soils.

In order to study and characterise clay mineral composition in these soils four agricultural surface soil subgroups (0–12 cm depth), representing the Ap horizon, were collected from the southwest of the Province of Buenos Aires in the Pampean region of Argentina. Soils were classified as three Mollisols and one Entisol: Typic Argiudoll (A1), Pachic Argiudoll (A2), Entic Haplustoll (A3), and Typic Ustipsament (A4). Soil samples were air-dried at room temperature, ground, and sieved through a 2-mm stainless steel sieve to obtain the <2 mm size fraction. The clay fraction (<2 µm) was obtained by sedimentation techniques using Stoke's law.

X-ray powder diffraction (XRD) studies were performed on each soil clay fraction, using CuKα (1.5406 Å) radiation (45 kV, 35 mA) on a Philips X-Pert PW 3710 diffractometer in a range of $2^{\circ}<2\theta<70^{\circ}$. The diffractometer was equipped with a 1º divergence slit, a 0.1-mm receiving slit, and a graphite monochromator. From these patterns quartz (4.27, 3.34 Å) and Na-rich feldspars (6.40, 4.05, 3.24, 3.21 Å) hematite and goethite were identified. For clay mineral analysis additional patterns were obtained in the $2\theta=2$–35° range using CuKα radiation, a 0.01º 2θ step, and a counting time of 30s per 2θ increment. The untreated clay fraction and residues from Mg-saturation followed by glycerol-solvatation, and K-saturation followed by heating to 550 ºC were examined, using the same equipment as above, at 36 kV, 18 mA, with a Ni filter. These patterns showed the presence of poorly crystalline materials, such as expandable clays of the smectite group and irregular and no quantitative amounts of interstratified illite-smectite (10.00-15.06 Å). Also, illite (10.00 Å) was identified. These results showed the presence of phyllosilicates related to the parent materials. Weathering processes of moderate intensity from illite to irregularly interstratified illite-smectite were observed as well. For the four soil samples clay mineralogy was quite similar. In addition, these results supported the traditionally assumed homogeneity of Pampean soil clay minerals.

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Effect of soil properties on the herbicide mesotrione adsorption

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Keywords: mesotrione, adsorption, clay minerals, soil organic matter, 13C NMR

Mesotrione, a member of the triketone family, is a recent selective herbicide developed for use in maize culture. The aim of this study was to estimate the effect of mineral and organic soil constituents on adsorption/desorption of mesotrione and its main metabolite – AMBA. Four soils with a different genesis have been chosen and investigated in detail: Chernozem (Russia), Luvisol (Russia), Red Soil (Abkhazia), Vertisol (France) in order to examine a wide as possible range of soil parameters which could affect the behavior of this weakly acidic herbicide (pKa = 3.12). The physico-chemical properties of the topsoils studied differ greatly: pH ranges from 5.8 (Red Soil) to 7.9 (Vertisol); CEC 18-73 cmol kg^{-1}. Although the silt fraction prevails in all the soils studied (47-60 %), the clay content (18-33 %) and composition are different: those of Chernozem and Vertisol are dominated by montmorillonite and beidellite, respectively. In Luvisol, the clay fraction contains interstratified illite-smectite, illite, kaolinite and visible amount of fine quartz, and that of Red Soil is smectite and kaolinite dominated with some goethite and fine quartz. Red soil is the richest in bulk and dithionite-citrate-bicarbonate extractable Fe_2O_3 (9.31% and 5.62% respectively). The OC content, ranges from 0.56 (Red Soil) to 2.91 % (Chernozem), is mainly composed of humic acids for Chernozem and Luvisol, and fulvic acids for Red Soil and Vertisol. The ^{13}C NMR data show that OC in all the studied soils is of aliphatic nature with an aromaticity index between 15-30%. The most abundant C- containing functional groups in all the studied soils are *O*-alkyls (up to 56 %).

The adsorption isotherms obtained for mesotrione and AMBA are almost linear and well described by the Freundlich equation. For mesotrione, the lowest K_f was obtained for Chernozem (1.03 $mg*kg^{-1}/mg*L^{-1}$), the highest for Red Soil (3.65 $mg*kg^{-1}/mg*L^{-1}$). The best K_f correlations were obtained with Fe_2O_3, the content of OC in *O*-alkyls (positive) and pH (negative). In case of AMBA, the K_f values for all the soils studied were lower: from 0.67 $mg*kg^{-1}/mg*L^{-1}$ for Vertisol to 2.29 $mg*kg^{-1}/mg* L^{-1}$ for Red Soil. The key parameter involved is Fe_2O_3. Nevertheless with AMBA, the role of pH and *O*-alkyls is less, but the effect of clay content is higher. The one-step desorption experiments show a better retention of mesotrione (up to 77 % desorbed) compared with AMBA (up to 85 % desorbed). AMBA presents a higher mobility, but mesotrione is also mobile [1].

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Influence of clay and iron mineralogy on copper sorption by meadow soils

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Keywords: copper adsorption, beidellitic clay minerals, soil iron minerals, analytical transmission electron microscopy, meadow soils

The role of clay and iron mineral composition of meadow soils in potentially toxic metal immobilization were investigated by batch Cu adsorption experiment and analytical transmission electron microscopy. Iron minerals such as goethite in a periodically aerated iron accumulation horizon and vivianite in a reductive soil environment were determined by XRD. Based on detailed clay mineralogical studies soil samples contain low and high-charge smectites as K saturation was followed by 15 Å peak shift to a broad 12-10 Å reflection. Swelling clay minerals are beidellitic and montmorillonitic according to Green-Kelly test. The maximum copper adsorption was 9.7 mg/kg for the iron accumulation horizon, 13.4 mg/kg for the soil sample with vivianite and 5.7 mg/kg for the gleyic horizon without XRD detectable iron minerals. According to ATEM results highest Cu uptake was observed by iron phosphate particles, whereas discrete iron (oxy)hydroxide and clay mineral phases from oxidized or reductive soil sample adsorbed less amount of Cu.

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Soil microaggregate formation by mineral-mineral interactions

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Keywords: microaggregate formation, soil minerals, surface charge, particle sizing, steric stabilisation

Aggregation in soils is a multi-cause process and the resulting microstructure has implications for many important soil functions. Formation of microaggregates, i.e., small structural units typically composed of clay minerals, secondary metal oxides, and organic matter, is thought to be primarily controlled by charge differences. Submicron scale particles (<20 μm) deriving from mineral-mineral interactions can be building units for larger microaggregates [1].

Here, we determined the effect of mineralogical composition and surface charge on the microaggregation by preparing mixed sequences of the model substances montmorillonite, fine grained muscovite, synthetic goethite, and freshly precipitated poorly crystalline Al and Fe oxides. Experiments were conducted for 40 min at pH 6 using particle concentrations of 5-500 mg l^{-1}. Surface charge was determined by zeta potential (ζ) measurements. After dispersion by ultrasonic treatment, particle sizes were measured by dynamic light scattering.

The particle concentration in suspension had marked effects on aggregate size. The lowest goethite concentration produced largest aggregates with effective diameters of 0.4 μm while at maximal concentrations effective diameters were smaller with 0.32 μm. The same was observed for negatively charged muscovite and is assigned to steric repulsion of particles [2], occurring at higher concentrations only. In mixtures of negatively charged muscovite and positively charged goethite strong aggregation (effective diameters at ~4 μm) was observed only at an amendment of 2 % goethite. Most probably this mixing ratio allowed optimum screening of the negative surface charge of muscovite. At mixing ratios unfavorable for aggregate growth, sizes of particles kept typical small with diameters of only up to 0.5 μm.

Particle sizes of Al oxides in the initial stages of formation were markedly smaller than those of Fe oxides, and sizes of fresh Fe oxide precipitates depended strongly on the initial Fe concentration. At concentrations ≤0.5 mM effective diameters were about 0.1 μm whereas they increased to about 10 μm in the Fe concentration range of 1-5 mM. Slight decreases of sizes over time indicated age-dependent morphology, most probably affected by ordering and polycondensation reactions. Our data suggest that besides surface charge and mixing ratio of minerals also particle concentration is a crucial factors for microaggregate formation.

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Palygorskite and sepiolite genesis in Barzaman Formation, United Arab Emirates

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Keywords: Dubai, mineralogy, palygorskite, neoformation, pedogenesis

The origin of the palygorskite could be diagenetic from the transformation of the pre-existent mineral content or by neoformation from solution under specific conditions. In our case mineralogical study on material taken from trenches and drill was undertaken on samples from a clayey layers liying in the Barzaman Formation in western UAE. This Formation was deposited as a series of fluvial sediment sequences along the western margin of the Ophiolitic Hajar Mountains of Oman and UAE during Miocene to Pliocene under humid climate. These sequences are dominated by variably cemented conglomerates characterized by the presence of ultramafic clasts. The aim of the study was the identification, quantification and understanding of the occurrence and genesis of palygorskite and sepiolite.

X-ray diffraction (XRD) on bulk and clay fraction (<2 µm), petrographic thin sections and Scanning Electron Microscopy (SEM), coupled with Energy Dispersive X-Ray Spectroscopy (EDS) helped to identify the conditions prevailing during the pedogenesis. This last, occurred in the deeper level in well cemented conglomerate which constitutes the hard crust. The post depositional process of erosion started in marine phreatic or vadose zones attested by the neoformation of serpentine from the weathering of olivine. The neoformation of palygoskite, sepiolite and halite occurred under evaporitic conditions (sebkha environment) at the upper levels in calcareous silty clay and calcareous siltstone facies. The study also highlighted associated minerals formed during the whole process under different condition.

Clay minerals in the Zmajevac loess-paleosol section, Baranja (Eastern Croatia)

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Keywords: loess, paleosol, clay minerals, X-ray diffraction, quaternary

As part of an ongoing multi-proxy study of the Zmajevac loess-paleosol section in Baranja in Eastern Croatia, with the purpose to reconstruct the palaeoenvironment and understand the palaeoclimate in the investigated area, detailed clay mineralogical analyses were performed using the X-ray powder diffraction (XRPD). The investigated loess-paleosol section is located on the south-western slope of the Bansko Brdo hill near the village of Zmajevac. Bansko Brdo represents an asymmetric tectonic horst built up of Miocene age basalt-andesite and volcanoclastic breccias covered with Quaternary loess-paleosol deposits [1, 2].

About 30 m thick Zmajevac section consists of six loess horizons, five paleosols and laminated alluvial sediment. Based on the infrared stimulated luminescence (IRSL) dating results of loess from Zmajevac and surrounding area (e.g. [2, 3, 4]), the Zmajevac loess-paleosol section represents a detailed Penultimate and Last Glacial sedimentary record.

XRPD patterns were recorded on random mounts of bulk samples and oriented mounts of the <2 μm fraction. Oriented mounts of the <2 μm fraction were record after the following treatments: a) air drying, b) saturation with K^+ and Mg^{2+} c) ethylene-glycol solvation, d) glycerol solvation, e) heating to 400°C and 550°C. The main mineral components of the loess-paleosol are quartz, illite/muscovite, chlorite and smectite. Mixed layer illite-smectite, plagioclase, carbonate (calcite and dolomite) and kaolinite are present in a lesser quantity. In some samples negligible amount of amphiboles are present. Such mineralogical content is typical for loess. A significant increase of smectite content below the 9 m depth of the profile is observed. According to the provenance analyses based on heavy minerals associations of the silty fraction, the main sources of the material were predominantly located in the Alpine region and subordinately the Dinaride Ophiolite Zone in Bosnia [5]. A greater amount of smectite in the older horizons of loess may indicate a stronger input of local volcanic rocks during that period.

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Nanostructural changes in montmorillonite upon cyclic wetting-and-drying: An electron diffraction study

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Keywords: montmorillonite, energy filtered TEM, electron diffraction, wetting-and-drying, nanoparticles

Montmorillonite is one of the main inorganic soil components, its physico-chemical properties have a key role in the evolution of the soil, its quality and agricultural value. Under nowadays climatic conditions in Hungary, large areas of cultivated land use to be drowned by water yearly which is followed by periods of drought. These inland inundations are modeled in laboratory by cycling wetting-and-drying of standard montmorillonite minerals (SWy, Istenmezeje, SAz) with the aim to reveal nanostructural changes that might be significant in soils on the timescale of several years.

Transmission electron microscopy was applied to characterize the morphology, particle thickness and relative orientation of the montmorillonite particles before and after more than 100 wetting-and-drying cycles. According to correlated thickness measurements using log-ratio method and electron diffraction analysis we observed that the average particle thickness decreases under wetting-and-drying conditions reaching a single TOT layer thickness in case of SWy which means an increase of the specific surface. This is probably due to the low layer charge of this montmorillonite.

The turbostratic character decreased after wetting-and-drying and the intensity distribution of the individual spot-like diffraction patterns was analysed. The dominant 4.5 Å and 1.5 Å reflections were interpreted in terms of particle orientation with respect to the electron beam and vacancy distribution [1] inside the individual particles.

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Weathering of glauconite: a case study from the Paleogene regolith cropping out in Zabierzów (Poland)

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Keywords: glauconite, goethite, weathering, XRD, Mössbauer spectroscopy

The aim of the present research was to study the weathering of glauconite which took place most likely during Paleogene within regolith developed on Cretaceous glauconite-marls. Samples used in the present study were collected from a profile cropping out in Zabierzów Quarry located in Krakow area, Southern Poland. Unweathered Cretaceous glauconite-marls and the regolith were sampled. Bulk rocks, the separated clay fractions, and the magnetically separated glauconite pellets were analyzed using X-ray diffraction (XRD). Thin sections prepared from bulk rocks were examined using optical microscopy. Mossbauer spectroscopy was used for determination of Fe^{2+}/Fe^{3+} in separated glauconite pellets. Separated fine clays were also analyzed using Fourier transform infrared spectroscopy (FTIRS). Scanning electron microscopy - energy dispersive X-ray spectroscopy (SEM-EDS) was used for observation and analysis of the thin sections and the separated pellets.

XRD analysis of bulk rocks showed presence of carbonates, glauconite, quartz and traces of pyrite and Fe-oxy/hydroxides (hematite and goethite). The regolith material was depleted in carbonates and pyrite, and enriched in glauconite, quartz and Fe-oxy/hydroxides in relation to the unweathered marls. Clay fraction separated from unweathered marls contained glauconite, kaolinite and traces of smectite-rich glauconite-smectite mixed layered minerals. XRD patterns of clay fraction from the lower (greenish horizon) of the regolith showed quite a similar picture with smectite-rich minerals being more abundant. Clay fractions from the upper regolith horizons contained smectite-rich glauconite-smectite, glauconite, kaolinite, and goethite. Concentration of the glauconite-smectite clays, and goethite increased while concentration of glauconite decreased up the profile. Similar trends were observed for separated glauconite pellets with purely glauconitic pellets separated from unweathered marls to pellets containing glauconite and goethite separated from the regolith material.

According to the results obtained, two main weathering processes can be recognized in the Paleogene regolith. Those are: 1. smectitization of glauconite leading to formation of smectite-rich glauconite-smectite minerals, 2. most likely dissolution of glauconite and precipitation of Fe in the form of goethite because of high pH due to the presence of carbonates.

Effect of iron oxyhydroxide removal on the metals' partition at particle level following their sorption in soil

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Keywords: DCB extraction, smectite, goethite, ferrihydrite, phase associations

Associations of iron oxyhydroxides and clay minerals could significantly modify the sorption capacity of the individual soil components. We studied this phenomena using competitive batch Cd, Cu, Pb and Zn sorption experiments carried out on two soil samples with contrasting characteristics before and after the removal of the soil iron oxyhydroxides by dithionite-citrate-bicarbonate (DCB) extraction. The sorption properties of the samples were characterized by sorption curve evaluation, whereas changes in their bulk mineralogy due to metals' sorption by XRD and FTIRS. TEM-EDS analyses were used to study the iron oxyhydroxide-clay mineral particle associations and their metal sorption capacities.

Submicron-sized smectite particles were found to be associated with tiny ferrihydrite and goethite particles in the acidic forest soil, whereas the alkaline meadow soil could be characterized by goethite and smectite particles attached to large carbonate grains. The DCB extraction of iron oxyhydroxides was found to be successful, whereas smectites with high Fe content (up to 10 at%) resisted.

Point chemical analyses carried out on such associations showed that significant metal separation may occur at particle level within the mineral associations observed. This is primarily obvious for Cu and Pb which are preferentially sorbed by iron oxyhydroxides over clay minerals particles. Highest affinity to clay minerals was found for Zn and it may be also characteristic for Cd in the acidic forest soil. However, decrease in available sorption sites and/or alkaline conditions may result in enhanced precipitation for the studied metals, primarily in form of carbonates.

After the removal of the iron oxyhydroxides, a slight re-arrangement was found in the metal partitioning at particle level, although sorbed metal amounts did not showed significant increase on the smectite particles. This can be due to increase in precipitation (as cerussite for Pb) and in sorption on soil organic material (for Cu) after iron oxyhydroxide removal. However, Fe-rich smectites still preferentially adsorb each studied metal over low Fe-smectites and other clay minerals, like illite.

Our results demonstrated the specific role of iron oxyhydroxide-smectite associations in the sorption of potentially toxic metals both in acidic and alkaline soil environment. Direct observation of metals' partition at particle level supports a deeper insight into soil-metal interaction.

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Weathering of glauconite in alkaline soils of temperate climate: a case study from Górniki, eastern Poland

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Keywords: weathering, glauconite, glauconite-smectite, kaolinite

The aim of the presented research was to study the weathering of glauconite in an alkaline soil profile developed on quartz-glauconite sand in Górniki (eastern Poland). Physical and chemical soil properties were determined for the collected samples. Bulk soil material (i.e. <2 mm fraction), separated clay fractions (<2 μm and <0.2 μm), and magnetically separated glauconite pellets were analysed by X-ray diffractometry. The fine clays were also analyzed using Fourier transform infrared spectroscopy. Fe^{2+}/Fe^{3+} ratio was determined for glauconite pellets separated from the soil parent material using Mössbauer spectroscopy. Thin sections prepared from undisturbed soil materials were examined using optical microscopy.

The pH measured in distilled water ranged from 8.6 in the lowermost soil horizon to 7.2 in the surface horizon. Separated clay fractions contained glauconite, smectite-rich glauconite-smectite mixed layered minerals, kaolinite and goethite. An increase in the concentration of glauconite-smectite, kaolinite and goethite was observed in the clay fractions up the profile. Particle size distribution and observations of thin sections indicated that no significant transport of the finest material occurred within the profile. The green pellets separated from the C horizon contained almost pure glauconite with traces of swelling glauconite-smectite. Fe^{2+} constituted only 4% of the total iron present in the glauconite. The pellets separated from upper soil horizons, except for glauconite, contained glauconite-smectite, kaolinite and likely goethite. Concentration of glauconite-smectite and kaolinite in the pellets increased up the profile.

According to the results obtained, glauconite smectitization, dissolution and formation of kaolinite and likely presence of goethite appeared to be the main weathering processes recognized in the studied profile. The exact mechanism of glauconite smectitization has not been recognized yet, however low Fe^{2+}/Fe^{3+} ratio measured for the glauconite separated from the soil parent material indicated that Fe^{2+} oxidation was not the main reaction leading to smectite formation.

Metal readsorption in soil and sediment clay – bacteria leaching systems

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Keywords: metals, clay, bacteria, soil, sediment

Metals readsorption is determined by the type and quantity of clay and oxide minerals, total organic carbon, pH and redox status during heterotrophic bioleaching. The purpose of this study was to evaluate these parameters of Cu and Zn readsorption by bioleached soil and sediment. Arsenic and iron extractions were enhanced in the presence of TOC during bioleaching [1]. The ability of clay - bacteria to uptake Cu, Zn cations was investigated in the next step of soil (K) and sediment (R) bioleaching with medium two times amended with 3mM Cu and Zn.

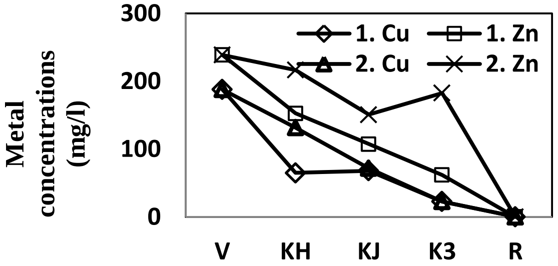

Fig. 1: Concentration of metals after leaching of samples; a) soil (KH- coarse grained , KJ – fine grained, K3 – iron rich 30 cm depth), b) sediment (R), c) V – measured initial concentration of Cu and Zn

The readsorption of Cu and Zn was increased to 100% from the Cu and Zn media after 14 days (Fig. 1) of the sediment bioleaching (R) and was decreased to 82 % in the abiotic sediment leaching (Table 1). Thus, Cu was readsorbed more effectively in the bioleached sediment-clay-bacteria systems. In soil with lower clay content, the readsorption of Cu and Zn was decreased with higher intensity than in sediment.

Table 1: Characterization of samples, pH changes and the readsorption efficiency of Cu and Zn

Samples	Clay content (%)	pH control / pH after BL	Readsorption Cu in control (%)	Readsorption 1.Cu /2. Cu in BL (%)	Readsorption 1. Zn / 2.Zn in BL (%)
KH	1.5	5-7.5 / 4.7-5.5	95	65/ 30	36 / 9
KJ	0	5-7.5 / 5.1-5.5	94	64/ 62	55 / 37
K3	1.7	5-7.5 / 5.2-5.5	88	88 / 88	74 / 23
R3	17	5-7.5 / 5.4-5.5	82	100/ 100	100 / 100

The readsorption in bioleached medium, is due to either direct sorption of the metabolites to the clay with the subsequent readsorption of Cu and Zn, or by enhanced sorption of the complex formed between Cu/Zn and chelate Na_3EDDS. In abiotic samples Cu and Zn were also precipitated, due to the buffering properties of the samples (pH increased from 5 to 7).

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Influence of montmorillonite, kaolinite and quartz on formation and peculiarities of Al-hydroxides in bauxite laterite profile

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Keywords: montmorillonite, kaolinite, quartz, gibbsite, biofilms

Montmorillonite (Fig. 1 a) and kaolinite are major components in the zonal laterite profiles. The first forms thick zones on weathered basic rocks (basalt, dolerite); moreover it is replaced by halloysite and/or kaolinite zones and Al-hydroxides (bauxites). In seasonal wet periods montmorillonite swells, tampons the pores and creates temporary reducing barrier. Under these conditions, Fe^{2+} is dissolved and leached out of the profile, creating white ironless zones of kaolin and bauxite. For these deposits the cryptocrystalline structure and close association of gibbsite $Al(OH)_3$ and boehmite AlOOH is characteristic. In the lateritized acid rocks kaolinite and quartz are dissolved, silica is taken out, and the numerous empty pores provide good drainage and the stable oxidizing environment. In the process of dissolution, quartz grains are repeatedly coated with biofilms which turned to the crusts of the euhedral crystals of gibbsite (Fig. 1 b) [1]. The abundant courses of boring organisms and walls of cavities were also covered with mineralized biofilms, and later on surface of biofilms the idiomorphic crystals of gibbsite grew up (Fig. 1 c).

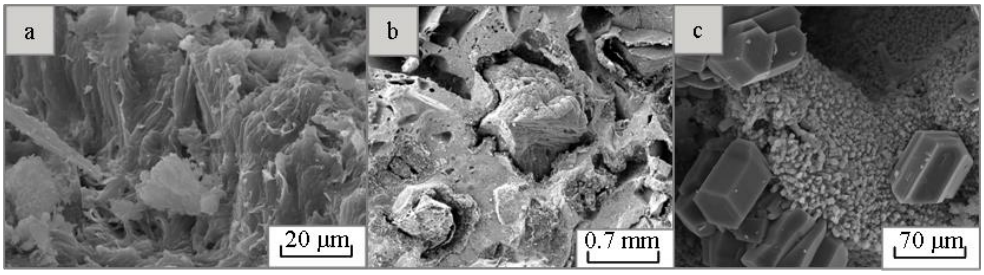

Fig. 1: Montmorillonite, quartz and gibbsite in the laterite profile (SEM): a - montmorillonite forms dense masses; b - porous spaces and crusts of the gibbsite crystals arise around the dissolved quartz grains; c- the gibbsite crust after biofilm.

The results of this study showed that peculiarities of boehmite and gibbsite depend on composition of the parent rocks, products of their weathering and presence of biota.

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Cation Mg^{2+} as indicator the depth of bentonite clays

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Keywords: montmorillonite, bentonite, dehydroxylation

The aim of the research was to found the crystallochemical features of bentonite from Vodopadnyi deposit of Sakhalin Island. Bentonite of volcanogenic-sedimentary origin occurs in coal-bearing seams. Thickness of the bentonite seam is 5 m, and the dip is over 60°. The number of sample was 6. They were investigated by Simultaneous Thermal Analysis (STA 449 F1 Jupiter "Netzsch") by heating rate 10 K/min in the closed crucibles in the air atmosphere, mass of a sample is about 40 mg. Chemical analysis by wavelength dispersive XRF spectrometr (Axios mAX Advanced "PANalytical"). As increases the depth of the layers of bentonite clay is increases their seal and the lithification degree and they go to mudstones and siltstones [1]. As the degree of substitution by magnesium in the octahedra and their vacant positions increase, the dehydroxylation temperature rises [2, 3]. With the increasing emplacement depth the pressure increases in the rock [4], and under this conditions the Mg^{2+} cation can migrate from interlayer site into octahedra [2], that is reflected in increasing of the dehydroxylation temperature with increasing depth. But the same migration could occur during temperature treatment in DSC furnace. This problem was solved by a comparison of the MgO content and amount of exchangeable cation of Mg^{2+}. With growth of the depth and the MgO content the value of the exchangeable cation of Mg^{2+} remains almost unchanged. Table 1 shows the change of dehydroxylation temperature, determined from the DTG curve, with the depth of the bed which confirms the possibility of such a transition at an elevated pressure.

Table 1 - The dehydroxylation temperature determined by DTG, the depth of location and the content of magnesium in bentonite

The hypsometric height, m	Serial number of the sample	T_{max} of weight loss during dehydroxylation, °C	MgO content (m/m%) by a chemical analysis (XRF)	Exchangeable cation of Mg^{2+}, mg-eq per 100g of dry bentonite
270	7	632	0.72	11.53
245	6_1	647	0.63	17.08
230	10_2	653	0.75	13.07
227	9_2	657	0.63	13.14
220	10_1	663	0.84	13.69
200	1	671	1.7	13.52

Acknowledgements: This study was supported by the Department of the Earth Sciences Russian Academy of Science (no. III.8.5).

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Use of clay minerals in the paleoenvironmental reconstruction of quaternary sediments case of Oued Zeïet, North East Algeria

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Keywords: mineralogy, paleoenvironment, Oued Zeiet, Algeria

In the continental environment, environmental reconstructions are often based on sedimentological, lithostratigraphic, and pollen analysis of sedimentary series. Our research has primarily used for mineralogical and sedimentological results. The identification of mineral phases (clay) of the sediment of Oued Zeiet terrace was performed on oriented preparations (natural, saturated glycol and heated to 550 ° C). X-Ray Diffraction spectra were obtained with a diffractometer equipped with a copper tube; it reveals the presence of clay minerals such as illite, kaolinite, and smectite. These clay minerals are also associated with quartz and calcite. The association consists of clay minerals such as smectite, kaolinite, illite, and sepiolite across the river terrace of Oued Zeïet, where smectite is usually the dominant mineral. The lack of variation in mineral species throughout the stratigraphic series and state of crystallinity indicates that these clay minerals are inherited and smectite in level 12, blackish in color, rich in organic matter is formed in confined low oxygen (no drainage).

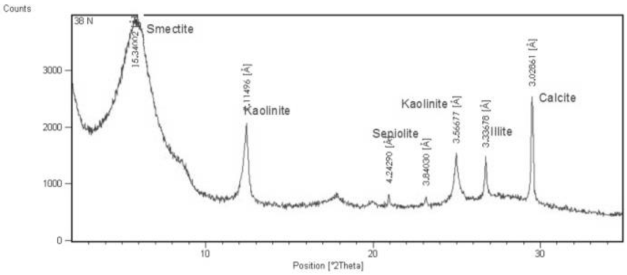

Fig.: Diffractogram of clay minerals

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Low-grade, medium pressure regional metamorphism of the pelitic succession in the Horváthertelend Unit: microstructural and thermobarometric evidences (NW foreland of the Mecsek Mts., Hungary)

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Keywords: Pannonian Basin, Horváthertelend, slate-metagreywacke, low-grade metamorphism

In this study the microstructural and thermobarometric examinations of the metapelitic sequence of the Horváthertelend Unit (Hh–1; NW foreland of the Mecsek Mts., Hungary) were carried out. Along the northern margin of the Tisza Unit, near the Zagorje–Mid-Transdanubian Zone, two low-grade metapelitic units are known. These unique epimetamorphic complexes are the Szalatnak and the Horváthertelend Units located among medium to high grade metamorphic and non-metamorphic Mesozoic formations. The studied well cuts through Cenozoic sediments and sedimentary rocks across 720 m. Below the depth 720 m, a black slate sequence with metasandstone intercalations was revealed in the thickness of 70 m. The underlying succession of the slate is a dark grey polymictic conglomerate-sandstone rock body. The slate and conglomerate bodies were correlated with the Silurian flysch-like Szalatnak Slate Formation.

In this work the upper slate sequence was studied which consists of mainly black and dark grey, in the lower section pale grey, slate with metagreywacke and metasiltstone lenses. The studied rocks contain grain supported, well sorted arkose clasts from millimetre to centimetre scale. The studied slate samples have K-white mica + chlorite + quartz + albite + anatase mineral assemblage. The slates have a distinct metamorphic continuous foliation in acute angle with the bedding.

The full width at half maximum (FWHM) values of the 001 and 002 XRD peaks of K-white mica and chlorite were measured in highly oriented <2 μm grain size fraction of the slate. The low FWHM values (Ms_{001}:~0.117 Δ°2θ, Chl_{002}:~0.147 Δ°2θ) and the crystallite sizes calculated using the Scherrer-equation (Ms_{001}: 1121±70 Å, Chl_{002}: 700±86 Å) suggest epizonal metamorphism. The $b_0=6d_{(060,331)}$ value of K-white mica was determined using nonoriented <2 μm grain size fraction. In the examined samples the average calculated b_0 value ~9,022 Å suggests medium P-T gradients during metamorphism.

High content of autochthonous carbonaceous material (CM) in the rocks enabled Raman-spectroscopic thermometry based on the evolution of CM's first order Raman bands. The calculated maximum temperature of the metamorphism arisen from three different empirical thermometers is ~350 °C.

The presented observations and data suggest Barrowian type low-grade (chlorite zone ~350 °C) regional metamorphism and ductile deformation of the metapelitic sequence of the borehole Hh−1.

Very low-grade metamorphism of the Cisuralian basement formations (Korpád Sandstone, Gyűrűfű Rhyolite) near Kelebia, Békés-Codru Unit, Hungary

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Keywords: phyllosilicates, metamorphism, Permian, basement, Békés-Codru Unit

The Tisza Mega-unit forms the basement of the Pannonian Basin south of the Mid-Hungarian Zone. Within its pre-Alpine crystalline units, the low to medium-grade metamorphic rocks in the westernmost part of the Békés-Codru Unit belong to the Kelebia Complex. Non-metamorphosed Triassic carbonates and redbeds, corresponding to the Codru nappe system, Cisuralian rhyolite lava together with volcanosediments (Gyűrűfű Rhyolite Formation) and small erosive remnants of the underlying Korpád Sandstone Formation overlap the erosional surface of the metamorphic basement rocks in the area. A study combining petrographic data of drill cores and thin sections from the subsurface Permian rocks (Korpád Sandstone and Gyűrűfű Rhyolite, boreholes near the village of Kelebia, Hungary), microstructural observations, and mineralogical data (X-ray powder diffraction, XRD) has revealed a complex burial diagenetic to very low-grade metamorphic evolution. In thin section the studied Gyűrűfű samples are thoroughly recrystallised which texture is defined by equigranular mosaic of subhedral to anhedral quartz and feldspar in the matrix. Locally dense networks of closed, spherical spherulites also occur. The strongly altered, sericitised pumices are oriented, strike paralell to each other, showing continuous, coherent sericite bands interpreted here as a spaced foliation due to ductile shortening. The phenocrysts (quartz ± plagioclase ± biotite ± pseudomorphs after pyroxene) have symmetric quartz and K-white mica pressure-shadow. Additionally, quartz crystals locally exhibit undulose extinction with deformation lamellae. The underlying metapelitic rocks have an S_0-S_1 primary foliation and an S_2 zonal crenulation one, suggesting a late ductile deformation. Based on XRD data, the mineralogical composition of the Kelebia rhyolites is predominated by mica and quartz with subordinate amount of chlorite and feldspar. The studied slate of the Korpád Sandstone has almost the same mineralogical composition with some additional hematite. Clay fraction separated from both of the rhyolites and slate are composed of K-white mica (>90%; $d_{00,10}$=1.99 Å) with some chlorite (5–10%) and quartz. Trace amounts of hematite contributes to the clay fraction of the slate as well. Non-calibrated FWHM values of the K-white mica scatter $\sim 0.15\Delta°2\Theta$ suggesting (very?) low grade metamorphism. In the studied part of the Békés Unit (Codru nappe system), traditionally, the Permian volcanosedimentary sequence is regarded as non-metamorphic cover. The abovementioned features, however, demonstrate that these formations were affected by a much higher degree of ductile deformation and metamorphism than previously thought. **Acknowledgements:** This research has been supported by the Hungarian Scientific Research Found (OTKA; No. K 108375).

Inorganic geochemical components of Paleozoic source rocks associated with basin stratigraphy and depositional processes

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Keywords: black shales, lithofacies, mineral content, XRD, XRF

Black shales of the north-western part of the Dnieper-Donets basin have been investigated by XRD- and XRF-analyses to obtain information regarding the inorganic composition, the conditions of formation and the depositional environment. A correlation between the distribution and variation of the mineralogical composition of 122 core samples of 15 wells, and the tectono-stratigraphic sequences of the basin took place, as well as the analyses of the relationship between mineral phases, trace elements and organic parameters.

The clay mineral content of the Devonian to Bashkirian black shales ranges from less than 20 to more than 80 Vol.% with a significant variability of the main components: kaolin-group and mica-group minerals. Mixed-layer illite/smectite is dominated by illite. The non-clays comprise primarily quartz, carbonates, feldspar and pyrite. Concerning the trace metals titanium shows the largest proportion. The total trace element content analysed by the Ni/Co-, and V/Cr-ratio reflects the euxinic milieu.

Within the stratigraphic succession the following significant lithofacial variations are observed: in some Devonian black shales feldspar exceeds 10 Vol.-% and glauconite occurs. An increased chlorine concentration indicates the effects of salt tectonics during the syn-rift phase. Significant for Tournaisian and Lower Visean are kaolinite contents up to 90 Vol.-% and pyrite contents which exceed 10 Vol.-%. The mineralogical composition of the Visean sediments reflects continental deposition suggested by increased Zr-, Nb-, Ti-values, and deposits of cyclic successions in fluvial, shallow marine and lagoonal environments [1]. In Upper Visean the amount of kaolinite decreases while the percentage of illite increases. On the north-eastern rim of the Srebnen and Zhdanivske Depression, samples of the Upper Visean (C1v2 19/20) show an increased amount of anatase. Apatite can be directly correlated with the phosphorus content. The amount of the TOC content [2] can be associated with the percentage of kaolinite, pyrite/marcasite and quartz. Overall, in the Lower Serpukhovian and the Bashkirian a decrease of kaolinite and mixed-layer clays and increase of chlorite, illite and the enhanced quartz content indicate the lithofacial change.

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Relative coherent stacking potential of fundamental particles of illite-smectite and its relationship to geological environment

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Keywords: I-S, fundamental particles, crystallites, expandability, coherent stacking

Interstratified illite-smectite (I-S) occurring authigenically in diverse earth crust environments reacts toward more illite-rich phases as temperature increases. For that reason, I-S is used for geothermometry when prospecting for hydrocarbons or ore mineral deposits. This study develops the mathematical relations for characterizing the coherent stacking potential of fundamental particles (FP) using the expandability ratio K, where K is defined as $(\%S_{MAX} - \%S_{XRD})/\%S_{MAX}$. The ratio can be applied to differentiating I-S samples from shales, bentonites, and hydrothermal alterations. In particular, patterns on a K vs. T diagram, where T is the average thickness of fundamental particles (FPs), appear to be indicative of the geological conditions related to I-S formation. Shale samples plot in the negative K domain of the diagram, possibly due to the intimate mixing of detrital particles. Both bentonitic and hydrothermal samples display trends of increasing K with T, which suggests the coherent stacking potential progressively decreases as FPs increase in thickness. Hydrothermal samples are more extensively distributed on the diagram than samples from bentonites. This result may reflect differences in particle growth conditions (nutrients and space) between bentonites (short supply) and hydrothermal alterations (good supply).

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Argillic alteration of Permian granite intrusion (Velence Mts., Hungary) by Triassic and Paleogene hydrothermal fluids

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Keywords: XRD analysis, argillic alteration, Triassic and Paleogene hydrothermal systems, Velence Mts.

In this study argillic alterations of a Permian granite intrusion (Velence Mts. Hungary) generated by Triassic and Paleogene hydrothermal systems were investigated. The hydrothermal fluid flow events can be characterized by different physicochemical properties; based on fluid inclusion studies the temperature (130-240 °C) and pressure conditions (400-500 bar) during the Triassic were significantly different from the Paleogene fluid flow (240-480 °C; 30-280 bar) [1].

The different hydrothermal alteration zones spatially often overlap and the elder mineral assemblages are locally overprinted by the younger hydrothermal systems. Therefore the isolation of the clay mineral generations of different age and origin is challenging. The main aim of our work is the spatial distinction of fluid-rock interactions of various ages and the characterization of the hydrothermal fluids (pH, T). XRPD, DTA and IR studies on variously separated and treated clay mineral samples were carried out in order to determine the domain size, illite polytypes and the Hinckley index of kaolinites. Argillic alterations of single mineral particles were studied by micro-XRD.

In the Triassic alteration zones the illite formed on the rim of the fractures and beidellite in the center suggest cooling of the hydrothermal fluids from 300 °C below 100 °C. Dickite and illite associated to hydrothermal breccias in the Palaeogene alteration zones indicate high-temperature (200-350 °C) and acidic to neutral pH of the hydrothermal fluids in agreement with the fluid inclusion studies.

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Synthesis of zeolites by alkali activation of calcined clays

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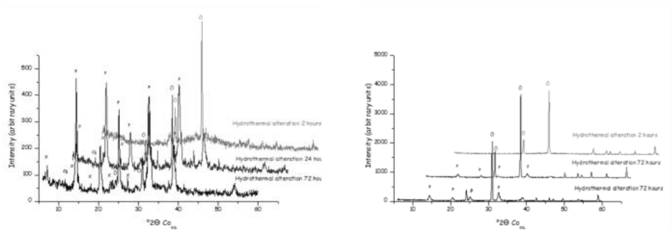
Keywords: geopolymer (AAA), compressive strength, zeolites

Growth of zeolite phases was detected in hydrothermally treated geopolymer mixtures (alkali activated aluminosilicates - AAA) prepared from two kinds of clays from Horní Bříza and Střeleč, respectively. Clays differing in the content of kaolinite and quartz were calcinated at 750 °C for 6 hours. The resulting metakaoline products were mixed with water glass so, that in both sets of samples the SiO_2/Al_2O_3 ratio around 3.4 was achieved. The cubes (20x20x20 mm) prepared from compact paste were treated at 140 °C for 2, 24 and 72 hours. Achieved compressive strengths of the AAA specimens are shown in Table 1 and their XRD analysis in Fig. 1.

Table 1: Compressive strengths of the AAA hydrothermal treated samples

Time of hydrothermal treating	Compressive strengths of AAA prepared from Horní Bříza clay (MPa)	Compressive strengths of AAA prepared from Střeleč clay (MPa)
2 hours	15.4	27.8
24 hours	9.3	10.0
72 hours	9.3	10.8



a) **b)**

Fig. 1: XRD analysis of AAA hydrothermal treated samples prepared from clays: a) Horní Bříza; b) Střeleč

The presence of X and P zeolites and chabasite was detected in hydrothermally treated samples. The types and quantity of the synthetized zeolites depended on the initial amount of kaolinite in raw materials. Compressive strengths were gradually reduced in dependence on the rising time of the thermal curing. The relative amount of kaolinite in clay samples did not affect the final compressive strength of the AAA systems after long term hydrothermal treating.

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Characterization and potential applications of zeolitic materials synthetized from perlite waste material

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Keywords: zeolites, synthesis, perlite, sodalite

Production of zeolite by treatment of volcanic glass with alkaline solutions is a common method described by many authors. Waste material (particle size <63 μm) derived from perlite milling process was used as a starting material in the present study. The goal was to optimize reaction conditions to produce zeolites effectively and economically (i.e. at low temperature, low NaOH concentration, and short reaction time). In addition, the potential applications for synthetized zeolitic materials were evaluated based on the additional sorption test on the removal of selected elements from aqueous solutions. The laboratory synthesis was carried out by mixing the perlite waste (11 g) with 80 mL of NaOH solution in the concentration range 1 – 5 mol.dm^{-3}. Different temperatures (50 – 80 °C) and various reaction times (24, 72 and 144 h) were used. For comparison, mixtures of perlite with distilled water (blanks) were prepared in the same way. After the synthesis the reaction solutions were collected and chemical compositions were determined. The solid phases were washed with distilled water until the pH was below 10. Then all solids were treated 3 times overnight with 1M NaCl. Excess soluble salts were removed by centrifugation followed by dialysis. Na-saturated samples were dried overnight at 60°C and passed through the 250 μm sieve. The Na-saturated reaction products were examined by X-ray diffraction (XRD), infrared spectroscopy (FTIR), scanning electron microscopy (SEM) and inductively coupled plasma (ICP) spectroscopy. The surface properties BET-specific surface area (SSA) and cation exchange capacity (CEC) were determined as well. The preliminary results showed that the reaction conditions strongly influenced the amount and type of zeolitization products. Sodalite was formed primarily at higher concentrations of NaOH solution whereas zeolite Na-P1 was found primarily at NaOH solution of lower concentration. The amount of zeolites increased with increasing temperature and reaction time.

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Structure of layered materials intercalated with organic species solved by molecular simulation methods

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Keywords: molecular simulations, LDH, drugs, phosphonate, intercalation

In our recent investigations we have used molecular simulation methods to describe various types of layered materials intercalated with different organic species, especially those materials where the disorder prevents their direct description by X-ray diffraction and other experimental methods. Here, we present Zn_2Al/Mg_2Al Layered Double Hydroxides (LDH) intercalated with pravastatin anions and Sr-phenylphosphonate intercalated with 1,2-alkanediols.

LDHs are very interesting matrices which are to be explored as drug nanocarriers due to their biocompatibility and stability properties in human body. The anionic forms of bioactive drugs can be intercalated into the interlayer to store them and preserve drug decomposition in environment. Intercalation of pravastatin drug into LDH was performed in [1] by co-precipitation method. Molecular simulations showed a preferred orientation and different behavior in dependence on pravastatin anion concentration in the interlayer space. Pravastatin anions were anchored to layers, water molecules are mostly in the middle of the interlayer.

Metal phosphonates represent a group of compounds playing an important role in the design of two-dimensional inorganic-organic hybrid materials. The applicability of the layered phosphonates can be increased by intercalation of commercially interesting, for instance optically or pharmaceutically active molecules. We present influence of intercalated 1,2 alkanediol on changes in structural arrangement of Sr phenylphospohonate. It was found that the 1,2-diol molecules are coordinated to the strontium atoms of the host layer by both oxygen atoms of the hydroxyl groups in the free spaces formed by phenyl rings. The models with 1,2-ethandiol, 1,2-propandiol, and 1,2-butandiol showed an ordered arrangement of diols and water molecules. 1,2-pentadiol and 1,2-hexandiol led to disordered arrangement of the guest in the cavities and moreover alkyl chain jut out from the cavities formed by phenyl rings. All presented calculated models are in a good agreement with experimental data.

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Interlayer structures of zirconium phosphonates with sulfophenyl and phenyl groups solved by molecular modelling methods

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Keywords: zirconium phosphonates, molecular modelling, sulfophenyl

Zirconium phosphates and phosphonates chemistry has grown in recent years because of its great potential for applications in photochemistry, molecular and chiral recognition, biotechnologies and catalysis. Structure of pure Zr phosphonate was solved back in 1960's [1] but nowadays many new compounds are being intercalated between the zirconium layers to reach desirable properties of resultant materials [2]. Generally, the zirconium phosphates are very insoluble and poorly crystalized. Therefore, it is difficult to deduce their structural characteristics. On the other hand the contemporary progress in the development of numerical apparatus for computer structural analysis and molecular simulation methods allows us to solve these large structures efficiently in reasonable time.

At first, the structures of zirconium phosphonate derivatives with sulfophenyl groups were analysed. This material with strong acidic -SO_3H groups in the interlayer works as good protonic conductor. Its optimized structures with minimal energies were obtained in Materials Studio modelling environment. Furthermore, structures with experimentally obtained specific ratio 1.3:0.7 of sulfophenyl and phenyl groups, respectively, were investigated. Calculated X-ray diffraction patterns of the final structures with the lowest potential energy were compared with the experimental diffraction. The structures of zirconium phosphonate layers with sulfophenyl and phenyl groups with the best agreement with experimental data will be presented.

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Grog-tempered Copper Age pottery in Southern Carpathians (Romania): technological choice or just a happening?

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Keywords: copper age, temper, grog, OM, EMPA

Grog (chamotte)-tempered pottery has been produced since the Early Neolithic and has become common during the subsequent time periods [1] [2]. The grog is often difficult to be distinguished from argillaceous rock fragments [3] [4].

The Copper Age Coţofeni pottery found at the Great Cave of Cerişor (Southern Carpathians, Romania) contains frequent fragments of grog – here referred as ceramoclasts. In order to find if the grog was intentionally added by the potter, a study was performed based on optical microscopy (OM) and electron microprobe analysis (EMPA). The sherds consist mainly of quartz, illite, muscovite, feldspars and heavy minerals, as well as rock fragments, ceramoclasts, clay pellets and soil concretions. Ceramoclasts have generally a subangular shape and are often surrounded by shrinkage rims. Microscopically, several compositional and textural types of ceramoclasts have been identified, some of 'ceramoclast-in-ceramoclast' type. OM and EMPA, as well as the elemental mapping revealed that the grog fragments have either the same, or different mineralogical and chemical composition compared with the host-body. The chemical difference regards in particular the Mg, Ca and P content. The back scattered images show in many cases different texture of the ceramoclasts.

The results suggest that the use of crushed older potsherds for producing pottery was a custom for the Coţofeni population.

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Technological interplay: Relationships between painted and shell-tempered pottery at Cucuteni – Cetățuia (Eastern Romania)

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Keywords: chalcolithic, Cucuteni culture, XRD, LA-ICP-MS, SEM

Cucuteni-Cetățuia (Iași County, Eastern Romania) is the eponymous site of the Cucuteni culture which offers detailed information on the cultural relationship between the Eastern Carpathians and the Dniester River during 4600 – 3600/3500 cal BC. The site is located in a hilly region, east of the Siret River and was systematically investigated in 1909-1910 and 1960-1966. The archaeological deposit, 1.70 m thick, includes all three phases of the Cucuteni culture and contains large amounts of painted pottery and, also, a large assemblage of shell-tempered pottery which is considered as an intrusive element in the Cucuteni culture area.

The aim of this work is to study the development of this settlement, through the production and the technology of ceramics considered of local production (the painted one), and the trade relations with the communities coming from the "Great Steppe" region through the shell-tempered pottery.

A total of 50 pottery samples was analyzed by means of laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS), X-ray diffraction (XRD) and scanning electron microscopy (SEM). Additionally, fifteen clay samples from the area were analyzed by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). By using LA-ICP-MS we could determine the nature of the inclusions and establish the origin of the raw materials, while XRD and SEM analysis offered us information about the mineralogical and structural characteristics of the pottery samples.

Preliminary results showed that although major textural differences can be observed among the analyzed ceramic bodies, inclusive of the same chronological period, there are no significant differences in the chemical and mineralogical compositions, which suggest that the sources of the raw material and manufacturing techniques could have remained the same in all three phases of the Cucuteni culture. This work opens a new challenge in the research of the shell-tempered pottery, especially, the one present in late phases of the Cucuteni culture which may represent an imitation of the "Great Steppe" pottery technology rather than imported goods.

Monumental sculptures in terracotta of the monastery of Alcobaça (Portugal) - raw materials and technological processes assessment as tools for provenance, conservation and restoration

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Keywords: terracotta, sculptures, provenance, conservation

The monastery of Alcobaça, classified by UNESCO as a world heritage site since 1987, is the first example of Gothic architecture in Portugal being, simultaneously, the best preserved Cistercian Abbey in the European context. This monument has a vast collection of valuable monumental sculptures in terracotta, with approximately 2 meters tall, that fall in the wide ceramic production which notes throughout history in the surrounding region, and that, especially from the 17th century, is considered a major center of ceramic production and export.

The conservation and restoration intervention intended to prepare implies the knowledge of the present state of the support material, in this case terracotta. Possible local and regional clayey raw materials were also studied.

The analysis carried out involved the mineralogical characterisation by x-ray diffraction (XRD) and the chemical composition by x-ray fluorescence spectrometry (XRF). Physical tests were made on terracotta samples, such as: open porosity, water absorption and density. Ceramic tests were also done on studied raw materials.

The obtained results point to local sources of their raw materials, very similar (illitic-kaolinitic clays to marly clays), despite the pieces showing different frameworks. Production is local, made by integral modeling of sculptures and cut into *tacelos* for easy handling, drying and cooking. Cooking would have been carried out in furnaces that did not allow an homogeneous optimal temperature cooking, some pieces very well cooked, with formation of new crystallographic phases, as gehlenite (occurring at temperatures in excess of 850º C) and other pieces showing still evidences of clay phases, such as kaolinite (collapsing at temperatures above 550º C). The ceramic properties of terracottas are in relation to the water absorption (within the normal parameters for this type of materials).

Investigation of chlorite schists (*pietra ollare*) by IR-spectroscopy and thermal analysis

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Keywords: archaeology, pietra ollare, chlorite, IR-spectroscopy, thermal analysis

Vessels made of different varieties of pietra ollare, ultramafic rocks affected by low grade metamorphism, showing characteristic tracks of the manufacturing by means of a lathe, have been found at several localities along the Croatian Adriatic coast [1]. In recent years chlorite-schists varieties found in Roman villa rustica in Červar Porat located close to the town Poreč (Istria peninsula, Croatia) have been studied in order to determine their provenance i.e. to determine ancient trade routes [1] [2]. Adequate raw materials for production of the vessels cannot be found in Istria and its nearest surroundings therefore import of this kind of vessels should be presumed. This kind of material could be found in Dinaridic ophiolite zone, but there is no evidence in the literature for the use of this material for production of stone vessels, therefore the investigated material most probably has Alpine origin in some of the main production centers of the ancient times. Hence in order to make database of possible source rocks chlorite rich pietra ollare samples were collected in Valli di Lanzo, Valle d' Aosta, Valchiavenna and Val Malenco, localities known as important production centers of pietra ollare in Italian Alps [3].

Pietra ollare provenance studies performed so far were based mainly on petrographic characteristics, chemical composition [4] and recently on X-ray powder diffraction data [2]. The aim of the present study was to determine if IR and TG, DTG studies could be used to distinguish samples originating from different localities. The obtained results showed that samples from different localities have dissimilar IR-spectra, due to different Mg for Fe and Al for Si substitutions. IR spectroscopy proved as valuable complementary method in the provenance studies of pietra ollare artefacts made from chlorite schists.

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Boom Clay retains its self-sealing capacity after 15 years of interaction with high pH solutions

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Keywords: Boom Clay, self-sealing, hydraulic conductivity, micro-CT, geological disposal

The self-sealing is an important property of clay host rocks considered for long-term geological disposal of high level radioactive waste and spent fuel. The self-sealing of Boom Clay has been demonstrated on artificially fractured fresh Boom Clay cores in the laboratory at ambient temperature and during heating and cooling cycles up to a temperature of 80 °C [1]. As a geological disposal system in Boom Clay could include components made of concrete, such as for instance the lining of galleries or the secondary packages for the wastes, it is important to evaluate if clay in contact with cementitious materials over a long period retains its self-sealing ability. For this purpose, we used Boom Clay samples that were percolated with young cement water (YCW, pH of 13.2, KOH dominated) and evolved cement water (ECW, pH of 12.5, $Ca(OH)_2$ dominated) for about 15 years. After dismantling of the percolation cells, we created artificial planar fractures in the middle of the cores perpendicular to bedding planes. The self-sealing was followed by means of hydraulic conductivity measurements using constant volume permeameter cells and 3D imaging by micro computed tomography (micro-CT) scanning.

In the case of ECW, the self-sealing is demonstrated by hydraulic conductivity (k_f) measurements rapidly decreasing to a values of 1.99×10^{-12} m/s, which is less than three times the k_f of the same core (7.35×10^{-13} m/s) measured prior to artificial damage. Despite this relatively limited k_f increase, the fracture was still visible in the μCT scans.

In the case of YCW, the self-sealing is evidenced by a modest increase of k_f to value of 3.13×10^{-12} m/s after fracturing and self-sealing, compared to a value of 1.67×10^{-12} m/s determined prior to artificial damage. Again, the fracture is still visible on the micro-CT images acquired immediately after termination of the permeameter cell tests. However, the fracture gap colour changes from black (air) to dark grey indicating the presence of material with a density lower than the density of the surrounding clay. The presence of the low density material can be explained by the swelling behaviour of clay in the fracture space.

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Microstructure and pore structure of binary cement systems based on diatomite

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Keywords: diatomite, pozzolanic reactivity, cement, microstructure, pore structure

This manuscript introduces clayey diatomite from Jelšovec deposit in Slovakia. Natural clayey diatomite (CD) and calcined clayey diatomite (CCD) were used for substituting 5 to 15 wt. % of the ordinary Portland cement CEM I (PC). CCD was prepared from CD by calcination at 900 °C for 1 hour. Frattini test was applied for the estimations of the pozzolanic reactivity. The pozzolanic reactivity of CCD is comparable with traditional natural and industrial pozzolans, and that of CD is only slightly lower compared to that of CCD (Fig. 1). Both clayey diatomites are reflected as high-efficient pozzolans when partially substituting the PC.

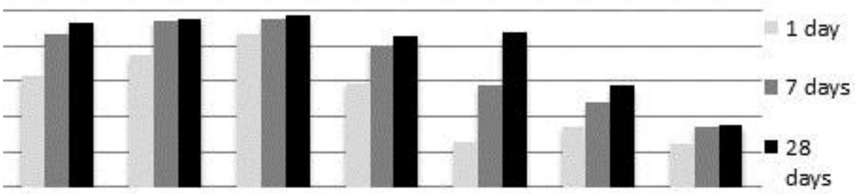

Fig. 1: Percentage comparison of pozzolanic reactivities

Cement composites of constant solids to water ratio of 0.5 with substitution rate of PC by CD and CCD ranked between 5 and 15 wt % were used for the tests. The specimens were studied by X-ray and thermal analysis as well as mercury intrusion porosimetry after 28 and 365 days compressive strength tests. Composites exhibited larger $Ca(OH)_2$ consumption, higher volume of gel-like hydrate phase (Table 1) and finer pore structure relative to the reference cement paste (PC).

Table 1: Thermogravimetric analysis evaluation after one-year water cure

Content [wt. %]	PC	5 %CD	10%CD	15%CD	5%CCD	10%CCD	15%CCD
Water in CSH	10.3	11.1	10.8	10.7	10.7	10.8	10.9
$Ca(OH)_2$	20.0	15.4	13.7	12.5	15.8	13.6	10.5

Present findings indicate Slovak diatomite from Jelšovec as perspective pozzolan used in cement-based materials with similar utility and microstructure properties than those gained with traditional natural and industrial cement modifiers. Moreover, cement substitution by CD and CCD is reflected in the decreases in energy costs and amounts of CO_2 released into atmosphere during the production.

Effect of desiccation on hydro-mechanical behaviour of compacted bentonite based buffer material

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Keywords: Calcigel bentonite; swelling pressure; permeability; desiccation; suction

In deep geological repository, the buffer made of compacted bentonite based material plays a decisive role in long term safety evaluation. Hydro-mechanical parameters like saturated hydraulic conductivity and swelling potential are key design parameters. In this study, the effect of suction and temperature induced desiccation on hydro-mechanical behaviour of compacted buffer material is investigated. Compacted Calcigel bentonite specimens were first desiccated in two different ways, at 80℃ using the oven and using vapour equilibrium technique (VET) at 80℃. After the suction equilibrium, shrinkage strains were measured in axial and radial direction. The experimental results show that the shrinkage strain first increases linearly with soil suction ranges from 40 to 400 MPa and it became constant for suction higher than 400 MPa. The swelling pressure of these specimens was then measured using UPC Isochoric cell with one step wetting with two folds in applied boundary conditions, the free swelling condition for swelling strains equals to initial shrinkage strains followed by constant volume condition. Finally, saturated hydraulic conductivity was also measured under constant head condition. Comparing the swelling pressure tests results, the swelling pressure of the desiccated samples apparently increases with little influence on the saturated hydraulic conductivity.

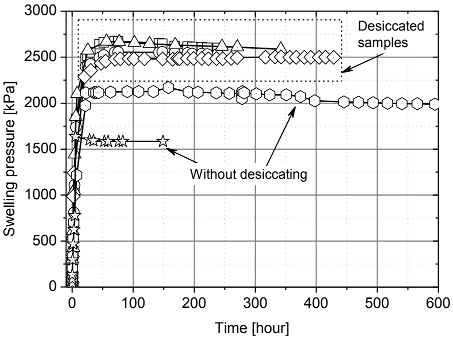

Fig.: Effect of desiccation on swelling pressure

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The core principles of the theory of strength of composite soil cement-based materials with carbon nanostructures

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Keywords: strength, clay, carbon nanotubes, cement, composite

The new theory of strength of composite soil cement-based materials with carbon nanostructures (CNT) has been developed from new positions of the structural-energy concept. Changes of strength of composite soil cement-based materials with CNT are the product of the binding energy of the structure of the film of new formations and the degree of disorder in the system, occurring with changes in the content of its individual components. The new classification of the microstructure of cement CNT composites has been developed; the classification features three levels: classes, types, and kinds. The classification is based on soils with different level of dispersion. The main feature of this classification, in contrast to the existing classifications of cement in coherent sedimentary soils, is the isolation of microstructures considering quantitative parameters: the strength of the composite and the binding energy of the films of the new formations of varying structure; i.e., it is based on the nature and strength of the structural relationships. Ultrafine CNT are an additional element of composite reinforcement. The composites are assuming elastic-plastic properties. Introduction of mono-layered and multi-layered CNT additives increases the strength of the composites by an order of magnitude compared with the baseline (i.e., without CNT additives) due to a structural component of a new, more durable matrix and the CNT additives reinforcement effect. If the CNT content increases from 0.01% to 1%, their activity and the resulting strength properties are reduced. The optimal CNT concentration in composites of the same formulation has been established. Carbon additives effectively modify different types of cement (CMC-90 and ЦЕМ I 42,5) in the composites of the same formulation. Moreover, reduction of the concentration of the additives by an order of magnitude from 0.1% to 0.01% increases the strength by 15-40%, at other equal conditions. At the same content of additives, multi-layered CNT with matted-fiber, disordered-structure of nanotubes are most effective. The film thickness of the new formations and its uniformity are the key parameters that allow accounting for the effect of the content and the type of cement and the content and structure of CNT, these parameters also allow predicting and controlling the strength of cement composite materials based on soils of varying dispersion, with addition of CNT. The dielectric losses are the integral parameter determining the binding energy of the new formations in the composite, depending on the structure, formulation, and the film thickness of the new formations. The compositions of composite materials, which can serve as tires and coatings technogenic, geochemical barriers, screens with record performance properties that protect against electromagnetic radiation, from man-made pollution and can be used in road construction and civil engineering.

Influence of carbon nanostructures on the clay minerals in the soil-based cement composites

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Keywords: clay, carbon nanotubes, cement, composite, structure

The study of carbon nanotubes represents a serious interest both fundamentally and applied. The impact of CNT on the structure formation of composite materials essentially depends on their properties. The properties of multi-layer and single-walled carbon nanotubes of different electronic structure have been studied [1]. Installed microstructure of carbon nanotubes and its relationship with the absorption of electromagnetic energy in the super-high-frequency range. Cements and clay soils are energetically heterogeneous systems and have a high concentration of electrons and spin-polarized electrons (bound water) and it allows you to adjust their electronic states both for charge and spin. The introduction of highly active ultrafine carbon additives in cement composite based on a fine-grained soil allows, first of all, a change in the molecular structural state of the bound water of clayey soils. It was found that for optimal content of CNT, the strength of cement composites based on loam were an order higher than that without additives, ceteris paribus. This is due to the increase of thickness of growth film and changes in its structure and to coordination of interaction bound water films of clay minerals fraction with carbon nanostructures. The microstructure of growth films in soils of different dispersion and its relationship with the strength of cement composites have been defined [2]. Increasing the number of spin-polarized electrons in bound water of clay films and reducing the size of pores in the soil promotes the effective modification of cement composites with carbon nanostructures. For the first time it was found that with an increase in dispersion of the soil and a decrease in the concentration of CNT to the optimum concentration, the binding energy of the growth film in the composite increases, ceteris paribus. For the first time it is quantitatively explained that the strength of the studied composites depends exponentially on growths film thickness with increasing soil dispersion. Stabilization of the growth kinetics of strength in composites with CNT occurs over a longer period of hardening (~ year). Structural and energetic patterns for cement composites based on soils of different dispersion with carbon nanotubes are established.

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Preliminary testing of the long-term efficiency of geosynthetic clay liners

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Keywords: geosynthetic clay liners, bentonite, landfill, final cover

Geosynthetic clay liners (GCL) are factory-manufactured hydraulic barriers consisting of a mineral (bentonite) and geosynthetic component (geotextile or geomembrane). Over the last several decades, their application has increased intensively in various engineering projects for environmental protection purposes, including landfills. In Croatia, there is also a significant number of landfills with GCL incorporated as an integral part of protective systems, most often as the landfill final cover. Since protective systems have to fulfil their designated function over a longer period of time, usually, laboratory tests of the GCL durability and landfill monitoring are being implemented in order to identify long-term functionality of GCL.

This study presents laboratory tests carried out on 23 samples of GCL that were installed at one real landfill near Zagreb between three and nine years ago, as well as sample of manufactured bentonite in its original state left over after installation. Following analyses were performed: XRD, ICP-MS, cation exchange capacity, pH, electrical conductivity, moisture, colour, index properties (free swell index, water absorption capacity by Enslin-Neff test, fluid loss) and hydraulic conductivity.

Montmorillonite is predominate mineral followed by quartz, K-feldspar, plagioclase, goethite, anatase and micaceous material. CEC ranged from 51.96 meq/100g to 75.47 meq/100g. Index properties for all samples are summarized in table 1. It can be concluded that the properties of all samples were deteriorated with time in comparison to the reference sample test results. Moreover, none of them fulfils the required values according to some recommendations nowadays. However, conclusions about the influence of the cover layer thickness and the time passed since the installation date cannot be precisely divided yet. Therefore, some additional investigations will be carried out.

Table 1: Test results

Instalation date	Liquid limit (%)	Plasticity index (%)	Free swell (ml/2g)	Water absorption capacity (%)	Fluid loss (ml)
2004	125-146	82-92	12-17	208-324	16-89
2009	112-190	67-157	8-13	163-293	52-86
2010	149-205	114-173	11-13	213-268	51-64
Ref. sample	420	382.4	27	453	20
Required*			>20	>450	<18

*DGGT (2002): Empfelungen zur Anwendung geosynthetischer Tondichtungsbahnen EAG-GTD, Ernst&Sohn.

Density determination of clay soils - A method comparison

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Keywords: density, porosity, drying, pycnometry

Density as a measure of the "compactness" of matter may be calculated from a separate mass and volume measurement. Various methods for determining the density of the soil are regulated in standards because of the importance of this material parameter for geotechnical practice. Depending on the preparation of the material and the nature of the methods used, however, different results are measured particularly for clay soils.

On samples of bentonite and lacustrine clay different density determinations were made: simple measurement of regular bodies, mercury intrusion porosimetry, dipping and weighing in silicone and water, and pycnometry with the different media (DryFlow®, helium, ethanol and water). Furthermore the influence of various kinds of sample preparation (i.e. drying) procedures was investigated: air drying, oven drying, shock freezing in liquid nitrogen with subsequent vacuum drying, and the water exchange process with methanol and diethyl ether.

The different drying procedures (provided that the sample was dry afterwards) have no influence on the measured grain density. The pycnometry with distilled water as the measuring medium is the standardized measurement. However, just this method could not deliver the desired accuracy of the results because of problems in the measurement due to swelling and self-sealing of the clay which could even not be avoided using ethanol. As the most accurate method the helium-pycnometry was found. The measured (dry) bulk density, however, was, as expected, strongly influenced by the applied drying method. The simple air or oven drying showed due to the shrinking processes the strongest influence on the soil structure and porosity and consequently on the determined density. The determined density was too high. On the other hand, the freeze drying and the water exchange resulted in only slightly overestimated bulk densities compared to the density determined on non-dried samples and afterwards corrected according to the water content. The different measurement methods itself provide reliable results. Nevertheless, the standardized methods (dipping) showed the largest variations depending from operation skills. As the most accurate method the DryFlow®-pycnometry on non-dried samples using the large sample chamber was found. The mercury intrusion provides good reproducible results for grain and bulk density. However, the grain density is an apparent grain density because of the fact that mercury cannot introduce into pores <3.6 nm and the bulk density is influenced by the drying procedure with the connected changes in the pore structure. The shock freezing and the water exchange methods showed the lowest impact on these results.

AUTHOR INDEX

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Work protective devices
Devices for eye protection - goggles, shields, other basic safety equipment such as gloves, coats, pants and a selection of basic hygienic and cosmetic products.

Glassware and porcelain
Laboratory cooking vessel made of borosilicate glass, beakers, flasks, standard joint glass apparatus and parts, such as glass measuring cylinders, flasks, pipettes and burettes, sample bottles, desiccators, bowls, cups and annealing below.

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Instruments for mechanical treatment of samples
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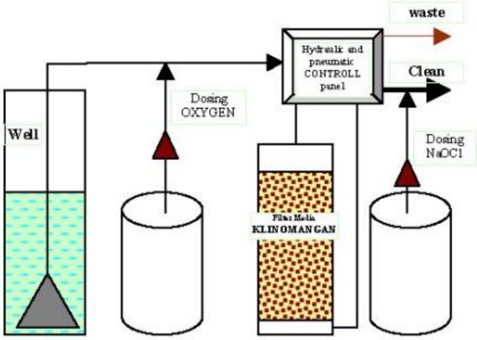
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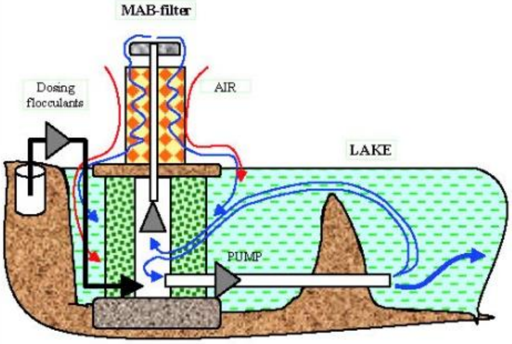
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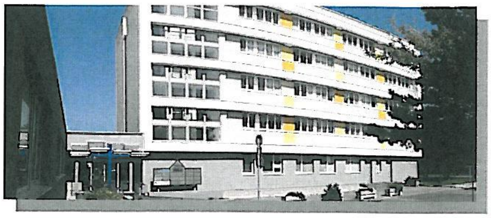

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