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HYDROGEN STORAGE AND DYNAMICS IN A NANO-CLAY MATERIAL

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Countries around the world have set a target of decarbonizing the planet by 2050. Several approaches need to be developed in parallel for this purpose. One of them is the implementation of negative emission technologies. Another is the use of green hydrogen. Hydrogen is the carbon-free fuel per excellence because its combustion, or its use in fuel cells, emits only water. At present, the limiting point to a massive deployment of technologies using hydrogen for energy purposes is its storage. The recent discovery of high hydrogen contents in clay-rich rocks [1] shows the potential of clays for hydrogen storage. However, this has been largely unexplored up to now.

We have found that pre-laponite, obtained as an intermediate stage of the synthesis of laponite [2], has promising storage characteristics at ambient temperature and under moderated pressure, where pressurization represents only a few % of the total energy stored. X-ray scattering and Infra-Red spectroscopy show that the local structure of pre-laponite is similar to that of laponite, while long-range order is strongly reduced (lateral dimension of the particles~4nm).

To understand the highest H_2 storage capacities of pre-laponite, we have performed inelastic neutron scattering (INS) experiments (spectrometer PANTHER at Institut Laue Langevin). INS is extremely useful in probing locally the direct vicinity of adsorbed molecular H_2. The INS spectrum of a free H_2 molecule is characterized at low temperature by a sharp and well-defined rotational feature at an energy of 14.7 meV corresponding to the transition of H_2 from a para- (molecular spin S = 0, angular momentum J= 0) state to an ortho- (S = 1, J = 1) state. The para-to-ortho transition line J_{01} has a three-fold degeneracy which is lifted as a function of the local symmetry of the adsorption site, with line-shifts that are dependent on the interaction between the H_2 molecule and the adsorption site. At 41K, the J_{01} peak exhibits a fine structure which is fitted by two gaussian lines with an intensity ratio of 2:1 (low energy component: high energy component). The splitting is in line with H_2 axis lying parallel to the adsorption site and attractive potential wall V~ -53 K. At lower temperature, a second type of adsorption site, with smaller potential value |V|<6K, is evidenced.

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ZEIN-SEPIOLITE BIONANOCOMPOSITE MAGNETIC FOAMS FOR REMOVAL OF POLLUTANTS IN WATER

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There is currently a growing interest in the exploration of clay minerals with fibrous morphology, such as sepiolite and palygorskite, to develop a wide variety of functional and multifunctional materials. The high surface area and the presence of silanol groups aligned along their fibers offer the opportunity to anchor a large number of nanoparticles, which makes these clays very attractive to be used as nanoplatforms for various applications [1]. Thus, for example, magnetite nanoparticles can be easily assembled to sepiolite fibers from a ferrofluid, introducing in the resulting material superparamagnetic properties while preserving the main properties of the clay, as for instance its capacity to adsorb cationic dyes [2]. In the present communication, we have explored a new application of this type of Fe_3O_4-sepiolite nanoplatform that is here used as a filler in the preparation of superparamagnetic bionanocomposites. Specifically, we have prepared bionanocomposites based on zein and sepiolite shaped as foams and we have explored two alternative ways to introduce superparamagnetic properties in them. In a previous study, we had used zein, a protein obtained from corn, as a modifier of sepiolite and palygorskite to produce bioorganoclays of potential use in the development of additives for bioplastics [3]. Now, we have used zein as a biopolymer in which sepiolite or Fe_3O_4-sepiolite is incorporated to obtain bionanocomposite foams for removal of organic contaminants present in water. The idea is to take advantage of the hydrophobic properties of this protein to produce bionanocomposite foams capable of remaining stable in aqueous media. Various aspects related to the characteristics of the superparamagnetic foams prepared by infiltration of magnetite nanoparticles present in a ferrofluid versus those produced using Fe_3O_4-sepiolite as nanofiller will be discussed. Finally, results of their use in adsorption processes of a model contaminant, the herbicide 4-chloro-2-methylphenoxyacetic acid, will be introduced confirming the utility of this type of adsorbent bionanocomposite foams, which can be easily recovered from the aqueous medium using a magnet, for decontamination applications in open waters.

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EVOLUTION OF A LATERITE PROFILE DEVELOPED ON THE ALTER DO CHAO FORMATION (PRESIDENTE FIGUEIREDO, AMAZONIA, BRAZIL): INSIGHT FROM CRYSTAL CHEMISTRY OF KAOLINITE

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Crystal chemistry can be used to single out various populations of kaolinites that formed in different conditions at the scale of a weathering profile (e.g. Balan et al., 2007). In addition, from the pioneering study of Balan et al. (2005) on Amazonian weathering profiles located in the Manaus region, dating kaolinite with electron paramagnetic resonance spectroscopy (EPR) has been applied on laterites from India, Brazil and Australia (see Mathian et al., 2022 and references therein). In all cases, these studies revealed major discrete weathering episodes that could be related to the paleoclimatic or geodynamic evolution of the region. The study of laterites from the Manaus region revealed two major weathering episodes with contrasting kinetics, the first one in Paleogene followed by a rejuvenation of profiles at late Miocene, (Balan et al., 2005; Guinoiseau et al., 2021). Here, we present new results on a profile developed on Alter do Chão formation in Amazonia, Brazil, and located 120 km north Manaus. We use EPR data to distinguish between populations of kaolinites according to their degree of local crystalline disorder and concentration of dilute structural Fe^{3+}. In addition, preliminary EPR dating of kaolinite using an improved protocol will be compared to ages previously acquired in the Manaus region. Results will be discussed in terms of profile evolution and climatic forcing.

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CANISTER CORROSION ACCELERATED BY 14 KGY GAMMA-RADIATION: IMPACT ON BENTONITE PROPERTIES

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High level radioactive waste repositories are multibarrier system, where the waste is confined in a metal canister surrounded by a compacted bentonite barrier. At the canister / bentonite interface, different processes (temperature, irradiation, hydration and corrosion) will affect the bentonite properties. The objective of the study is to analyse if the integrity of the bentonite barrier is maintained upon a gamma-irradiation accumulated dose of 14 kGy, representative of a dose expected after 40 years of repository operation. This irradiation may accelerate metal corrosion, affecting the geochemical properties of the interface.

Four different types of samples were prepared to simulate the metal canister / bentonite interface in different scenarios. They consist on cylindrical samples of 1 cm in diameter and 1 cm thickness, made of compacted bentonite clay: (1) alone, or covered with (2) a Cu disc representative of the Swedish container concept, (3) a C-steel disc customary of the Swiss concept or (4) a thin layer of powdered magnetite, positioned over one of the clay surfaces. Each of these four sample types was prepared at two clay compaction densities (1.4 and 1.6 g/cm^3) and at two different water saturation degrees (60 or 100%), by hydrating the clay with the corresponding pore water. Reference powder phases of each material were also studied for comparison.

Compacted and powdered samples were gamma-irradiated, in a pool-type facility with ^{60}Co source during eight days, achieving the required an accumulated dose. Afterwards, samples were dismantled and bentonite, metal discs and oxides were analysed by different techniques (FTIR, SEM, DLS, zeta potential,…) to identify gamma-radiation induced changes, in comparison to their non-irradiated reference state. The impact on microbial activity is analysed elsewhere on equivalent samples, as additional agent accelerating corrosion.

In bentonite samples, where no additional material was included, no significant structural, compositional or stability changes were observed. The bentonite samples with Cu discs did not show significant changes either, because Cu disc corrosion was limited. However, C-steel discs experienced appreciable corrosion and magnetite showed appreciable structural alteration as well. The released corrosion products altered the physico-chemical state of bentonite and the overall impact on the barrier performance at the long-time should be considered.

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EXPANSION BEHAVIOUR OF BENTONITE COMPACTED AT DIFFERENT DENSITIES IN FRACTURES OF WIDER APERTURES

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Compacted bentonite barriers in high-level radioactive waste repositories must meet specific containment, retention, swelling and sealing properties to ensure long-term safety. When the bentonite barriers is hydrated with water coming from the host rock, the clay dispersion [1] and the developed swelling pressure promote the expansion of the clay in the surrounding fractures [2]. This expansion can deplete the mass of the clay barrier compromising its properties.

This work experimentally analysed the expansion of compacted bentonite samples in custom artificial smooth horizontal fractures made up of methacrylate to visualise and quantify the expansion [2]. Bentonite samples were compacted at different densities (1.2 to 1.65 g/cm^3) and emplaced in the centre of fractures with variable aperture (0.2 to 0.6 mm). Experiments were carried out with a commercial Na-homoionised bentonite, previously equilibrated with 10^{-3} M NaCl, used to fill-in the fractures. The clay was hydrated under stagnant conditions, the expansion process was monitored taking periodic photographs during 30 days, time after which the fractures were dismantled to quantify the mass of eroded clay in each case.

Results showed that the clay expansion lengths in the fracture, and the total expanded mass, depend linearly on the compaction density, the higher the density the higher the expansion, in all fracture apertures analysed. This result contrasts with clay free dispersion studies carried where the dependence with sample compaction density was exponential [3]. This suggests that the fracture aperture and the physical-chemical conditions of the expanded material (gel nature, viscosity,…) play an important role, limiting the expansion. The data obtained contribute to the development of predictive models for bentonite barrier erosion, under real repository conditions.

The research leading to these results was partially funded by the Swedish Nuclear Fuel and Waste Management Company (SKB) under BENERO and by the Spanish Ministry of Innovation and Science (PID2019-106398GB-I00, ARNO Project).

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EFFECT OF PUMICE SCRAPS ON TECHNOLOGICAL PROPERTIES IN SILICATE CERAMIC TILES

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The effects caused by the global pandemic first and the conflict between Russia and Ukraine in Europe later, caused a change in the supply chain of ceramic raw materials. By considering a typical composition for sintered ceramic tiles, it contains about 40% of kaolinite and ball clays, about 45% of feldspars and about 15% of quartz. Nowadays, Italy is highly dependent on foreign raw materials as it has a very low production of clays and feldspars compared to the actual demand. Clays have been imported mainly from Ukraine and Germany but, unfortunately, due to the conflict, the supply chain of Ukrainian clays has stopped causing a sharp decrease in the quantities available. On the other hand, feldspars come from Turkey. These are non-renewable natural raw materials and therefore in the long term can have problems in their supplying, so it is necessary to find alternative solutions to their use.

The goal of our work, derived from the collaboration between Academia and the ceramic company, was to totally replace the foreign feldspars, partially reduce the clay content and replace the foreign clays, to a small part, with Italian clays, as well as to reduce the total number of raw materials used in ceramic body production. The first step was to develop a mix that could replace feldspars maintaining the properties made from pumice, feldspar and fired scrap tiles "chamotte". Pumice and feldspar used are Italian extraction scraps. The ceramic mixture was balanced to obtain approximately the same amounts of oxides and crystalline phases as the mixture in use by comparing the chemical and mineralogical analyses of the raw materials. The mix was characterized to verify that it did not negatively affect the rheological properties of the suspension. Then the mix was inserted inside the ceramic body, produced in the company, replacing the Turkish feldspars; the resulting slip and the fired sample were characterized (viscosity, density, linear shrinkage, water absorption and raw tensile strength). The thermal and densification behavior of the ceramic batches were evaluated by DTA-TG and dilatometry techniques, respectively.

The experiment was carried out simulating the industrial cycle at laboratory scale, but the samples were glazed and fired in the company's production cycle (48 minutes, 1210°C). This mix of residues allows to obtain ceramic tiles with technological properties similar to commercial ones, reducing the amount of non-renewable natural raw materials. According to UNI EN 14411 ISO 13006, the obtained tile samples could be classified in the BIa group (WA≤0.5%, B.S>35 MPa).

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ONSET OF THE CARNIAN PLUVIAL EPISODE: A RECORD BY CLAY MINERALS FROM THE MISURINA STRATIGRAPHIC SERIES (DOLOMITES, ITALY)

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The Carnian Pluvial Episode (CPE) was a climate and biological crisis that occurred in the early Late Triassic (ca. 234 to 232 million years ago) and is recorded worldwide in both marine and terrestrial successions [1]. The CPE has been linked to large igneous province volcanism, which would have injected large quantities of volcanic CO_2 into the Carnian atmosphere and triggered global warming and a strong enhancement of the hydrological cycle [1]. To understand the physical-chemical weathering processes that occurred at the onset of the CPE, we analyzed the clay mineral composition of 112 samples taken from a basinal stratigraphic series outcropping near Misurina (Auronzo di Cadore, Dolomites, Italy). In the marine sedimentary succession of Dolomites, the CPE is marked by a crisis of the early Carnian microbial-dominated high-relief carbonate platforms and an increase of siliciclastic deposition. The Misurina section consists mainly of claystones and marls, in which a transition from prevalent grayish and light brown pelites (San Cassiano Formation) to dark gray marls (Alpe di Specie member of the Heiligkreuz Formation) is recorded. We performed whole-rock sample (bulk) XRD analysis from which the overall quantitative mineralogical composition by Rietveld method was obtained. Analyses on oriented mounts of the <2μm fraction in air-dried, ethylene-glycol saturated, and heated form, were also performed for the accurate identification of clay minerals. The quantitative analysis of the mineralogical phases shows that the predominant fractions are represented by clay minerals (70.24–23.13%) and carbonates (70.30–21.76%). Among the clay minerals, the predominant phase is represented by interstratified illite/smectite (I/S = 63.88–19.70%), while an enrichment in kaolinite (+1.70%) and illite (+1.01%) is observed at the San Cassiano–Alpe di Specie transition. The increase of kaolinite and illite is parallel to an increase of pyrite. Higher kaolinite content, which is also documented in other marine and terrestrial settings during the CPE [2][3], suggests intensified hydrolysis processes in continental landmasses and can thus be interpreted as the evidence of stronger hydrological cycle and higher chemical weathering. This mineralogical change appears to be coeval with the onset of the CPE, i.e., the first negative C-isotope excursion as observed in the same stratigraphic interval in a nearby section of the Dolomites.

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THE ROLE OF CLAY MINERALS IN THE PRESERVATION OF MARTIAN ORGANICS, ANALYSES OF MARS ANALOG SAMPLES AND IMPLICATIONS FOR THE CURIOSITY ROVER ON MARS

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On early Earth, clay minerals may have provided a likely substrate where organic matter could have been concentrated and possibly transformed by abiogenic catalytic reactions to polymeric organic networks that were the forerunners of biopolymers. Ancient organic molecules such as chlorine and sulfur-bearing organic compounds, fragments of alkyl and aromatic compounds, and medium-chain length alkanes were recently discovered in samples containing clays by the Sample Analysis at Mars (SAM) instrument onboard the Curiosity rover. Among the many types of organic compounds of fundamental importance for life, it is amino acids that have attracted a lot of attention, because they are the building blocks of proteins and were found in Martian meteorites. However, amino acids have been not, up to date, detected by Curiosity rover instruments. To understand possible limitations of the rover instruments in detection of amino acids and evaluate the derivatization and extraction efficiency of the SAM instrument, we prepared four SWy-2 montorillonite-glycine samples with the glycine solutions corresponding to 0.5, 1, 2 and 20 CEC (cation exchange capacity) of SWy-2. Four SWy-2-glycine samples with varying glycine concentration were characterized by XRD and FTIR-ATR analyses to verify the presence of glycine in the interlayer of SWy-2. These samples, without and with Mg perchlorate (to study an effect of O_2 evolved during heating in SAM), were further analyzed by lab EGA (evolved gas analysis) and pyrolysis GCMS instruments under SAM-like operating conditions and the data were compared with the data of Martian samples containing clay minerals. Lab EGA data showed that trends in CO_2 evolved from the glycine-smectite samples is not fully consistent with the CO_2 from Martian samples, but when perchlorate is added there are similarities. In SAM analyses this CO_2 could derive from the thermal breakdown of oxidized organic compounds (e.g., oxalate minerals) or from the oxidation of reduced organics during heating; our data suggests that oxidation of interlayer amino acids could produce some of that CO_2. SAM-like wet chemistry results indicate that glycine was only detectable at the two highest glycine concentrations (2 and 20 CEC) and that flash-pyrolysis experiments (fast heating up to 300°C) were more efficient for the detection of glycine. Although flash-pyrolysis cannot be performed with SAM, an increase in the ramp rate up to 70°C/min may be considered for future experiments on Mars to improve the extraction and derivatization efficiency of amino acids.

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STUDY OF CLAYS AND DEFLOCCULANTS INTERACTIONS BY THE STATISTICAL METHOD OF MIXTURE DESIGN

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In the production of ceramic tiles, the clays and the other raw materials are reduced in size and homogenised by milling. Usually, this stage process is conducted by continuous wet-grinding in cylindrical or conical mills. To guarantee a high solid content (65-72 wt%) with a suitable viscosity, deflocculants, suspending and dispersing agents are used. Deflocculants are substances that increase the fluidity of the ceramic slips by two different actions: as fluidificant (reducing viscosity) and as dispersant (increasing the repulsive forces). They guarantee good particle dispersion by increasing the Z potential and so avoid flocculation.
Inorganic substances (such as silicates, phosphates and carbonates sodium salts) or organic additives, generally polyacrylates of sodium or ammonium salts with different molecular weights, are common, used. They are normally poly-electrolytes with steric, electrosteric properties and sequestrating complex action.
In literature, only a few papers consider the combined effect of two or more deflocculants in the clay suspension while in industrial production this is the usual practice. In this way, the apparent viscosity values and the time-dependent behaviour observed using the most efficient deflocculant might be obtained with an appropriate mixture, but at a lower cost. A deeper knowledge of the mutual interaction between the additives can allow an optimisation of the ceramic process.
In this study three clays a kaolinitic, an illitic-kaolinitic and an illitic -chloritic, widely used in industrial ceramic production were chosen. The chemical additives used were: anhydrous sodium, metasilicate (NaSil); sodium tripolyphosphate (NaTPP) and sodium polyacrylate (NaPol). For each clay typology, concentrated suspensions (55-70 wt%) were prepared by fast ball mill grinding for 20 min with different amounts of additives. The rheological behaviour was investigated by Rotational Rheometry at room temperature using a cylindrical concentric sensor[1]. The influence of two or more additives was investigated by the statistical method of mixture design, a part of the design of experiments (DOE)[2]. Correct experimental planning generates a 3D map of the response over a specified region of the formulation with this methodology it is possible to discover the critical variables, define mathematical models and engineer the rheology of suspensions.

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DIFFERENT KAOLINITE GENERATIONS IN BAUXITE PROFILES FROM NORTHERN BRAZIL: CONSEQUENCES FOR THE ALUMINA PRODUCTION AND BAYER PROCESS

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The Pará state (northern Brazil) holds several world class bauxite deposits, besides the second world's largest alumina refinery (Hydro Alunorte), with a nominal capacity of about 6,3 million tones/year. The main ores are typical gibbsitic bauxites whose profiles exhibit complex structuration in terms of horizon succession, including two bauxite levels separated by a ferruginous crust (Negrão et al., 2018). Since gibbsite is typically formed from the breakdown (hydrolysis) of kaolinite, one observes a progressive decreasing content of the latter, from the base to the top of the profiles, and inversely, an upward increasing of gibbsite.
Upper bauxite horizons are usually low-grade ores because of the high kaolinite contents, the so called HRSB, High Reactive Silica Bauxites (Smith, 2009). Besides that, new kaolinite generation – probably resulting of silicification of underlaying gibbsite horizons – are usually high disordered (high-defect) kaolinites.
Nowadays, the high-grade bauxite ores of the most important mines in the amazon region are rapidly exhausting, which turns the exploration to the HRSB. The processing of such lower grade bauxites became a challenge because in the conventional conditions of the Bayer process, the kaolinite is undesirably leached by NaOH solution, and then precipitated as sodalite. The formation of this phase brings a significant increase in process costs, both by increasing the processing time as the irreversible loss of NaOH withdrawn from the system to form sodalite, which is then discarded in the residues (red mud) basins.
Given this metallurgical problem, in this work, sodalite has been synthesized using bauxites from different parts of the profile in order to investigate the crystal chemistry of sodalite formed in conventional conditions of the Bayer process, so that, from these results, studies to reduce these losses of the process and facilitate the processing of HRSB can be developed in the future. Residues (red muds) obtained from the processing of the different bauxite horizons were also evaluated in order to better understand the mineralogical conditions of such wastes.

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SWELLING BEHAVIOUR AND INTER-AGGREGATE POROSITY EVOLUTION IN COMPACTED BENTONITE

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Karlsruhe Institute of Technology (KIT) has developed a hydraulic sealing system called the Sandwich sealing system [1], which is intended for use to seal high-level radioactive waste shafts in underground repositories. The system consists of sealing layers (DS) of compacted bentonite alternating with equipotential layers (ES) of higher hydraulic conductivity. This design promotes even hydration of the DS layers, resulting in improved functionality and better overall sealing performance. Therefore, this system is adapted by the German authorities in their concepts for deep repositories in claystone formation (i.e., Opalinus clay) [2]. Within this framework, the Sandwich Support Project 1(Sandwich-SP1), a joint project of KIT and Ruhr-Universität Bochum (RUB), investigates the swelling behavior and heterogeneity of two German bentonites, Securisol UHP is from Ruppach, Lower Saxony, Germany, and Calcigel is from Bavaria, Germany. Within the framework of the Sandwich-SP1 project, the present study aims to achieve two main goals. Firstly, to identify the kinetic model for cation exchange that takes place when bentonite comes into contact with a saturation fluid containing different cations than those already present in the interlayer of the smectite phase in the bentonite. Secondly, it aims to visually and quantitatively analyze the porosity development in the bentonite during saturation, while also monitoring the development of the swelling pressure. To achieve these objectives, the raw bentonite material is processed and purified to obtain smectite-rich and homo-ionic material [3]. Additionally, cells suitable for X-ray micro-computed tomography (μCT) were developed, which enable recording of the swelling pressure of the sample, as well as conducting μCT measurements.

We will present preliminary results from the Sandwich-SP1 project, which include the mineralogical and chemical properties of raw and purified bentonites, as well as recorded swelling pressure curves from natural bentonite samples with different dry densities and sample heights. Furthermore, we are currently processing μCT 2D and 3D images recorded before and after the hydration of the bentonite samples. This work is expected to yield valuable insights into the evolution of inter-aggregate porosity in compacted bentonite samples during the hydration process, as well as the optimal sample size needed to capture this evolution of porosity and the associated changes in swelling pressure curves.

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EFFECT OF CLAY PARTICLES' PREFERENTIAL ORIENTATION ON THE DIFFUSION OF WATER IN CLAYEY MEDIA

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Due to their ability to significantly slow down the diffusive transport of water and solutes when compacted, clay minerals are widely used as the main components of natural and artificial barriers that isolate municipal and radioactive wastes from surrounding ecosystems. Although significant research has been conducted on diffusion in clay-rich materials, a quantifiable evaluation of the impact of the preferred orientation of lamellar clay particles is still lacking. Regarding clay-rich media, some authors (e.g., [1]) have reported that the effective diffusion coefficient (D_e) of a water tracer is approximately six times higher when measured parallel to the sedimentation plane of the particles compared to when it is measured perpendicularly. In 2020, Dabat et al. [2] established experimentally a quantitative link between the anisotropy of water diffusion tensor and the degree of anisotropy in clay particles' preferential orientation for porous media made from non-charged/non-swelling clay (i.e., kaolinite), which only exhibit interparticle porosity. Within this framework, the current study investigated the correlation between the degree of anisotropy in clay particle orientation and the anisotropy of the water diffusion tensor in porous media made from clay particles characterized by a significant negative layer charge.

The porous media used in this study were made from two high-charge clay minerals: Na-Vermiculite, which is a swelling clay, and Na-Illite, which is a none swelling clay. The porous vermiculite media exhibit dual porosities (i.e., interparticle and interlayer), that are both accessible to water, whereas the Na-Illite media only exhibit interparticle porosity. Na-vermiculite was chosen for its lack of osmotic swelling when saturated with water, which maintains a clear separation between interparticle and interlayer porosities [3]. Through-diffusion (TD) experiments were conducted on two Na-vermiculite and two Na-illite porous media, all designed to have a similar volume of interparticle porosity but varying degrees of preferential particle orientation. The latter was quantified through the order parameter $\langle P_2 \rangle$ obtained from X-ray scattering analyses [2], with values ranging from 0 to 1 for purely isotropic and anisotropic media, respectively.

TD results showed a considerable decrease in the D_e of HDO for porous media characterized by higher $\langle P_2 \rangle$ values for both clay minerals. Additionally, the De values measured perpendicularly to the sedimentation plane in vermiculite media were nearly identical to those obtained from kaolinite and illite media with a total porosity value comparable to the interparticle porosity in the vermiculite media. The results suggest that the contribution of HDO diffusing in the interlayer porosity of vermiculite media is insignificant compared to the HDO diffusing in the interparticle porosity. Additionally, the experimental results were in reasonable agreement with those obtained from Brownian Dynamic (BD) simulations conducted on analogous virtual porous materials. Further details will be discussed during the presentation.

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NEW INSIGHT ON THERMAL STABILITY OF ARTIFICIAL RADIATION-INDUCED DEFECTS IN KAOLINITE: REINFORCING THE PROTOCOL FOR EPR DATING

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All natural kaolinites contain several radiation-induced defects (RIDs), among which one, the so-called A-center, is stable at a geological time scale and is used as a geochronometer (Balan et al., 2005; Allard et al., 2018). Stability at room temperature is extrapolated from isothermal annealing experiments and was well-established for natural RIDs in reference kaolinites (Clozel et al., 1994). However, the stability of artificially produced defects used for dosimetry and subsequent dating of the clay mineral formation has never been studied. In this study, we aim to verify on KGA-2 and disordered soil kaolinite that artificial A-centers used for dating are also stable enough defects. Our experiments include the following steps: (i) the production of defects in kaolinites by irradiation with He^+ ions to simulate the effect of ionizing radiations, (ii) preliminary heating of samples at 250 °C to remove unstable RIDs, (iii) annealing kinetics at the temperatures of 350°C, 375°C, and 400°C over 120 hours, (iv) Measurement of A-center concentration by EPR for both naturally- and artificially-irradiated samples. The results provide a comparison of the kinetics of natural and artificial defects decay. The kinetics parameters of the annealing were calculated by considering a second-order reaction, as a first-order function does not fit the data. Activation energy E_a of the reference and natural samples ranges between 2.6 to 1.7 eV, and the half-life values extrapolated to room temperature for artificially-irradiated samples are consistent with the previous studies, i.e., $t_{1/2} > 10^{12}$ yrs. Consequently, our results show that artificial A-centers are also stable at the geological time scale and thus mimic natural ones, reinforcing the methodology of EPR dating with kaolinite.
Keywords: Kaolinite; EPR; RID’s

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REVEALING WEATHERING EPISODES IN LATERITE DEVELOPED ON THE PROSPERANÇA FORMATION (AMAZONIA) USING ELECTRON PARAMAGNETIC RESONANCE SPECTROSCOPY OF KAOLINITE

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Geodynamics and climate strongly impact the formation and evolution of weathering covers at the Earth's surface. Among them, laterites sensu lato cover 1/3 of emerged continents and 80% of the Amazon Basin (overlying on different parent rocks), extending to an overall surface of about 6.1×10^6 km^2. Despite their relatively simple mineralogy (mainly kaolinite and associated Fe oxides), laterites are complex open systems that could experience several weathering episodes. Therefore, it is essential to differentiate generations of secondary minerals and reveal the time frame of the evolution of weathering profiles. Crystal chemistry of kaolinite, especially with electron paramagnetic resonance spectroscopy, was shown to be appropriate to this objective through the combination of parameters of order/disorder and geochronology [1-2]. Together with (U-Th)/He dating of iron oxides, or K/Ar and Ar/Ar dating of Mn oxides, it participates in the growing knowledge of the time evolution of laterites in the Amazon Basin. Dating of kaolinite was initiated in the Manaus region on laterites developed over the Alter do Chao sedimentary formation [1]. Major weathering episodes were recognized in Paleogene (at depth) and at the end of the Miocene (in the topsoil), indicating a rejuvenation of the profiles [1-3]. Here, we studied a lateritic profile that developed on the siliciclastic sedimentary sequence of Prosperança formation in the Presidente Figueiredo district 120 km from Manaus, with a different parent rock and occurrence of a duricrust. With this study, we aim to characterize the geochemical and mineralogical properties of the horizons and reveal by EPR the kaolinite generations throughout the profile formed in different conditions. The next step, i.e., kaolinite dating of these generations, will help to understand the evolution of the profile and the relation of major weathering episodes with paleoclimatic conditions.
Keywords: Amazon basin; Laterites; Kaolinite; EPR Spectroscopy.

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PALYGORSKITE USE AS CORROSION INHIBITOR FOR INDUSTRIAL METALS AND ALLOYS

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The study deals with the use of palygorskite as corrosion inhibitor of two metals, aluminum and zinc, and their alloy (aluzinc), in a 0.5 M hydrochloric acid medium. The study was carried out by monitoring the free-corrosion potential and performing dynamic polarization measurements (Tafel curves) at different concentrations of inhibitor in solution. The measurements suggested that in a 0.5 M acidic medium, the surface of each of the three materials was attacked. The decrease in current density was very noticeable in aluminum and zinc at a level of 2 gL-1. A weak tendency to passivity was noticed for zinc and aluzinc. The experimental results obtained showed a decrease in the current intensity in the presence of the corrosion inhibitor in the acidic medium. The maximum inhibitory efficiency rate reached for the metals and their alloy was higher than 99 %. This percentage was obtained for aluminum and zinc in the presence of 4 gL-1 of palygorskite and 3 gL-1 for aluzinc.
Keywords: palygorskite, corrosion inhibitor, dynamic polarization.

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INVOLVED MECHANISMS WHEN EXPOSING OPALINUS CLAY FROM THE LOWER SANDY FACIES OF MONT TERRI SITE TO HIGHLY SALINE AND ALKALINE SOLUTIONS

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Nowadays, claystone is a subject of interest for researchers as it is considered as potential host rock for deep geological repositories in several countries due to its favorable hydraulic and mechanical properties as well as its good retention for radionuclides. During Excavation, a Damaged Zone (EDZ) is generated in the host rock. This EDZ is expected to be sealed with the infiltration of underground water (under a neutral pH and in absence of salinity). However, during the exploitation of the repository, alkaline plumes may seep from concrete degradation and saline plumes may seep from saline waste increasing the pH and salinity of the underground water. Thus, it is of paramount significance to study the chemical-hydro-mechanical behavior of claystone especially at the microstructural level to investigate the different involved mechanisms.

Two Opalinus Clay samples from the Lower Sandy Facies (LSF) of Mont Terri site were exposed in an oedometer cell for 31 days (1) to a synthetic water having the same chemical composition (osmotic suction 1 MPa and pH (7.5) as the underground water and (2) to a sodium nitrate solution having an osmotic suction of 34 MPa. A third sample was exposed for 17 days to a hyper-alkaline solution at pH=12.5. The pore size distributions of the three samples were determined through mercury intrusion porosimetry and nitrogen adsorption-desorption tests.

It was found that the pore network of the LSF Opalinus Clay is mainly composed of macropores (pore size > 50 nm) and mesopores (2 nm< pore size < 50 nm) according to the International Union of Pure and Applied Chemistry (IUPAC) classification. Also, while a higher density of macropores was detected at 34 MPa, a higher mesopore density and a more pronounced BJH peak were found at 1 MPa. These results were due to the transfer of water from the meso to the macro pores under the imposed osmotic gradient and due to the contraction of the clay particles as a result of the shrinkage of the diffuse double layer. As for the impact of alkalinity, a higher macropore density was recorded at pH=12.5 and the BJH peak increased from 3.81 nm at pH=7.5 to 3.87 nm at pH=12.5. These results were due to the acid-base attack, concentrated at the edges of the clay particles that have led to a dispersed structure with higher repulsive forces and to the dissolution of the clay minerals. In addition, the dissolutions of non-clay minerals (quartz and calcite) are to be considered. The results of this study help understand the evolution of the microstructure of the Opalinus Clay with salinity and alkalinity which is crucial for the assessment of the hydro-mechanical behavior of the claystone.

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INVESTIGATION OF ADVANCED SURFACE COMPLEXATION MODELING TO DESCRIBE OXYANION ADSORPTION ONTO MAGNESIUM-IRON LAYERED DOUBLE HYDROXIDES

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The clay mineral/water interface plays an important role with regard to the mobility of elements in the environment. There are a number of approaches to describe the behavior on the clay mineral surface, including different types of models. Of the various clay minerals, anionic clays, i.e., layered double hydroxides (LDH), are particularly interesting for environmental applications due to their ability to influence the mobility of both cations and anions. However, the main drawback of current studies is the modeling approach to describe the adsorption behavior, i.e., the predominant use of basic empirical models, which do not allow a detailed description of individual adsorption mechanisms. In contrast, surface complexation modeling (SCM) enables the description of specific binding arrangements to the surface of solid materials, thus providing more detailed information about the ongoing surface processes. Therefore, the use of advanced SCM, which is still rare for LDHs, appears more promising compared to empirical approaches. To fill this research gap, this study aimed to investigate the adsorption behavior of arsenate and phosphate on Mg-Fe LDHs using two different types of SCMs, i.e., the simple diffusion layer model (DLM) and the more advanced charge-distribution multisite complexation model (CD-MUSIC). The main advantage of using DLM is the relatively low number of input parameters, especially those related to the material structure. In contrast, the CD-MUSIC model allows to consider more material-unique characteristics and thus provides a better description of surface complexation mechanisms. Before the actual modeling, detailed analyzes of the solid phase were carried out, where it was found that at higher As/P concentrations and lower pH values, the removal mechanisms of these oxyanions are significantly affected by the structural changes of LDHs, i.e., formation of Fe-arsenates/phosphates. Therefore, the application of the newly developed SCMs was limited only to data with a preferential surface complexation mechanism, i.e., lower As/P concentrations. In general, a better fit was obtained using the CD-MUSIC model when combining two types of surface complexes: 1) an inner-sphere complex (i.e., chemical adsorption) at lower pH values, and 2) an outer-sphere complex. (i.e., physical adsorption) at higher pH values. Subsequently, the resulting model was successfully verified in competing As/P systems. It should be emphasized that our study is the first to propose a complete modeling approach using CD-MUSIC for LDHs. One of the advantages of this modeling approach is the possible implementation of outer-sphere complexes, which, according to our previous observations, also affect the resulting mechanisms in the case of oxyanion adsorption onto LDHs, and cannot be described by simpler models (e.g., DLM). The resulting models can subsequently be beneficial for studies dealing with the application of LDHs in environmental engineering systems and/or in the implementation of the LDH phase as a reactive surface in more complex modeling approaches, e.g., reactive transport models. However, in addition to LDHs, attention should also be focused on investigating new advanced SCMs describing the surface behavior of other clay minerals, especially those commonly found in soils, to elucidate in detail their role in influencing the mobility of elements in the environment, which is in current modeling approaches often insufficiently addressed.

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STUDY OF ENHANCED FLUORESCENCE OF CATIONIC DYE CRYSTAL VIOLET AFTER INTERACTION WITH EITHER PRISTINE OR BY ETHYLENEAMINES MODIFIED MATRIX OF SYNTHETIC HECTORITE.

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This work reports the effect of negatively charged layers of synthetic hectorite (Hec) on the spectral properties of adsorbed cationic dye – crystal violet (CV). CV exhibits very complex ultrafast excited state decay, which occurs in a few picoseconds [1]. Dye adsorption on the surface of the clay is expected to hinder the twisting of the phenyl ring that causes an emissive complexed state which can be relaxed by fluorescence. The only problem is that a high concentration of planar CV in the interaction with clay forms molecular aggregates. Two main types have been recognized: J- and H-aggregates. The H-aggregates are mostly nonluminescent and often exhibit properties of quenchers [2]. In the first place, two-component hybrids (Hec-CV) were examined. Besides, to improve the fluorescence of two-component systems, ethyleneamine compounds were introduced into the clay-dye systems. The measurements of absorption spectra of Hec-CV dispersions revealed the presence of all three species: main band related to monomers with a slightly hypsochromic shift of its maxima to the ~ 585 nm compared to CV in solvents (590 nm), shoulder at higher energies linked to H-aggregates ~ (500-550 nm), and distinguished band related to J-aggregates at ~ (615-680) nm. Modification of Hec-CV by ethylenamines led to ~ 5 nm shift of the main absorption band to lower wavelengths, suppressing the intensity of the shoulder and disappearance of the band related to J-aggregates. Moreover, bands belonging to J-aggregates in absorption and excitation spectra were noticed only in the samples with low concentration of the dye. Interaction of CV with hectorite particles caused the increase in the fluorescence intensity, but the trend was directly proportional only up to a certain concentration of the dye. Thus the additional amount of the dye had the opposite effect. With increasing dye concentration, the maxima of the main band of emission spectra of Hec-CV samples were shifted from ~ 655 nm to ~ 675 nm. Fluorescence lifetimes of CV in the proximity of Hec augmented lifetime from picosecond (CV in solution) [1] to the nanosecond scale. Further modification by ethyleneamines overall enhanced fluorescence intensities to the extent at least one order of magnitude higher than Hec-CV. Fluorescence spectroscopy showed new emission bands at lower wavelengths with much higher intensities than those observed in Hec-CV. However, the intensities of the bands at higher wavelengths were also significantly enhanced. Maxima of the main emission bands were observed to be in the range of 603-610 nm. The shift occurred due to the increasing concentration of the dye. Enhanced emission in the surfactant-modified samples was supported by the finding that species with longer lifetimes were populated to a higher extent.

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INTERACTION OF BEIDELLITE AND SAPONITE CLAY MINERALS WITH POLY(2-METHYL-2-OXAZOLINE): A DENSITY FUNCTIONAL THEORY STUDY

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Advanced materials based on clay minerals and polymers have gained considerable attention in the last decade due to their use in a variety of fields, such as biomedicine [1]. The development of clay-polymer nanocomposites aims to improve the thermal stability, mechanical strength, and barrier properties relative to the individual components. Unlike conventional micro fillers, even a small amount of clay minerals (< 5 wt%) as a nanofiller in a polymer matrix can significantly enhance its overall properties [2][3].
The layered structures of smectites, such as beidellite (Bd)) and/or saponite (Sap), consist of tetrahedral (T) and octahedral (O) sheets connected through apical oxygen atoms. The isomorphic substitution of trivalent ions (e.g., Al^{3+}/Si^{4+}) in the tetrahedral sheets and/or divalent ions in octahedral sheets (e.g., Fe^{2+}, Mg^{2+}/Al^{3+}) generates a negative layered charge. The interlayer cations, e.g., Ca^{2+}, Na^{+}, Li compensate this negative charge. Due to the cation exchange ability the polymers can be intercalated into the interlayer space of clay minerals. Other specific properties such as affordability, eco-friendliness, and abundance of the smectite clay minerals are prominent advantages for using it as a potential filler for clay-polymer nanocomposites[4]. The strong interfacial interaction between clay minerals and polymers explains the transfer of the load from polymers to clay minerals which results in better mechanical strength of the clay-polymer nanocomposites [2]. It is difficult to fully understand the interfacial bonding between clay minerals and polymers through experiments only, so the use of *ab initio* quantum mechanical methods such as density functional theory (DFT) method is an effective tool to obtain deep insight into the interactions between clay minerals and polymers [5].
This work reports the study of the interaction of beidellite and saponite clay minerals with the pentamer of poly(2-methyl-2-oxazoline) (PMeOX) by the DFT-D3 method. For the description of exchange-correlation energy, the Perdew, Burke, and Ernzerhof (PBE) functional based on the generalized gradient approximation (GGA) theory was used. The structural stability of both models, beidellite with the pentamer of poly(2-methyl-2-oxazoline) (Bd-PMeOX) and saponite with pentamer of poly(2-methyl-2-oxazoline) (Sap-PMeOX) were examined through hydrogen bond analysis and intercalation energies.

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CLAY MINERALOGY AT MIDDLE MIOCENE CLIMATIC OPTIMUM LOW BOUNDARY IN LACUSTRINE SEQUENCES IN THE ALCUBIERRE SIERRA (EBRO BASIN, NE SPAIN)

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The studied materials are dominantly lacustrine lutites and marls of the Lower Miocene in the Alcubierre Sierra, central Ebro Basin, dated from 17.7 to 16.2 Ma (Perez-Rivarés, 2016), thus embracing the lower boundary of the Middle Miocene Climatic Optimum (beginning ≈ 17 Ma).

The mineral assemblage of sheet silicates in the clay fraction is +illite, ± chlorite, ± smectite, ± kaolinite, and with minor contents of ± pyrophillite, ± palygorskite. Non-sheet silicate assemblage in the whole rock is + quartz, + potasium feldspar, + plagioclase, + calcite, ± dolomite, ± ankerite, ± siderite, with minor contents of ± gypsum, ± hematites, ± pyrite. The observed values for "illite crystallinity" measured as FWHM of 001 reflection of illite are in the range 0.100 – 0.350 º (2 theta , Cu K alpha 1). Based on the illite FWHM, two distinct intervals are observed below and above 17 Ma, with a marked increase of the average values above this age, indicative of an increase of chemical weathering in the source area. Similarly, the (illite + chlorite) / (kaolinte + smectite) ratio shows a decreasing trend, representing a decrease of the physical / chemical weathering ratio.

The delta ^{18}O measured on calcite of limestones and marls of the studied section evolves towards less negative values above 17 Ma, which can be related to a decrease in the evaporation / precipitation ratio, which is consistent with the aforementioned evolution of the clay mineral based proxies.

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RECYCLING TIONITE IN ROOFING TILE MANUFACTURING: AN EXAMPLE OF INDUSTRIAL SYMBIOSIS

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Tionite is the insoluble residue from the titanium-bearing mineral dissolution process in the sulphate TiO_2 production process. The residual acidity coming from the acid-leaching solution wetting the solid is neutralized by adding CaO and/or $CaCO_3$. Tionite is a fine-grained material with D_{50} = 7 microns, consisting of gypsum, rutile, pseudobrookite (iron titanate), calcite and a large fraction (around 50%) of amorphous components. It's coulor as received is brown/reddish, and the substantial presence of titanium dioxide confers to the virgin material some photocatalytic activity. The feasibility of including tionite in the raw materials for brickmaking has been previously assessed by Dondi et al. [1]. In the present work, the use of tionite in the production of roofing tiles is assessed, both with laboratory tests and with industrial pilot production. The influence of up to 15% tionite substitution on the cake body working moisture, drying sensitivity, shrinkage and bending strength in the green and fired conditions, water absorption, bulk density, efflorescence, and colour has been determined.

The clay quality and the process firing temperature have been found to play an important role in the performance of the fired materials. Carbonate-rich bodies are affected by tionite more during drying than during firing; carbonate-poor bodies range from little changes to consistent performance worsening especially when low firing temperatures are used and less liquid phase is formed at high temperatures. The tionite extent of washing before filtration affects the amount of retained sulphates, and thus the amount of gypsum after neutralization. More gypsum increases tile permeability and affects performance. The presence of tionite has no influence on the penetration of oxidation in the body during firing, and no efflorescence was observed. On the contrary, a slight whitening of the surface colour occurred when using red clay at the highest tionite content, while no significant colour variation has been observed when using a clay with less iron and more calcium, giving a clearer shade.

The possibility of valorizing tionite and using it in the production of roof tiles is an interesting example of industrial symbiosis. The production of 1 ton TiO_2 generates about 1,75 tons of copperas ($FeSO_4 \times 7H_2O$), 1,56 tonnes of ferric sulphate monohydrate and 0,25 tons of tionite, using 1,78 tons of titanium-bearing minerals. About 20000 tons/year tionite are produced by the plant located near Scarlino (Gr) in Tuscany, which is nowadays totally landfilled. Vice versa there are several furnaces producing bricks and roof tiles throughout Tuscany, taking advantage of the region's clay deposits. The recycling of tionite in the making of roof tiles would have the benefit of eliminating landfilling of the 20000 tons/year tionite, and reducing excavation of virgin clays for an equivalent amount.

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HEAVY METALS REMOVAL FROM POLLUTED WATERS USING ZEOLITE FORMED FROM NATURAL SOURCES AND WASTE

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Water pollution represents an increasing problem in most countries around the world, and heavy metals remediation is one of the major concerns. Several strategies have been proposed to reduce the level of these pollutants using chemical processes including eco-friendly methods based on the use of natural sorbents as alternative and green extractive materials, such as biomaterials or minerals. Among minerals, zeolites have been widely used to solve environmental problems due to their peculiar structural features. The attention to polluted water remediation using such minerals has widely focused on the application of natural/modified zeolite [1], although many synthetic equivalents exhibit similar or higher properties [2]. In addition, synthetic zeolites can be produced at lower cost from waste [3] in accordance with the principles of sustainable circular economy and they have successfully used for heavy metals removal from aqueous solutions [4].
In this work, synthetic zeolites obtained combining natural sources (bauxite and obsidian), pure alumina/silica reagents, and waste material (red mud) were tested for heavy metals removal. The efficiency of the formed sodalite and zeolite with LTA and FAU topology (zeolite A and X, respectively) was evaluated in distilled water, tap water and wastewater treatment plant effluent, focusing on the mechanism controlling the remediation process. Thermodynamic and kinetic experiments demonstrated that all the newly-formed zeolites are able to remove the pollutant elements. The toxic metals adsorption mechanism is due to the ion exchange and the precipitation on the synthetic zeolites. Based on XRPD Rietveld analysis, it was found that host–guest interactions between the framework oxygen atoms, co-adsorbed water molecules and cations take place inside the zeolite channels, according to the type of the newly-formed mineral.
Finally, the magnetic properties of the synthetic products, along with their adsorption capability under relevant environmental conditions, makes these zeolites excellent candidates for heavy metals removal from polluted water.

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TRANSFORMATION OF SI-MG(-AL) GELS INTO MAGNESIAN CLAYS BY HYDROTHERMAL REACTION IN SEAWATER. THE CASE OF STRýTAN ALKALINE VENT (ISLAND)

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Hydrothermal circulation of seawater through the oceanic lithosphere has played a major role in the prebiotic chemistry and habitability of the oceans. This is due to the permanent chemical disequilibrium conditions that exist between the silica-rich alkaline hydrothermal fluids and the acidic primitive ocean. Submarine hydrothermal fields located near Iceland (Strýtan) are considered as possible analogues of places on the early Earth that could have hosted the emergence of life due to the existence of significant ionic gradients capable of sustaining life in inorganic membranes.

Strýtan is a shallow hydrothermal system consisting of three columnar structures 25-55 m high located 65 m deep on the eastern slope of Eyjafiord in North Iceland [2]. Hydrothermal activity occurs primarily in the largest structure, with a flow of about 50 L/s of a fluid at a temperature of 60-72 °C. It is a low-salinity, silica-enriched, alkaline fluid with a non-significant H_2S and metal content. The chimneys in Strýtan are composed mainly of amorphous silicates, magnesian clay minerals, and occasionally carbonates.

This project aims to elucidate the processes of chimney formation by precipitation of the constituent minerals. Synthesis experiments were conducted to simulate underwater hydrothermal conditions at low temperatures and pressures (50, 80, 110°C). The starting material was magnesium (aluminum) silicate gels obtained by coprecipitation from the mixture of Na2SiO3 and MgCl2 (AlCl3) solutions, to obtain a Si:Mg ratio close to saponite [3]. Two types of gels were prepared, a SiMg (4:2.3) gel and a SiMgAl (4:1.7:0.4) gel. The hydrothermal treatment was carried out with synthetic seawater for 1 to 6 months, and the solid products were characterized by XRD, SEM-EDS, TEM-AEM.

After aging for 1 to 6 months, the starting gels show partial transformation into a low crystallinity phyllosilicate, characterized by diffraction bands at 1.54-1.53 Å. The gel grains were formed by rounded nanometric particles, being more compact in SiMg gel. Small flakes and honeycomb structures developed on the surface, which are characteristic of smectites. No difference in composition was observed from particle to particle. Nanodomains with 2-4 layers of 7 Å periodicity were identified by TEM. Temperature apparently favored the gels transformation, but no relevant differences were observed with time. Compared with natural samples, gels seemed to mimic the first stage of crystallization of Mg-silicates in Strytan, although further evolution was not observed under our experimental conditions (temperature, time, absence of flow). The absence of flow in the experiments prevented the development of characteristic structures associated with flow conditions. Currently, experiments are being conducted in conditions closer to those observed in the submarine vent.

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UNRAVELLING AND CHARACTERIZING HALLOYSITE DEPOSITS IN PEGMATITE PROVINCES FROM SOUTHEASTERN, BRAZIL

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Kaolin is a rock formed by hydrated aluminum phyllosilicates, which may contain impurities such as quartz, mica, feldspar, iron oxides, etc. Mineralogically, it consists mainly of kaolinite and halloysite. More rarely, dickite and nacrite may also occur.

Halloysite is a kaolinite polytype that has one more water molecule in its structure, differing mainly by its tubular shape and reduced size. Because of these properties, there has been a growing interest in the study of halloysite due to applications in different sectors of nanotechnology with an emphasis on health and agricultural areas.

The clay mineral occurs in two types: 10Å-halloysite ($Al_2Si_2O_5(OH)_{4}.2H_2O$) when water molecules are present in the interlamellar region and 7Å-halloysite ($Al_2Si_2O_5(OH)_4$) when such molecules are missing.

Halloysite deposits can be classified as primary, when formed *in situ* due to alteration of silicates by weathering or hydrothermalism, or as sedimentary/secondary when originating from sedimentary processes. Primary deposits are more common being halloysite generally associated with intrusive acidic rocks, granites, anorthosites and pegmatites.

The objective of this study was to identify and characterize different occurrences of halloysite from four samples of weathered pegmatites from southern Brazil. Under a hand magnifying glass, these pegmatites are whitish in color, friable and the main mineralogy is composed by quartz grains, feldspar, muscovite/biotite and kaolin. The samples were also analized through X-ray diffractometry (XRD), scanning electron microscopy (SEM) and X-ray fluorescence (XRF).

XRD indicates the presence of kaolinite/halloysite at 7Å (001), quartz at 3,34Å and 4,25Å, mica at 10Å, K-feldspar at 6,48Å and 3,24Å, plagioclase in one sample at 3,18Å, goethite at 2,4Å and gibbsite in one sample approximately at 5Å. Images generated by SEM showed kaolinite in booklet format and tubular halloysite. Chemical analysis by X-ray fluorescence indicated the predominance of SiO_2, Fe_2O_3, Al_2O_3 and K_2O. Based on these results, it is possible to confirm the presence of halloysite in several pegmatites in the states of Rio de Janeiro and Minas Gerais (southern Brazil), nonetheless open regarding its true economic potential in the region.

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CHARACTERIZATION OF BRAZILIAN MONTMORILLONITE AND PALYGORSKITE SAMPLES AIMING THEIR APPLICATION AS ANTIBIOTICS ADSORBERS

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Pharmaceuticals belong to the class of emerging pollutants that have been identified in low concentrations in the environment and that can negatively affect human and environmental health [1]. Among the classes of drugs, antibiotics stand out, which have numerous applications in both human and veterinary medicine. Thus, several studies have focused on the remediation of these contaminants, through adsorption. Clay minerals are one of the most important adsorbents due to their high abundance, large specific surface area, negative charge, and hydrophilic surface. In Brazil, among the clay minerals used for adsorbent purposes, palygorskite and montmorillonite [2,3] stand out. Both are 2:1 aluminosilicates, presenting two tetrahedral layers containing silicon (Si) and oxygen (O) and an octahedral layer containing di- and trivalent metals, such as aluminum (Al), magnesium (Mg) and iron (Fe), which they can be isomorphically replaced by less charged cations, promoting a charge deficiency [4]. This charge deficiency is the factor that determines its negative surface charge, allowing the adsorption, in particular, of cationic species. The objective of this work is the ore dressing and characterization of two Brazilian clay minerals (montmorillonite and palygorskite) to evaluate their adsorptive potential in antibiotics removal presented in water bodies. For this, the samples were homogenized, subjected to grinding, wet granulometric classification, dried and adequately disaggregated. After these steps, the samples were characterized by X-ray diffractometry (XRD), X-ray fluorescence (XRF), Cation Exchange Capacity (CEC) and surface charge measurements by means of Zeta potential. The results indicated that the studied montmorillonite has associated minerals such as kaolinite and dolomite, which may influence its adsorbent properties. Palygorskite sample presented CEC within the expected range and a negative surface charge in the entire pH range studied. Therefore, both clay minerals are promising with regards to positively charged species adsorption.

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GEOLOGY CHARACTERIZATION OF PALYGORSKITE OCCURRENCES FROM PARNAÍBA BASIN, PIAUÍ, BRAZIL

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Guadalupe is a city in the state of Piauí which is the only region in Brazil where has exploitable deposits of palygorskite. It is inserted in the geological context of a Fanerozoic Basin, the Parnaíba Basin, specifically in the sequences of Carboniferous and Permian, represented by the Piauí, Poti and Pedra de Fogo formations (Pôssa and Bertolino, 2022). The economic importance of this clay mineral is directly related to its unusual structure and physicochemical properties, which give it a wide variety of uses in industry. This clay mineral from Guadalupe has studies investigating its applicability, mainly due to its adsorption properties as adsorbent of oils, heavy metals, glyphosates and others (Simões et al., 2017; Câmara et al., 2020; Nascimento et al., 2023). The formation stability field of palygorskite is very limited, which makes deposits of this clay rare around the world. The objective of this study was the geological and mineralogical description of palygorskite occurrences in the Guadalupe region looking for their geology characterization. Six occurrences were studied, and 25 samples were collected. These raw samples were processed to concentrate particles with size smaller than 44 μm. X-ray diffractometry (XRD), scanning electron microscopy (SEM/EDS), density and particle size analysis were performed. Most of the samples were composed by palygorskite, quartz and kaolinite. However, according to the diffractograms, there are three samples with the absence of palygorskite, two with the absence of kaolinite and one with presence of dolomite. Based on these results, it is possible to correlate hypotheses for palygorskite formation with the local geological context. The environmental conditions of Piauí and Pedra de Fogo formations were favorable to this clay mineral formation. The association of dolomite and palygorskite in an upper layer may indicate a greater association with Pedra de Fogo Formation, however the fields descriptions, as the levels of silexite, and the analyses results are not enough to define in which one of these formations the occurrences of palygorskite are inserted.

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ROCKJOCKML DATABASE MANAGER: A TOOL FOR CREATING AND IMPROVING DATABASES FOR QUANTITATIVE PHASE ANALYSIS BY FULL-PATTERN SUMMATION OF X-RAY POWDER DIFFRACTION DATA

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Full-pattern summation (FPS) and the Rietveld method are popular whole-pattern fitting methods for quantitative phase analysis of mineral mixtures, both of which have advantages and limitations. In the Rietveld method, an X-ray powder diffraction (XRPD) pattern of a mineral mixture is modeled as a linear combination of the XRPD patterns of individual phases, calculated from known crystal structures and adjusted by optimizing the peak shape function parameters, unit cell parameters, and even preferred orientation. This allows the analyst to leverage libraries of thousands of published crystal structures and account for small differences between the phases present in a sample and those in the database. However, the Rietveld method cannot be used to identify/quantify multiple amorphous phases, and it is difficult to apply to clay-bearing samples without sophisticated structural modeling. In the FPS method, the XRPD pattern of a mixture is modeled as a linear combination of experimentally derived patterns from a library of standards, and quantification is accomplished via measured reference intensity ratio (RIR) values. This approach works fairly well for identifying/quantifying amorphous phases, and both for quantifying clay minerals and at least narrowing down their identification to a few major groups. However, FPS requires labor-intensive sample preparation, so the time needed for generating a large database of standards can be prohibitive. Notwithstanding this difficulty, differences in peak shapes and positions between phases in the sample and those in the database reduce quantitative accuracy, so it is advantageous to create the database using the same instrument on which samples are analyzed. Finally, it is very difficult to find pure samples of some geologic phases for inclusion in such a database.

We are attempting to mitigate many of the limitations of the FPS method using the program, RockJockML Database Manager, which is a companion to the FPS program, RockJockML. In the database manager, one may easily perform the following tasks: 1) importing and analyzing XRPD patterns to create database standards, 2) removing and correcting for the influence of impurities in standards, and 3) using simulated XRPD patterns based on crystal structures to generate new standards with identical peak-shape characteristics to chemically and structurally similar experimental standards. These features will allow analysts to dramatically increase the size and quality of FPS databases, and we demonstrate this by using the program to analyze and improve the standard RockJock FPS database published by the United States Geological Survey.

RockJockML Database Manager is programmed in MATLAB, but is deployable in a standalone format for Windows, Macintosh, and Linux operating systems with no requirement for a MATLAB license. It can be downloaded at http://geol.byu.edu/bickmorewiki/, where documentation and training materials can also be found.

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PHOTOACTIVE HYBRID FILMS COMPOSED OF SAPONITE AND PHLOXINE B EFFECTIVELY ERADICATE STAPHYLOCOCCAL BIOFILMS

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Hybrid films based on clay minerals functionalized with bioactive molecules, such as photosensitizers, have been studied due to their potential antimicrobial properties [1, 2]. *Staphylococcus aureus* is a Gram-positive bacterium forming strong biofilms on the surface of medical devices, such as catheters and joint implants, associated with life-threatening infections. Surface modification of medical devices with a layer of antimicrobial film can potentially scale up anti-biofilm activity. This research analyzed the efficiency of a photoactive nanocomposite film on polyurethane (PU), composed of clay mineral saponite (Sap) modified with poly(diallyldimethylammonium) cations (PDDA) and photosensitizer phloxine B (PhB).
Sap particles were modified with PDDA (1.5 $mmol \cdot g^{-1}$) to change their surface charge to positive. PhB solution was used for the functionalization of the PDDA/Sap complex. The colloidal mixture was filtered on polytetrafluoroethylene (PTFE) membrane and coated with a thin layer of PU resin. The composite surface anti-biofilm activity was tested using standard strain *S. aureus* CCM3953 and methicillin-resistant *S. aureus* (MRSA) L12.
The L12 strain was confirmed to be resistant to oxacillin, ciprofloxacin, and norfloxacin (MIC > 256 μg/mL, MIC > 32 μg/mL, MIC > 256 μg/mL, respectively, MIC – minimal inhibitory concentration), while CCM3953 was sensitive to tested substances. The efflux activity evaluated by the ethidium bromide agar screening method [3] was higher for L12 strain compared to *S. aureus* CCM3953. Quantitative PCR showed 7.51 times higher expression of the efflux *norA* gene for L12 biofilm formed on PU without modification compared to CCM3953 set to 1. Preliminary testing the new hybrid film was performed with strain CCM3953 on PTFE membranes. The hybrid films prepared with different ratios (0.5, 1.0, and 1.5 mmol/g) demonstrated after the irradiation with laser the inhibition in a log scale: 2.03, 3.37, and 9.02 (100%), respectively. Based on these results, a hybrid containing n_{PhB}/m_{Sap} ratio of 1.5 mmol/g was functionalized on PU. Results showed inhibition determined in a log scale: 2.84 and 2.64 after irradiation for CCM3953 and MRSA L12, respectively.
These results suggest a promising potential of hybrid films with photoactive properties in the eradication of staphylococcal biofilms, even MRSA biofilm with the up-regulated *norA* efflux gene.

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CHARACTERIZING PHYLLOSILICATES ON MARS AND WHAT THEY REVEAL ABOUT ANCIENT GEOCHEMICAL ENVIRONMENTS

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Spectrometers orbiting Mars and other planets provide information about the surface mineralogy and composition. The Compact Reconnaissance Imaging Spectrometer for Mars (CRISM) instrument on the Mars Reconnaissance Orbiter collected visible/near-infrared (VNIR, 0.4-3.9 μm) spectra at 18 m/pixel surface resolution for >15 years and has enabled mapping a variety of phyllosilicates and alteration assemblages that reveal information about former aqueous environments including potentially habitable regions [e.g., 1,2]. Analyses of hyperspectral CRISM imagery suggest distinct aqueous geochemical environments on Mars including paleolakes, evaporites, hot springs, and subsurface hydrothermal systems. Phyllosilicates are the most abundant alteration mineral found on Mars and these are excellent indicators of the ancient climate and environment. Martian phyllosilicate assemblages reveal planet-wide warm water environments that produced extensive deposits of Fe/Mg-smectite. More localized outcrops of clay/sulfate assemblages and Al-rich phyllosilicates likely formed in acidic environments, potentially resulting from volcanic gasses and surface brines. Smectite/chlorite assemblages occur in other regions that are often accompanied by serpentine, talc, prehnite, zeolite, or carbonate and reflect higher temperatures due to impacts, volcanism, or geothermal processes.

Correlating the phyllosilicate assemblages detected on Mars with field and lab observations enables an improved understanding of the aqueous environments at the time these minerals formed or altered, and reflectance spectra are needed of these minerals and mineral assemblages [e.g., 3] in order to detect them on planetary surfaces. For example, assemblages of smectite, hematite, and jarosite are observed at cinder cones and fumerole sites in volcanic environments, while smectite, kaolinite, opal, and gypsum are found in some evaporite settings. However, thick deposits dominated by smectite are more prevalent in warm wet/dry cycling environments and frequently form from pyroclastic material. Diagenetic environments include mixtures of smectite with high temperature phyllosilicates, sulfates, zeolites, and/or carbonates. Alteration in glacial environments results in higher abundances of poorly crystalline phases and fewer crystalline clays and iron oxides. Reflectance spectra of analog samples from field expeditions, coupled with alteration experiments in the lab, are improving our ability to discern minerals on Mars in complex, natural mixtures. The martian surface regolith includes elevated S and Cl compared to terrestrial soil, and brine experiments in the lab provide clues to the potential evolution of phyllosilicate assemblages through alteration in martian brines. Dehydration experiments in the lab also provide constraints on how hydrated minerals on Mars will change over time. The cold, arid surface environment of Mars today does not support formation of phyllosilicates, but many of them will persist long-term once formed. Through coordinated lab-field-remote sensing studies we can retrace the ancient lacustrine, evaporite, and geothermal environments from the martian past.

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IRON-RICH AND POOR AUSTRALIAN KAOLIN FOR VARIOUS ADSORBENTS DEVELOPMENT

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Kaolin minerals (kaolinite and halloysite) has been discovered in the Cloud Nine deposit in Western Australia. Iron poor and rich variations of kaolin lithologies were identified (Biswas et al. 2023). The iron rich kaolin samples contained elevated amount of mica/illite as the primary source of iron. Agricultural and environmental applications of these kaolin species are receiving increased attention due to their economic value. While kaolin minerals often require physicochemical modifications to achieve desired properties, the nature of iron impurities needs to be taken into consideration. In this contribution, we test the physical and chemical modification of adsorbents and evaluate their performances in order to establish the role of these iron impurities. Among them, alkali activated kaolinite and iron nanoparticle composites on delaminated surfaces has been developed. We show that the performances as adsorbents of gases or mixed metals varied upon the kaolin mineral species and the presence or removal of iron impurities/associated mineral species (mica/illite).

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BACTERIOLOGICAL IDENTIFICATION OF ALGERIAN PALYGORSKITE

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In this work, we verified the no existence of bacteria found at the macroscopic scale in Algerian palygorskite called Sif Pal [1] for use of this material in the pharmaceutical and parapharmaceutical field in the future. With the same fibrous clay [2, 3], one parameter is studied, it's the particle size to evaluate the nature and the quantity of bacteria in the palygorskite. The first step is to prepare our sample of palygorskite at different particle sizes 1mm, 2mm and 90µm. The second step involves the process of extracting the bacteria from the three samples named Pal 2mm, Pal 1mm and Pal 90µm. The third and last step is essentially based on the identification of the bacteria extracted from the sample by isolation and bacterial culture.
The results obtained for the three samples Pal 2mm, Pal 1mm and Pal 90µm show that in the first sample Pal 2mm, two bacteria Raoultella planticola (8.10^6 Bacteria/mL) and Escherichia coli ($5.5.10^6$ Bacteria/mL) were identified. For the second sample Pal 1mm, two bacteria Escherichia coli ($6.6.10^6$ Bacteria/mL) and Bacillus sp (9.10^4 Bacteria/mL) were found. Furthermore, a single Enterobacter cloacae complex bacterium (5.10^4 Bacteria/mL) was identified in the Pal 90µm sample. The results allow us to conclude that the best size of particle of Sif Pal that can be used on a pharmaceutical and parapharmaceutical field is a size less than or equal to 90 µm.

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HYDROPHOBIC ORGANIC COMPOUND–CLAY MINERAL INTERACTIONS AT THE CLAY–WATER INTERFACE: INSIGHTS INTO THE ROLE OF MINERAL CHARACTERISTICS AND COMPOUND HYDROPHOBICITY

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Hydrophobic organic compounds (HOCs), such as halogenated aromatic hydrocarbons, can be very persistent in the environment and lead to adverse effects on humans and other biota. Sorption processes are highly relevant for the assessment of their environmental fate and risk. In this context, especially the interactions between HOC and organic matter are intensively studied. However, significant adsorption of HOC can also take place on mineral phases [1].

For further mechanistic elucidation of HOC–clay mineral interactions at water/clay interfaces, adsorption experiments with different HOC–clay mineral systems were performed in the present work. Therefore, five halogenated benzenes (log K_{ow} 2.6–6.5) were used as HOC representatives and 20 smectite-rich bentonites were used as mineral phases.

The experiments showed a large mutual influence of the characteristics of HOC and clay minerals on the extent of adsorption. The determined solid-liquid adsorption coefficients K_d varied over several orders of magnitude for specific HOC–clay mineral interactions. The hydrophobicity of the HOC played a relevant role for the level of adsorption, but to a lesser extent than the mineral properties. This can be illustrated by the example of two selected HOCs (A: log K_{ow} 2.6 and B: log K_{ow} 5.6), whose adsorption varies depending on the clay minerals by up to a factor of 5 for substance A (log K_d 1.8–2.5), but by up to a factor of 90 for substance B (log K_d 2.1–4.0). The interpretation of results is based on clay minerals characteristics such as specific surface area, pore distribution, charge density, cation exchange capacity and cation occupancy. In terms of particle morphology, especially the pore size distribution is discussed as factor for the interaction of HOC with clay minerals. The sorption processes are further interpreted on the basis of molecular simulations [1,2] additionally considering the aqueous phase.

The results show the great influence of specific HOC–clay mineral interactions for the estimation of the distribution behavior of HOC. Furthermore, the results illustrate the general influence of clay minerals on the adsorption of HOC and their importance for the fate and transport of HOC in the environment, e.g. in long-term source/sink phenomena in soils and sediments.

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ION EXCHANGE REACTIONS ON CLAY MINERALS IN AN ACIDIC ISR (IN SITU RECOVERY) CONTEXT: COLUMN EXPERIMENTS AND ASSOCIATED REACTIVE TRANSPORT MODELING

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Uranium (U) roll-front deposits with relatively low U content are generally mined by acidic *in situ* recovery (ISR). This mining technique involves injecting a sulphuric acid leaching solution into highly permeable sandy sediments and pumping the resulting pregnant solution to the surface for further metal extraction at a processing facility. ISR mining has a more limited environmental footprint than traditional mining technologies (*e.g.,* waste-rocks, mine tailings). The fate of swelling clay minerals, such as smectites, in this geological context is of key importance due to their role in the mobility of cationic elements by diverse geochemical processes, including ion exchange reactions and dissolution. Despite the importance of ion exchange processes in regulating pH, no experimental study coupled with numerical modeling to date has demonstrated H^+ exchange on clays in the context of acid ISR mining.

Column experiments, coupled with numerical models, were performed on an arkosic sand containing ≈5 wt.% smectite from the Zoovch Ovoo uranium roll-front deposit in Mongolia. The experiments simulate the different phases of fluid circulation during and after acid exploitation, *i.e.,* circulation of a sulfuric acid solution (pH≈2), followed by circulation of a reference aquifer water until initial physico-chemical conditions are reached. For each experiment, pH and the concentrations of metals (major and trace) and anions were measured by ICP-MS, MP-AES and ion chromatography.

Results show a pH evolution at the output of the column similar to that observed *in situ* during real ISR tests. The circulation of a reference aquifer water is characterized by an increase in pH in two well-defined steps. A reactive transport model (HYTEC) was developed to simulate the water chemistry evolution. The model generally reproduces the concentrations of major cations, including H^+, suggesting a significant role of ion exchange processes in the control of aqueous compositions. Additional experiments were performed to investigate ion exchange processes by injecting solutions enriched in monovalent and divalent cations (Na^+ and Mg^{2+}) into the column following acid circulation. Results demonstrate the crucial role of cation nature and concentration in the rate of pH increase with time, with divalent cations showing a higher efficiency for acid reduction. Experimental desorption curves were well reproduced by numerical models, further confirming the role of ion exchange processes in the control of H^+ mobility in the sand column.

The present study demonstrates that clay-bearing sand from the studied aquifer can be described to a first order as an ion exchanger, and that the general behavior of pH and major cations can be modeled using only ion exchange reactions. This confirms the key role of clay minerals in controlling geochemical conditions through ion exchange processes in the context of acid ISR mining. These results show how chemical reactions at the clay/water interface can be integrated into reactive transport models to better assess U production and remediation strategies.

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THERMALLY ACTIVATED SURFACE ADSORPTION TO IMPROVE THE PHOTOACTIVITY OF AN ORGANIC LUMINOPHORE

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The interaction of organic dyes and clay minerals and dye molecular aggregation have been hot topics for the last decades. The objective of this work was to introduce a new phenomenon of a significant increase in the photoactivity of an organic pyrazinacene dye in hybrid colloidal dispersions of the clay mineral saponite (Sap). Pyrazinacene butterfly-shaped molecule (*butterfly pyrazinacene*, BP) consists of a quadruply benzo-fused fluorubine core with six hydrophilic oligo(ethylene glycol) chains to achieve better solubility in polar solvents. BP exhibits strong luminescence in organic solvents, but in aqueous solutions forms molecular aggregates of a significantly weaker photoactivity. Achieving highly photoactive systems in aqueous environments is one of the fundamental challenges of *green photochemistry* and is necessary for photobiological applications. The high photoactivity in an aqueous environment was achieved in the systems of Sap colloidal dispersions, however, the adsorption alone was insufficient. On the other hand, the combination of the adsorption on Sap particles and heating of the hybrid system led to the breaking of BP molecular aggregates, redistribution, and irreversible fixation of BP molecules on the surface of Sap particles. This led to a multifold increase in luminescence and photoactivity compared to the BP aqueous solution, confirmed by several spectral methods. The photoactivity of the resulting systems was comparable to the dye solutions in organic solvents. Thermally assisted irreversible adsorption of BP onto Sap particles represents a simple strategy to suppress the formation of dye molecular aggregates. This strategy can be applied to various organic dyes to improve their photophysical properties and extend their use to aqueous systems in biological applications, for photodisinfection, as photosensitizers, luminescent sensors, or probes.
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ANTI-BIOFILM EFFECTIVENESS OF POLYURETHANE NANOCOMPOSITE SURFACES FUNCTIONALIZED WITH ORGANOCLAY AND PHLOXINE B.

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Antimicrobial surfaces, especially of technical polymers, are gaining more attention due to their medical applications. The main objective of this work was to design an effective way of preparing antimicrobial surfaces based on polyurethane (PU) nanocomposites. The principle of PU modification was the formation of a thin layer of PU/organoclay nanocomposite, that was functionalized with the photosensitizer phloxine B (PhB). A thin layer of organoclay reacted with the penetrating molecules of the liquid polymer precursor. The key feature of the modified PU was the concentration of PhB, as an active ingredient, only on the surface of the materials, while the polymer matrix was without the dye and organoclay particles. In addition, the surface properties allowed the controlled release of the active PhB molecules, important from the view of surface activity. Factors such as synthesis conditions and reactant compositions were tested using infrared spectroscopy, X-ray diffraction, contact angle measurements, and UV-Vis and fluorescence spectroscopy to achieve optimal surface properties. The antimicrobial properties of the PU surfaces were investigated in experiments with biofilm formed by methicillin-resistant *Staphylococcus aureus* (MRSA); L18, L12, and S61 strains. Surfaces modified with organoclay without PhB also exhibited anti-biofilm properties. However, the PhB-containing composite material in combination with irradiation reduced biofilm growth by about 1000 to 10,000-fold, demonstrating a great anti-biofilm effect. The impact on cell destruction was confirmed by scanning electron microscopy. This high effectiveness was observed despite of resistance of MRSA strains to conventional antibiotics and the confirmed activity of the NorA efflux pump. Results showed increased regulation of the *norA* gene in 24-h biofilms of L12 and S61 MRSA strains, formed on the PU/organoclay functionalized with PhB. Moreover, significant up-regulation was observed after irradiation in the S61 strain (20.8-fold compared to methicillin-sensitive *S. aureus*). Polymer surface modification via the formation of composite thin films opens up new possibilities for the targeted modification of polymers with a focus on practical applications.
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PHOSPHATE REMOVAL CAPACITY AND CHARACTERIZATION OF POROUS AND NON-POROUS LAYERED DOUBLE HYDROXIDES (LDH)

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Phosphorus (P) in the form of orthophosphate ($H_xPO_4^{(3-x)-}$) is a limited and non-renewable resource extracted from phosphorous rock [1]. It is an essential nutrient and used as a fertilizer in agriculture. Recovery and reuse of phosphate is in line with a circular resource economy and a possible solution is by the removal of phosphate from polluted water by anion-exchange materials such as layered double hydroxides (LDH) [2].
LDH ($[M(II)_{1-x}M(III)_x(OH)_2]^{x+}[A^{n-}]_{x/n}\cdot yH_2O$, $0.20 \leq x \leq 0.33$), with M(II) = Mg and Zn and M(III) = Al has extensively been investigated for phosphate recovery since they have limited toxicity and a high affinity for phosphate [2]. Coprecipitation (Co) using a strong base is a popular method for the synthesis of LDH and results in powder samples. However, isolation of these from solution occur by filtration or centrifugation and would be hard to implement on large scale. Contrary, porous monolithic LDH with a high surface area can be synthesized by the sol-gel (SG) method, involving epoxide and phase separation processes, and result in LDH in tablet form [3].
Here, a comparison of the phosphate removal capacity and stability of LDH synthesized by both coprecipitation and the sol-gel method is presented. Samples were detailly characterized using powder X-ray diffraction (PXRD), solid state NMR- (^{1}H, ^{27}Al, ^{31}P, ^{35}Cl) and infrared spectroscopy (FT-IR), BET, scanning electron microscopy (SEM) and inductively coupled plasma (ICP-OES) to investigate how structure and function is related.
Preliminary studies of porous LDH synthesized by the SG method showed a high surface area (55-163 m^2/g), whereas LDH synthesized by coprecipitation had a surface area of 35 m^2/g. Furthermore, MgAl-LDH (Co) removed 45 mgP/gLDH and MgAl-LDH (SG) removed 55 mgP/gLDH reaching equilibrium within 30 min. From PXRD, the LDH phase is maintained after P exposure, but a decrease in crystallinity is observed. ^{27}Al MAS NMR gave important insight into the Al environments and show that LDH synthesized by SG method contain multiple Al sites, whereas the LDH from coprecipitation is phase pure. ^{31}P MAS NMR provided insight into the phosphate removal mechanism.
The LDH synthesized by the SG method may present a possible solution as pellet sized LDH/ coating is possible ideal for the big scale recovery of phosphate and need further investigation.

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PICKERING EMULSIONS STABILIZED BY HALLOYSITE NANOTUBES: A VERSATILE SYSTEM FOR COATING AND CULTURAL HERITAGE APPLICATIONS

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Nowadays, Pickering emulsions are extensively employed in various applications due to their numerous advantages over surfactant stabilized droplets, such as low or no toxicity, ease of storage, low production costs, etc. In this regard, particles obtained from eco-sustainable sources have been employed for their design in order to satisfy the need for environmentally friendly materials. Among them, halloysite clay nanotubes can act as interfacially active inorganic particles, and we recently proposed a novel protocol for the preparation of wax/halloysite based Pickering emulsions characterizing their stability and structure. Moreover, we designed new green coatings based on biopolymers (chitosan and pectin) [1] and geopolymers filled with wax/halloysite microspheres. Within this, the fillers combined with the aforementioned biopolymers were successfully employed to fabricate composite films with enhanced mechanical properties. A significant hydrophobization of the biopolymeric films was also detected by water contact angle measurements designing novel biocompatible nanocomposite systems that can protect the artwork surface from the aging process caused by environmental conditions. Microwax particles obtained from Pickering emulsions were also embedded in halloysite-based geopolymers developing a new hybrid material with heat storage capacity and enhanced flexural performances [2]. The incorporation of microwax into the geopolymers was confirmed using various techniques, including thermal analyses, spectroscopies, microscopies, and contact angle experiments. The homogeneous dispersion within the geopolymeric network improved again the coating's physico-chemical properties by increasing the hydrophobicity. Furthermore, the Pickering emulsions were employed for the treatment of waterlogged wooden samples [3]. Compared to archaeological woods treated only with wax, the inclusion of nanotubes led to a notable enhancement in mechanical properties such as stiffness and flexural strength, making this method useful for treating larger-sized shipwrecks. The discussed approaches suggest the development of wax/halloysite Pickering emulsions with versatile functions for both eco-friendly coating and cultural heritage applications.

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DEVELOPMENT OF ONE-PART ALKALI-ACTIVATED MORTARS FROM INDUSTRIAL BY-PRODUCTS

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The production of bioenergy from fluidized bed combustion of biomass is increasing worldwide as it is considered CO_2 neutral. However, this process generates huge amounts of biomass fly ash (BFA) and biomass bottom ash (BBA) that are usually disposed of in landfills. So, more sustainable management practices must be investigated, such as their recycling in construction materials. Further, the valorization of other by-products, such as blast furnace slag (BFS), from the iron production process, has been studied in the production of a wide range of construction materials.

In this work, the feasibility of one-part geopolymer mortars production, cured at room temperature, using BFS and BFA as precursors and BBA as aggregate was evaluated.

BFS, BFA, and BBA were characterized in terms of chemical composition (XRF), particle size distribution (by sieving for the BBA and by laser diffraction for BFA and BFS), and morphology (SEM). The influence of the substitution amount of BFS by BFA (0, 25, 50, 75, and 100 wt.%) on the workability, density, water sorptivity (by capillary and immersion), compressive strength, and durability to 25 consecutive freeze–thaw cycles of the prepared mortars was evaluated.

Results have indicated that the compressive strength of the mortars after 28 days of curing decreases with the increase of the BFA content (71.7 MPa for 0 wt.%, 57.0 MPa for 25 wt.%, 46.8 MPa for 50 wt.%, 13.5 MPa for 75 wt.%, and 0.2 MPa for 100 wt.%). The other evaluated properties were not significantly affected. Moreover, it was verified that the developed compositions support 25 freeze–thaw cycles being resistant to extreme conditions. Therefore, it was concluded that BFS, BFA, and BBA can be effectively used in the production of one-part alkali-activated mortars, with the amount of BFA incorporation depending on the intended application, contributing to a more sustainable construction industry.

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POLLUTANTS RECOVERY FROM INDUSTRIAL WASTEWATER-SYNTHESIS OF NEW FUNCTIONALISED MINERALS

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Within the framework of the various strategies studied to cut down the polluting agents in water, both from anthropogenic and natural sources, the adsorption processes are among the most widespread techniques. In this context, the LDHs (anionic adsorbers) play a fundamental role, but industrial wastewater often contains both anionic and cationic species. In this study, a composite material consisting of a MgZnAl-based LDH and montmorillonite (cationic exchanger) was synthesized to test its adsorption capacity for both cationic and anionic pollutants.
Four different compounds were prepared: two (ZnMg)Al LDHs (both nitrate and carbonate intercalated, (Zn_3 Mg)/Al = 2), throughout hydrothermal and coprecipitation syntesis and the composites materials made up of LDHs and montmorillonite. The compounds were characterized by means of Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES), X-ray powder diffraction (XRPD), Field Emission Scanning Electron Microscopy (FE-SEM), Transmission Electron Microscope (TEM), Fourier Transform Infrared Spectroscopy (FT-IR) and Differential Thermal Analysis/Termogravimetry (DTA-TG). The materials have been tested on two different industrial wastewater and the results compared.
The best results in terms of yields and extraction performance are shown from LDH and composites containing nitrate anions in the interlayer space.

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METAKAOLIN/RED MUD-DERIVED ALKALI-ACTIVATED MATERIALS FOR WASTEWATER TREATMENT

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Red mud (RM) is a highly alkaline and hazardous waste generated in the Bayer process were the conversion process of bauxite into alumina, with a production of about 150 million tonnes per year [1]. Over the years, around 4 billion tonnes of RM have been stored in dams/lagoons due to lack of appropriate recycling strategies [2,3]. Numerous studies have been carried out in recent decades to develop a more sustainable management strategies, but still the industrial reuse of these wastes is insufficient (only about 3% of annual production is reused) [1]. Alkali-activated materials (AAMs) can be an alternative to RM reuse, as these new binders can be produced with precursors that have a similar composition to RM [4]. However, RM is known to have low reactivity in an alkaline environment, which hinders its use in structural applications. However, AAMs can be used in other added value applications [5]. One very interesting application could be the use of AAMs as heavy metal adsorbents [6].

In the present work, it is proposed to use RM and metakaolin (MK) as solid precursors to synthesize porous AMMs coupling hierarchical porosity with suitable compressive strength (4.5 MPa) and enabling their use as bulk-type (not powder) sorbents to treat lead containing synthetic waters. The porous AAM showed rapid lead removal capacity, the removal efficiency of the sample reaching 99.5% after 6 hours (6 g of AAM/L, $[Pb^{2+}]_0$= 100 ppm). The pH of the adsorption tests has a decisive influence on the lead removal capacity, with a significant increase from 3.5 to 99.5 % when the pH is increased from 2 to 5. This property is related to the competition between H^+ ions and Pb^{2+} ions for the active sites on the AAMs. Another influencing factor is the initial lead concentration, as the lead concentration increases the adsorption increases, reaching a maximum adsorption of 30.7 mg/g of AAM ($[Pb^{2+}]_0$ of 600 ppm. Increasing the volume of the solution from 50 mL to 200 mL, while maintaining the same amount of AAM, increases the uptake from 7.35 to 17.44 mg/g. The opposite tendency is observed in the removal efficiency, which decreases from 99.5 % to about 75 %. This behaviour can be explained by the decrease in the number of active sites, as the mass of the adsorbent did not change. RM-based AMMs showed promising lead extraction capacity (fast and high removal capacity), and this strategy (e.g., using red mud derived bulk-type bodies to treat heavy metal-bearing wastewaters) can mitigate the environmental impact of RM while providing a high added value alternative for wastewater treatment. Moreover, the use of centimetre-sized bodies in wastewater treatment is a safer and easier way than using nano- or micro-size powders, which require an expensive post separation step.

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ORGANIC-INORGANIC HYBRID PIGMENTS BASED ON PILLARED ORGANOCLAYS AND EOSIN Y: AN ARCHEOMIMETIC APPROACH

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Problems involving fading or changing color with time of many bright red dyes such as eosin-based pigments in Van Gogh's masterpieces have inspired scientific inquiries in the pigment degradation issue. In this context, the organic-inorganic hybrid approach has been applied to design new archeomimetic pigments capable of facing the action of time, light and other environmental changes. Here, eosin-derived pigments were prepared with modified Saponite and Bentonite samples by using aluminium pillaring and silylation with 3-aminopropyltrimethoxysilane both loaded with eosin Y dye. The prepared hybrid pigments were characterized by CHN elemental analysis, XRD, FTIR, TGA/DTG, TEM, zeta potential and spectrocolorimetric measures. The effect of eosin loading at pH 5 and pH 10 were also evaluated. Photoaging effects were simulated by exposure of the prepared pigments to white light irradiation for 244 h, using a LED lamp set to provide 60 Klx of illumination intensity. This light dose is equivalent to about 24 years in a museum gallery illuminated at 200 lux (10 hours of light exposure per day; 6 days per week; and 50 weeks per year). CHN results showed a greater incorporation of the organosilane in Saponite than in Bentonite samples and a highest value of adsorbed eosin were then observed for silylated Saponite. Thermal analysis and infrared spectroscopy showed both silylated and pillared samples indicated the presence of eosin dye after loading process. XRD and TEM results suggested dye incorporation preferentially in the interlamellar spacing, with intercalation being the main mechanism of interaction in all samples. Although the anionic form is the main eosin speciation at both pH studied, the best loading results were observed at pH 5 for all samples and are related to the less negatively charged surfaces. Based on the results, only the dye-loaded silylated samples prepared at pH 5 were submitted to the photodegradation study. The microfading tests indicated the colors acquired lighter tones after light exposure with a lightly shift towards the green and blue region in most samples. Saponite-based samples presented more fading than the Bentonite based pigments. This fact may associate to the content of eosin loaded in both samples. In general, all prepared eosin-based pigments presented a relative photostability with low color differences values (ΔE*) even after 244 h of light exposure. The results highlighted the chemical modifications carried out on Bentonite and Saponite samples and allowed them to be applied as new hybrid pigments with improved photostability properties than eosin dye.

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CLAY HYBRID MATERIALS: AN EMERGING AREA IN MEMBRANE ASSISTED WASTEWATER TREATMENT TECHNOLOGY

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Most of the recently developed NF membranes are composite membranes whose support layer is covered with an active layer. Among different ceramic support materials currently used as a support layer, α-alumina supports are an integral part of the membrane, which is made of artificial materials like alumina and thus adds to the high price of the membrane. This draws our attention to making low-cost support material of natural clay which aims to be excellent membrane support as it possesses high mechanical strength, high permeability, narrow pore size distribution, and low manufacturing cost. As an active layer for the ceramic membrane, titania is preferred over Al_2O_3 membranes due to a slew of benefits ranging from its small crystallite size and self-cleaning property to its highly efficient photocatalytic material. It has been observed that if titania is immobilized onto clay support, its photocatalytic action increases tremendously. One of the problems encountered when photocatalysts are immobilized on support is the detachment of the microparticles from the support for high flow rates of liquid effluent. This can be overcome by using montmorillonite as a support material, as it has outstanding binding capacity. Not enough effort has been made in the literature to evaluate the specific features of these catalysts concerning practical use and to optimize their design to their characteristics. Thus optimization of such a nanoreactor may be helpful in the separation of heavy metal ions from wastewater and in recovering ions such as Pb^{2+} and Cd^{2+}, which latch onto clay composite membranes.

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ASSESSMENT OF ADSORPTION PROPERTIES OF BENTONITES WITH THE PLATE TEST AND METHYLENE BLUE ADSORPTION

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Bentonites are utilized for their adsorption capacity for various inorganic and organic molecules such as water and dyes, including the methylene blue (MB) dye. Water adsorption capacity with the plate test has been used to assess suitability of bentonites in iron ore pelletization. Also the MB adsorption test is a standard test for bentonites in foundries, which indicates both the smectite content and the binding properties of the bentonites. In this study, we examined the adsorption capacity of 30 bentonites from Greece, South Africa, India Turkey, Morocco and the USA for water with the plate test and for MB adsorption. Quantitative mineralogical analysis of all samples was performed by X-ray diffraction (XRD) with the Rietveld approach (BGMN code, Autoquan© 2.80 software). Water adsorption was determined with the porous plate test (ASTM E946, 1996) and MB adsorption was determined according to the API 13B-1 method (API, 2003). Three types of bentonites were examined, natural Na-bentonites, industrially Na-activated bentonites and Ca-Mg bentonites. The Ca-Mg bentonites were activated with 1-4% Na_2CO_3 according to the smectite content, determined by the Rietveld approach and the water adsorption and MB adsorption tests were repeated. In addition, XRD showed that most Na-activated bentonites were partially activated. In these samples Na-exchange was completed by addition of distilled water to form a paste for 16h, followed by drying and both tests were repeated.
The smectite content in the bentonites varies between 48.7 and 96%. As expected, the Ca-Mg-bentonites displayed considerably lower water adsorption capacity than their natural Na-rich and Na-activated counterparts (146-183%, 457-522% and 260-867% respectively). Addition of water promoted Na-exchange to the incompletely Na-activated bentonites and increased water adsorption by 1-20%. Also, Na-activation of the Ca-Mg-bentonites increased water adsorption by 10-170%. Water adsorption with the plate test was affected by the type of exchangeable cation and the smectite content. After Na-activation the correlation was better expressed due to homogenization of the exchangeable cation composition. Similarly, MB adsorption depended both on the type of exchangeable cation and the smectite content of the bentonites. Na-activation increased the amount of MB that was adsorbed by the bentonites and the Na-activated bentonites followed the same trend as their natural Na-rich counterparts. Finally, the layer charge of smectite affected MB adsorption. Bentonites containing high charge Ca-smectites displayed higher MB adsorption than their low charge counterparts, due to the formation of H-type MB aggregates rather than J-type aggregates or H-dimers in the exchangeable sites.
In conclusion, both the ceramic plate test and the MB test are useful for assessing the adsorption properties of bentonites and provide a rough indication of the smectite content. However, smectites should be Na-homoionic before testing, in order to obtain reliable comparisons.

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MINERALOGY AND GEOCHEMISTRY OF A BENTONITE PROFILE FROM AGIA IRINI, DEPOSIT, MILOS ISLAND, GREECE: A GEOSTATISTICAL ANALYSIS

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The Angeria bentonite deposit in Milos Island Greece, is a world-class deposit with >100 Mt reserves of high-quality material. The deposit has an E-W strike and consists of three sectors, the Koufi, Angeria and Agia Irene from east to the west. In this contribution we examined the mineralogy and geochemistry of a ~75 x 20 m (length x height) bentonite profile from the south domain of the Agia Irini sector. Twenty-five bentonite samples were collected from the profile. Quantitative mineralogical analysis was performed with the Rietveld method (BGMN code, Autoquan© 2.80 software) and the chemical composition was determined by ED-XRF. The layer charge of smectite was determined with the modified K-saturation method (Christidis & Eberl, 2003) and the charge localization was estimated with the Greene-Kelly test after Li-saturation. The mineralogical and geochemical data were processed with geostatistical analysis using the Matlab code to draw conclusions for spatial variation and trends of layer charge, major mineral phases and major chemical elements. The samples are composed of Ca-Mg-smectite (58,7-88,9%), opal-CT (2,6-20,9%), quartz (0,5-7,1%), plagioclase (0,7-20,5%) and K-feldspar (0,6-9,7%) with traces of illite, calcite, jarosite, alunite, gypsum, anatase, hornblende and bassanite. High-charge smectites (>0,480 e/huc) predominate, with 6 samples containing moderate-charge smectites (0,425<layer charge<0,475 e/huc) and 6 low layer charge smectites (<0,420 e/huc). Most smectites are montmorillonites, 3 samples contain beidellite and 6 samples contain both montmorillonitic and beidellitic layers. The smectite content is positively correlated with the $MgO+Fe_2O_3$ contents of the samples, the K_2O content is directly associated with K-feldspar and the SiO_2-polymorphs with the SiO_2 content. In geostatistical analysis, an Ordinary Kriging approach was implemented in terms of an exponential variogram, to determine the samples spatial dependence, and showed that smectite content is maximized in the central-eastern sectors of the profile. The beidellitic layers dominate the lowermost sectors, whereas the tetrahedral charge is minimized in the highermost part towards the western sector of the profile. The beidellitic layers tend to have lower layer charge, whereas their montmorillonitic counterparts have intermediate and high layer charge. Therefore, both the total and the octahedral charge of smectite tend to increase from the bottom to the top of the profile. The estimation errors of the smectite content, layers charge and octahedral/tetrahedral charge distribution are minimized in the center and maximized in the boundaries of the profile. In conclusion, the use of geostatistics provides useful information about the distribution of smectite content and crystal-chemical properties of smectite in bentonites, thereby optimizing bentonite processing including Na-activation and classification of bentonite deposit in blocks of variable properties.

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EFFECT OF H2O ON THE INTERCALATION OF KAOLINITE BY AMIDE

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The kinetics of the intercalation of kaolinite by N-methylformamide (NMF) have been recently revisited by real-time near-infrared spectroscopy and X-ray diffractometry [1, 2]. These studies indicated that intercalation is a two-state, fast-switching phenomenon taking place at the level of individual interlayers or crystallites and described by lognormal sigmoidal kinetics. The intercalating capacities of commonly studied kaolinites such as KGa-1b, KGa-2 and Imerys Hywite Alum were measured to be significantly lower than previously estimated and decreasing further with increasing reaction temperature.

The present study introduces H_2O as an additional variable affecting the intercalation kinetics of the aforementioned kaolinites. The minerals were exposed to NMF:H_2O mixtures with up to 30 wt% in H_2O ($x_{H_2O}\leq 0.63$ molar) at 30, 45 and 70°C and the uptake of NMF was monitored for up to 3 days by the intensity of the 2νNH mode of the intercalated species at approx. 6700 cm^{-1}. Remarkably, at any liquid composition and temperature investigated, the position and width of this 2νNH mode was found to be independent of H_2O. This suggested that, even for the largest H_2O contents, H_2O is not entering the interlayer, NMF remains the sole intercalating species, and the interlayers/crystallites display the same binary behavior that was reported for the anhydrous end-members: They are either non-intercalated or fully intercalated, but never partially intercalated. Moderate additions of H_2O (up to 10wt%, $x_{H_2O}=0.34$) were found to shift the lognormal sigmoidal to shorter times with little effect on the shape of the sigmoidal and no effect on the final uptake. In agreement with the older literature [3, 4], this 'catalytic' effect was attributed to the de-structuring effect of H_2O on liquid NMF. Both, higher H_2O contents and increasing temperature caused a progressive decrease of uptake capacity and the broadening of the sigmoidal, presumably due to the antagonism between NMF and H_2O molecules for the edge sites of kaolinite.

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LAYERED SILICATES AS MATRIX FOR LIGHT CONVERSION MATERIALS

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Layered silicates are among the hydrated oxide inorganic materials commonly found in nature and can be prepared synthetically by hydrothermal synthesis. Layered silicates are formed by building blocks network of tetrahedrons and octahedrons that are combined in layers with defined ratios like 2:1 and 1:1 for e.g. smectites and kaolinite, respectively. Isomorphous substitutions occurring in the networks are responsible for the negative charge of the net oxygen network. The charge is balanced by external cations located in the interlayers[1]. These cations compensating the negative charge can be exchanged for other cations in cation exchange reactions. Rare earth elements (REE) are known as phosphors with emissions associated with rich electron transfer abilities between energy states of f-orbital levels[2]. In the presented study, layered silicates were used as a matrix for REE doping, to modify their properties and produce new optically active materials. In this work, the optical properties of synthetic and natural layered silicates were compared. The optical response of selected REE-modified samples was enhanced significantly in the case of synthetic sample in comparison to natural one, using thermal fixation of REE cation at elevated temperatures.

Keywords: Layered silicates, nanoparticles, rare earth elements, phosphors
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ATOMISTIC SIMULATIONS OF HYDROGEN ADSORPTION AND TRANSPORT IN HYDRATED NA- AND CA-MONTMORILLONITES FOR RADIOACTIVE WASTE AND SPENT FUEL DISPOSAL APPLICATIONS

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The management of radioactive waste, particularly high-level radioactive waste (HLRW) from nuclear power plants and other sources, requires appropriate disposal and storage procedures. In this regard, radioactive waste repositories must comply with various physical, chemical, and geo-thermo-mechanical conditions to ensure safe and effective management. Due to their favorable properties, clay-rich host rocks are favored for geological repositories of radioactive waste. In France, the Callovo-Oxfordian (COx) clay formation has been chosen as the host rock for a radioactive waste disposal facility due to its high clay mineral content (25-60%) comprising illite, smectite, interstratified illite/smectite, chlorite, and kaolinite, along with other phases [1]. The formation of gas in repository environments can result from several mechanisms, including alpha decay, anoxic corrosion of stainless steel waste containers, and water radiolysis reactions, leading to the production of hydrogen gas (H_2), which is the most frequently generated gas under waste storage conditions. The accumulation of hydrogen gas within the repository presents a potential risk of overpressure and fracture of the surrounding clay rock. To prevent this, it is essential that gases are either absorbed, diffused, or react with the constituent host rocks. Therefore, a molecular-scale understanding of H_2 adsorption and transport processes in clay is crucial to ensure the safe geological disposal and storage of radioactive waste.
We apply the techniques of classical molecular simulations to quantitatively investigate the adsorption and diffusional transport of H_2 gas in hydrated clayey materials and improve the fundamental comprehension of the physical and chemical processes governing the interactions between H_2, water and clay minerals. Our study aims to improve the fundamental understanding of the molecular mechanisms underlying these processes. Initially, we performed Grand Canonical Monte Carlo (GCMC) simulations to investigate H_2/H_2O binary mixture adsorption in Na- and Ca-montmorillonite at temperatures of 25, 50, and 90°C and pressures up to 120 bar. Furthermore, molecular dynamics simulations of H_2 adsorption and transport in hydrated Na- and Ca-montmorillonite interlayers are conducted to investigate not only the structural properties but also the dynamic properties. The simulation results show that the adsorption of H_2 gas exhibits a proportional increase with increasing pressure, while a decrease is observed with increasing temperature in accordance with the solubility behavior of hydrogen gas in water. It has been noted that the mole fraction of adsorbed hydrogen in hydrated clay interlayer sites is higher in comparison to its solubility in water.

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THERMO-PHYSICAL PROPERTIES IN CLAY-BASED BRICKS INCORPORATING GRAPE STALKS.

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Circular economy thinking is rapidly becoming a guiding force in business and construction materials production. However, is well known that a society exclusively relying on linear economy is an historical anomaly in terms of resource exploitation. The habit of reusing waste in clay-based materials is rooted in the past and represents a win-win circular economy solution for facing current sustainable challenges. This study investigated the possibility to introduce grape stalks in a standard clay mixture for minimizing environmental impact derived from the wine activity and for generating new value-added quality bricks. Although grape stalks are not intrinsically hazardous, the necessity to store and/or reuse the large quantity of waste from the wine activity is compulsory. Indeed, since wine production is concentrated in a period of the year, it poses potential implications for air/water pollution and global warming. Moreover, its disposal in landfills can rise other problematic circumstances, due to smells and noises. On the basis to all these needs, the possibility of reuse of grape stalks in brick production can support the Sustainable Development Goals (SDGs) of the Agenda 2030 under different perspectives: i) to reduce the use of new resources, considering the Life Cycle Assessment (LCA); ii) to obtain a high-quality final product, especially concerning the optimisation of its physical properties. The research was specifically addressed to assess the pore system and to verify the final physical-mechanical properties (water behaviour, thermal insulation, and durability to ageing tests) of the new brick produced. Results demonstrated that grape stalks combustion increases the porosity of the final product both in terms of abundance (total porosity, %) and of pore dimensions (up to 3-4 cm). The high abundance of large pores favours a good durability, reducing the pressure effects due to ice and salt crystallization, and decreases the heat transmission up to 40% with respect to a standard brick. Quantification and prediction of the effects of porosity on thermo-physical behaviour in building materials can have a great environmental impact in response to the increasing efforts required by the SDGs, enhancing awareness on eco-labelling and supporting the industrial sustainable development.

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UNDRAINED SHEAR STRENGTHS OF CLAYS: A STATISTICAL OVERVIEW

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Indirect undrained shear strength estimates of fine-grained sediments are commonly derived from clay properties and soil stresses. In the last decades, several site-specific, regional-based and soil class-based correlations were proposed to assess co-dependence among index parameters, soil stresses and undrained shear strength observations for practical use. Nevertheless, such correlations might pose a problem of pertinence when applied to new project-sites leading to biased prediction of undrained shear strength. In this study first insights of a newly compiled incomplete generic clay database are illustrated. A data collection in terms of undrained shear strength (i.e., remolded and vane strength) and clay properties (i.e., Atterberg's limits, index parameters) of different worldwide clay classes is presented. Main effort is focused on establishing generic interdependence among undrained shear strength and index parameters such as Liquidity Index. The high systematic uncertainties that inevitably arise in generic correlations are reduced through a Bayesian sampling scheme. The Bayesian approach, here applied, searches and identifies observations within the proposed database that statistically match site-specific geotechnical characteristic to further establish weighted correlations. A comparison with generic and site-specific literature correlations is provided which highlights the benefit of Bayesian updating approach for site-specific undrained shear strength prediction from clay properties.

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HF-ND ISOTOPES COUPLED TO CLAY MINERALOGY AS PROXIES OF ENHANCED CHEMICAL WEATHERING AND SUBSEQUENT COOLING DURING THE LATE CRETACEOUS

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The carbon cycle, which plays a major role in the evolution of atmospheric CO_2, is controlled over the long term (> 1Ma) by the degassing of mantle CO_2 (source) and by continental weathering which consumes CO_2 through silicate weathering reactions (sink). The aim of this study was to discuss the links between tectonic, long-term evolution of silicate chemical weathering intensity and climatic changes during the late Cretaceous, which is marked by a major global cooling representing the initiation of the last greenhouse-icehouse transition. Site DSDP 959 (Ivory Coast-Ghana margin) was then targeted to study the long-term evolution of silicate chemical weathering intensity on the West African margin. Detrital clay mineral evolution was used to track climatic evolution through kaolinite and smectite contents while the (illite+chlorite)/smectite ratio was used to track mechanical erosion. Such mineralogical proxies were coupled to the isotopic composition of Nd ($\varepsilon_{Nd(t)}$) in the clay fraction to assess local sources and to the new geochemical proxy $\Delta\varepsilon_{Hf(t)}$ defined by Bayon et al., (2016) in modern river sediment to track the local silicate chemical weathering. This index of weathering intensity measured in the clay fraction (<2 µm), is based on the decoupling behaviour of Nd and Hf isotopic systems during chemical weathering process of silicate rocks.

In this site, the clay mineral assemblages display a large dominance of smectites pointing to a relatively hydrolyzing climate with contrasted seasons associated to a low relief. while the evolution of the $\Delta\varepsilon_{Hf(t)clay}$ shows enhanced chemical weathering on the West African craton from the Santonian to the middle Campanian. At the same time is recorded a pulse of mechanical erosion highlighted by the ratio Quartz/Clays and Feldspar/Clays, suggesting a coupling between mechanical erosion and chemical weathering on the margin. The increase of kaolinite during the Maastrichtian up to 20% suggests however changes in humidity conditions or in sources on the craton at the very end of the Cretaceous.

These new data obtained at Site 959 are compared with those from sites 1259 (Corentin et al., 2023) and 356 (Corentin et al., 2022) on the eastern margin of South America. The results from these 3 sites, which are located on margins affected by different climatic, geological and tectonic conditions, suggest that chemical weathering markedly intensified at each site during the late Cretaceous. Hence, we propose a major role of tectonic uplifts affecting the southern Atlantic margins of Africa and South America in the silicate weathering and CO_2 budget potentially increasing the global cooling of the late Cretaceous.

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ON THE QUANTITATIVE DETERMINATION OF THE ELASTIC PROPERTIES OF CLAY MINERALS

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There exists a large diversity of experimental and theoretical estimates of the elastic moduli of clay mineral phases. These estimates are obtained experimentally on macrocrystals and macroscopic analogs or theoretically by molecular simulations and micromechanical inversions. These estimates are expressed as isotropic moduli or written following isotropic transverse symmetry.

Here, all the available data are compared using Voigt-Reuss-Hill (VRH) averages, which account for all the components of the stiffness tensor and allow us to reduce most of these estimates to equivalent isotropic moduli. The qualitative and quantitative comparison of all these data highlights the following four sets of results.

First, the elastic constants of 2:1 nonswelling minerals can be reasonably estimated by molecular modeling of the density functional theory (DFT) type. These experimentally validated numerical results can therefore be considered as first order estimates of the elastic coefficients of dry clay minerals. The models obtained by molecular dynamics (MD) provide much more dispersed results, which can be explained by the variety of local force fields used in the calculations.

Second, all the estimates obtained by molecular modeling on swelling minerals show that their elastic properties are sensitive to the presence of interlayer water: they globally decrease with the number of water molecules in the interlayer space. However, these theoretical estimates face a major difficulty: their experimental validation. The measurement on macroscopic analogs (e.g., macroscopic vermiculite crystals as analogs of microscopic swelling clay minerals) is again of interest in this context. It is recalled here that such analogues have been successfully used to study the diffusion properties of interlayer water.

Third, most of the values provided by micromechanical inversion of geophysical or geomechanical data acquired on clay rocks or clayey composites and the unjacketed bulk modulus K_s values measured in geomechanics are rather representative of clay mineral assemblages and not of a given single clay mineral, as it is often awkwardly considered in literature. Considering these mineral assemblages, the mechanical interactions between minerals or clay aggregates (e.g., friction between clay minerals possibly associated with buckling processes, mechanical interactions between clay aggregates themselves) and the fundamental role of interlayer water should be considered.

Fourth, the use of a simple micromechanical model applied to the isotropic VRH moduli illustrates the solid nature of interlayer water. The elastic properties of adsorbed water would be more similar to those of the solid mineral itself than those of ice, as the literature often suggests. This last result should be obviously validated by the experimental measurement of all the elastic constants of hydrated clay minerals, which still remains an experimental challenge.

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GEOLOGY AND MINERALOGY OF THE S'ALIDERRU BENTONITE DEPOSIT (SARDINIA, ITALY): PRELIMINARY DATA

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The S'Aliderru bentonite deposit, identified for the first time in 1983, is located in north-western Sardinia Island, between the towns of Sassari and Alghero. The deposit developed from the alteration of several cycles of deposition of Oligo-Miocene pyroclastic materials, interbedded with sediments of proximal-to-marine environment, represented by conglomeratic and sandstones lens. The deposit is hosted within the Mesozoic carbonate tectonic basin, with an approximate NW-SE orientation. The present study aims to define the preliminary mineralogical, petrographic and chemical features of the deposit, as well as to define its genesis. The current open pit extends for about 1km N-S and 0.5 km E-W, with an average thickness of the mineable bentonite layer of about 50 m. The mineralization consists of several bodies with variable shape and size, showing different colours; light-colored varieties (pink, white, green) are of higher quality compared to red, grey and brown bodies. Intermixed with the mineralized lenses, sterile tufaceous and ignimbritic lenses, conglomeratic and arenaceous bodies and travertine deposits are present. The entire deposit is characterized by the presence of local faults, dislocating and tilting the mineralized beds. 141 samples were collected, and then selected and analysed based on lithology and location. Laboratory tests included X-ray powder diffraction analyses (both qualitative and quantitative), petrographic and SEM-EDS analyses. Mineralogical analysis (XRPD) allowed to define that S'Aliderru bentonites are essentially montmorillonitic, with subordinate amount of calcite, quartz, cristobalite, feldspars and muscovite. Three bentonite types were recognized: the first type includes bentonites mainly formed by montmorillonite, plagioclase and cristobalite; the second type includes bentonites composed exclusively of montmorillonite; the third type includes bentonites composed of montmorillonite and kaolinite. Qualitative mineralogical analyses pointed out that investigated bentonites show clay minerals contents ranging between 90% and 99%, with residues of plagioclase, muscovite, calcite and quartz. The petrographic analyses (polarized optical microscopy) were fundamental to determine some peculiar features of the deposit. Source volcanic rocks are composed almost entirely of plagioclase, with rare sanidine present in ignimbrite lithologies, chlorite and biotite immersed in an unaltered to strongly altered glassy matrix. The interbedded conglomerates are characterized by carbonatic (centimetric to decametric) pebbles, with presence of fossils such as foraminifera, red algae and echinoids. A regular echinoid spine was found in a bentonite sample, indicating a submarine depositional environment. Bentonite SEM analyses highlight the genetic link between glass and newly formed clays. EDS chemical analyses on clay minerals revealed significant contents of magnesium, thus classifying clays to montmorillonite-beidellite series (according to Weaver & Pollard 1975[1]), with samples showing anomalous iron content. Fe- and Mn-oxides, barite, hollandite, monazite, probably associated with late hydrothermal fluid circulation were recognised as accessory phases.

Preliminary data highlight the complexity of the S'Aliderru deposit, which was probably formed in a proximal-to-submarine environment, with different phases of marine intrusion, underlined by the presence of conglomeratic formations with marine fossils, and subsequent hydrothermal alteration phases that formed accessory minerals. Presence of travertine indicates continued and long-term secondary fluid circulation in the northern area of the deposit. Bentonite body thicknesses, combined with the ever-increasing bentonites application makes S'Aliderru a strategic deposit on the European scene.

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PRODUCTION OF LIGHTWEIGHT ECO-BRICKS BY ADDING WINE-MAKING RESIDUE

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In this research, in a bid to reduce clay consumption and recycle a waste product, wine pomace (grape skins, seeds, stems and wine lees) with three concentrations (2.5, 5 and 10 wt.%) was added to two clayey soils from Granada (Jun and Guadix, Spain) to manufacture handmade bricks that were fired at 800, 950 and 1100 °C. The chemical-mineralogical and physical-mechanical behaviour of the raw materials and fired bricks were analysed and discussed. The wine pomace was consumed during firing, leading to the appearance of voids where the pomace particles had once been present. In all the bricks, a less birefringent matrix was observed at 1100 °C due to vitrification. Vitrification reduced the porosity and increased the ultrasonic wave velocity, especially in the temperature range from 950 °C to 1100 °C. Conversely, the addition of wine pomace caused a fall in ultrasonic velocity. In general, the firing process resulted in the dehydroxylation of phyllosilicates, the crystallization of Fe oxides, the appearance of mullite at high temperatures and, when the carbonates were present, the development of Ca-(Mg) silicates such as gehlenite at 950 ºC and diopside, wollastonite and anorthite at 1100 ºC. The bricks made with added wine pomace had very similar mineralogy compared to those made without it.

After firing, the greatest colour differences were detected after increasing the amount of waste and the firing temperature, which generally resulted in yellower bricks.

The bricks made with wine pomace were more porous and absorbed more water under immersion. They also attained poorer mechanical strength, especially at low firing temperatures. The increase in firing temperature resulted in an improvement in mechanical resistance regardless of the composition of the bricks.

This research sheds more light on possible uses for wine pomace in the production of lightweight bricks for use in the construction industry. This could lead to environmental benefits by reducing the amount of clay required in brick production and by usefully disposing of a waste product, pomace that might otherwise end up in landfills. In addition, the production of lightweight bricks can achieve energy savings in both the transport of the bricks by road and in the construction of houses with better thermal insulation.

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CELEBRATING THE INTERNATIONAL YEAR OF MINERALOGY: THE IMPACT OF ZEOLITES ON TECHNOLOGICAL DEVELOPMENT

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For over 260 years, zeolites have gone from being a matter of curiosity to a key technological component of our age [1]. This transformation is highlighted in the section, “The Wonderful World of Zeolites: Probably the Most Outstanding Mineral Discoveries That Changed Humans’ Life”, in the chapter, “Mineral Discoveries That Changed Everyday Life”, of the book “Celebrating the International Year of Mineralogy: Progress and Landmark Discoveries of the Last Decades” [2], which is being published by Springer in 2023 in recognition of the International Mineralogical Association’s (IMA) declaration of 2022 as the Year of Mineralogy. This initiative was endorsed by UNESCO under the patronage of the International Year of Basic Science for Sustainable Development.

In this talk, I will provide an overview of the multifaceted mineral family of zeolites, discussing how they have contributed to technological developments, and how they continue to inspire sustainable solutions for the future. Special emphasis will be placed on the synergistic relationship between natural and synthetic zeolites, which enables a combination of mineralogy, chemistry, physics, and material sciences.

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AEROBIC CORROSION IN LONG-TERM IRON-BENTONITE INTERACTION: STUDY OF THE TRANSIENT STAGE IN THE PERFORMANCE OF THE ENGINEERING BARRIER FOR A DEEP NUCLEAR WASTE REPOSITORY

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Two long-term laboratory experiments, FB5 (14 years) and FB6 (15 years), in which FEBEX bentonite (B) has been in contact with iron powder (F), heated to 100 ºC, have been dismantled and characterized to investigate the iron-bentonite (FB) interaction processes at the interface. The FB experiments, implemented by CIEMAT (Torres el al., 2009), are composed of cylindrical columns of compacted bentonite (7cm in diameter, 8.9 cm in length, 1.6 g/cm^3, 13 %w water content) in contact with a disc of iron powder (40 µm, equivalent diameter grains) compressed to 1.3 cm thick.

FB5 was hydrated with Grimsel test site-like groundwater (HCO_3^--Na-Ca-<0.001 M) from the bentonite end, at ~20 ºC, thus creating opposite hydration and thermal gradients. FB6 was not hydrated. The SEM-EXD and XRD-powder analysis of FB5 (carried out in anoxic environment) revealed the predominance of the formation of Fe(III) oxides as corrosion products at the interface (hematite and maghemite), and minor magnetite and Fe-O-Cl oxides (green rust, akageneite). Chloride and magnesium are concentrated at the bentonite interface and their contents outline a chemical gradient front towards the heating zone, which includes a progressive increase in exchangeable magnesium from the hydration to the iron powder heated zone. The porosity of the iron powder disc was filled to a depth of 2mm with iron oxides developed from the bentonite contact interface. The iron grains are coated by a 10 µm oxide rim. The hydration front and the penetration of the iron into the bentonite have been examined by X-ray µ-CT. The iron-bentonite interface remained dry or partially saturated due to the heat front, as revealed by the preservation of macropores between the compacted bentonite grains. The depth of influence of iron in bentonite, captured by µ-CT image analysis, is heterogeneous, affecting a zone of less than 5mm.

FB6 has been run in dry conditions (with its original water content) and there is no evidence that the pores of the iron disc are filled with iron oxides. The Fe-oxide rims bordering the iron grains are less than 2 µm in size at the iron-bentonite interface. Under dry and hot conditions, corrosion is limited, the chloride-rich phases being absent.

The results obtained highlight the need to consider the initial anhydrous oxide layer (magnetite/maghemite/hematite) present on the corroded iron-steel surface, to model the transient towards anoxic conditions in long-term modelling exercises of the barrier system. The initial chloride-Mg rich geochemical environment in high-T corrosion zone can induce long-term changes in the clay mineralogy of the bentonite.

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MULTI-IONIC TRANSPORT AND SALTS CONCENTRATION PROCESSES IN UNSATURATED BENTONITE HYDRATED FOR 10 YEARS UNDER HIGH TEMPERATURE HEAT SOURCE

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The engineered barrier system (EBS) performance for the confinement of high level radioactive waste (HLW) has been proved in several underground research *in situ* tests at moderate temperatures (< 100°C). The heat produced in the decay of HLW radionuclides will induce perturbations in the water and solutes transport through unsaturated compacted bentonite buffer material. These processes are driven both by the temperature gradient that controls thermochemical equilibrium, and hence solubility of mineral phases, and by the hydration front progress from the host rock to the hot waste canister. High temperature (>100°C) is expected to favour, at least in a transient stage, the drying of bentonite near the heat source and the presence of a relevant gas (air, CO_2, H_2O)-aqueous solution-clay interface near the water saturation evolving zone. Then, dissolution-precipitation reactions related to concentration of ions in evaporative zones and the coupling with cation exchange distribution changes will take place. This work analysed the distribution of soluble minerals (i.e. calcite, gypsum, anhydrite, halite) and the distribution of bentonite (montmorillonite) exchangeable cations affected by the dissolution-precipitation reactions. A 50-cm long column of MX-80 bentonite pellets was heated on its base at 140°C while Pearson water (Na-Ca Cl-SO_4, 0.3 M, pH 7.6) was supplied through its upper surface at a very low pressure. The experiment was implemented at CIEMAT to simulate in the laboratory the conditions of the barrier material used in the HE-E in situ test (Mont Terri, Switzerland). After almost 10 years the cell was disassembled and the bentonite was sampled for its physical, geochemical and mineralogical characterization. The hydration behaviour of montmorillonite, its stability at crystal-chemical scale and the distribution of soluble ions and extractable cations (soluble plus exchangeable) were described in (Villar et al. (2023).
A detailed analysis of accessory mineralogy (soluble minerals represent < 1%) allowed to distinguish dissolution-precipitation zones related to temperature and evaporative processes. Gypsum precipitated at 50°C (17 cm from the heater), closer to the heater than the area of maximum sulfate solubility and concentration at 40°C, at 22 cm from the heater. This position showed high sodium concentration (extractable and soluble). Halite precipitated at 10 cm from the heater (60°C), where evaporative processes resulted in montmorillonite being partially dehydrated. Extractable sodium (exchangeable + soluble) decreased from the 40°C zone towards the heater, whereas extractable Ca concentration increased, although the soluble sodium content was overall ten times higher than the calcium one. Calcite precipitated in the area at two cm from the heater, and traces of anhydrite could be identified from 9 to 5 cm (60-100°C). Ongoing characterization using SEM localised analyses in clay masses free from salts along the column and montmorillonite basal spacing deconvolution detected the increased amount of divalent cations in the warmer zones. These data combined with clay-water interaction modelling will be used to assess the soluble minerals and exchangeable cations distribution driven by the simultaneous heating and hydration processes.

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TOWARDS A SCALABLE APPROACH TO ANTIBIOTIC DEGRADATION USING CLAY AND ENZYME-CLAY SUPPORTED BIO-GEOFILTERS

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The wide use of antibiotics, both in humans and in veterinary use, and the subsequent release of their residues into aquatic and terrestrial ecosystems is an issue that generates increasing concern in public health authorities and the population in general. However, the available scientific data are still limited, so it is necessary to broaden knowledge in order to prevent problems such as those associated with the generation of resistance to antibiotics due to repeated consumption of subclinical doses. The regenerated wastewater obtained from wastewater treatment plants (WWTP) is used for an efficient irrigation and fertigation. However, despite the tertiary treatments these waters may contain small concentrations of antibiotics. The scope of the research delves into the monitoring of antibiotic residues in intensive horticultural systems, while reducing or even eliminating their presence thanks to the combined effect of nanostructured geomaterials (as high surface area Mg-smectites and sepiolite) and enzymes produced by ligninolytic fungi capable of degrading organic molecules.

Biogeochemical strategies associated with adsorption-degradation of antibiotics have been implemented. In a first step, materials were prepared minimizing colloidal dispersion (used in 1mm size mineral grains, or by a remould-extrusion procedure heating hermetically at 300 ^{0}C, all mixed with 50 % quartz sand material). Then, small size (2×2 cm diameter and length) column experiments were performed to study the efficiency of adsorption-degradation of tetracycline hydrochloride (TCH) with or without immobilized clay (mg-clay stevensite) *Laccase* enzymes. Considering relatively high TCH concentration (100 µg/L) compared to < 1 µg/L measured in WWTP regenerated waters, a stable reduction to 15 µg/L during 4 days was achieved, with enzyme, at 1ml/min contaminated water flow, whereas a constant 50 µg/L concentration is reached in 2days without enzyme. The role of enzyme in overall efficiency was tested alone in batch experiments including TCH and sulphamide antibiotic families. Several bentonites showed adsorption-degradation efficiencies close to 100 %, that were higher than free enzyme (90 %) and also activated carbon (90%) and MOF (80%). The inclusion of redox mediators additions after the bio-geochemical step highly improved degradation. Both enzymes and redox mediators can be obtained from fungi culture or olive oil processing wastes. These processes are being improved in larger and multi-step strategies. The development of a real-scale bio-geofilter means minimizing the concentration of antibiotics in irrigation water from regenerated wastewater, which represents a solution to the current waste problems in intensive horticultural systems.

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MIGRATION PROPERTIES OF NICKEL IN BODA CLAYSTONE FORMATION

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(1) Centre for Energy Research

High level radioactive waste is planned to be disposed in deep geological repositories in Europe. In addition to the multi-component engineering barrier system, the host rock of the repository serves as a natural barrier to contain the radionuclides. In several European countries, argillaceous rock was chosen for the disposal of high-activity radioactive waste. In Hungary, the potential host rock is the Boda Claystone Formation (BCF). The aim of this work is to investigate the sorption and diffusion properties of the Ni^{2+} cation in order to evaluate the radionuclide retention capacity of the Boda claystone, which serves as a natural barrier. Using synthetic pore water, after kinetic tests on powdered and conditioned albitic claystone samples, sorption isotherm was recorded. Sorption tests were also performed on petrographic thin sections. The applied initial Ni^{2+} concentration of through-diffusion experiments was selected based on the obtained isotherm. The concentrations in the liquid phase were monitored by ICP-OES and TXRF. Although the porewater contains significant amount of salt (0.02 M NaCl), a reliable calibration could be obtained for TXRF. The solid phase was examined by microscopic X-ray fluorescence (μ-XRF) in order to obtain the diffusion profile. With appropriate sample preparation technique samples for transmission electron microscopy (TEM) were created to identify the sorbing minerals and study the distribution of sorbed nickel on the nanoscopic scale.
The sorption isotherm recorded on BCF core samples is very similar to the results reported for other clay formations. Correlation analysis of μ-XRF measurements on thin sections suggested that nickel is primarily bound to clay minerals (mainly illite and chlorite) which was confirmed by TEM measurements. Around illite particles a newly formed, nickel-rich few atomic layer thick phyllosilicate phase was identified. The discrepancy of the experimental and modelled sorption isotherm at high concentrations could be explained with this nickel-rich new phase. Based on the through-diffusion experiments the effective diffusion coefficient of Ni^{2+} (C_{in}=10^{-2} M) are in the same order of magnitude for the studied BCF sample as reported data for other clay-rich rock media.

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STRUCTURATION, DYNAMICS AND DIFFUSION OF WATER IN IMOGOLITE NANOTUBES

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Imogolite nanotubes (INT) with stoichiometry $(OH)_3Al_2O_3Si(OH)$ are clay nanomaterials formed of a rolled gibbsite sheet with isolated $SiO_3(OH)$ units inside. They can be synthesized by soft chemistry and Si atoms can be replaced by Ge ones. The inner diameters of Si and Ge-based INTs are respectively 1.5 and 2.9 nm.
We study nanoconfined water inside Si and Ge-INTs thanks to complementary experimental and numerical approaches, namely X-ray scattering, quasi-elastic neutron scattering, inelastic neutron scattering and classical or ab-initio molecular dynamics simulations.
A unique structure of the water layer adsorbed inside Ge-INT is revealed [1]. Water molecules form an ordered triangular lattice on the inner surface of the nanotube. To the best of our knowledge, this structure differs from that of any kind of two-dimensional water. Water dynamics remains harmonic from 10K to 300K, with no phase transition towards a liquid state up to room temperature.
In Si-INT, the adsorbed water layer is no more solid-like but it is structured periodically along the tube axis z. Water close to the nanotube wall diffuses along a ring in the (x,y) plane, while water in the central section of the pore diffuses rapidly along the z axis (A. D'Angelo et al., article in preparation).
Interactions at the interface are decisive for the transport properties. Comparison between carbon and imogolite nanotubes helps illustrate this point very well. Moreover, the subtle structural and morphological differences between Si and Ge-INTs explain the dissimilar water behaviour close to the nanotubes walls.

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THE ATOMIC STRUCTURE OF IMOGOLITE NANOTUBES: A 50 YEARS OLD ISSUE REINVESTIGATED BY X-RAY SCATTERING EXPERIMENTS AND MOLECULAR DYNAMICS SIMULATIONS

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Fine fibrous aluminosilicate clay particles, named imogolite, were first reported in 1962 in Japan [1]. Despite many studies, their structure remained a mystery during the ten years following their discovery. A first important milestone was the determination of the morphology of imogolite, as a hollow nanotube, by high-resolution electron microscopy in 1970 [2]. Two years later, in 1972, Cradwick and co-workers proposed its structural model in an article that is still a must-read [3]. The nominal composition of imogolite nanotubes (INT) is established to be $Al_2SiO_7H_4$. An imogolite nanotube consists of a curved di-octahedral gibbsite-like layer $AlO_3(OH)_3$ and of isolated $SiO_3(OH)$ tetrahedra connected by three mutual oxygen atoms to aluminium octahedra. Its point group is C_{2Nh}, N being the number of silicon tetrahedra along a circumference. The third important date in the development of research on imogolite is 1977, with the first synthesis of INTs [4]. There is now a consensus that synthetic INTs have a larger diameter (a larger N value) than natural ones and that this diameter (N value) may depend on the method of synthesis. However, diameters (N values) reported in the literature over the last fifty years are not consistent.

After an introduction that reviews the key steps in the studies on imogolite and the inconsistencies between some of the results, we present our work, which has been conducted on synthetic INTs for which external diameters ranging from 2.2 to 3.2 nm were reported, together with a value of N=12 [5]. We have performed X-Ray Scattering (XRS) experiments on nanotubes in suspension and on the same sample as a powder after removing water. The analysis of XRS diagrams is based on Molecular Dynamics simulations allowing us to obtain INTs with different values of N. We find that the sample is made of a mixture of nanotubes with N=13 and N=14 (A. D'Angelo et al., article submitted). Our study points towards strong deformation of the nanotubes in their dry state, which makes the analysis of XRS diagrams rather tricky. XRS investigations in the literature are discussed from the perspective of our results.

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PHOSPHATE AND FLUORIDE REMOVAL USING POSITIVELY CHARGED CLAYS : A SIMPLE AND EFFICIENT WATER TREATMENT PROCESS

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(1) Imerys Talc Europe

The removal of toxic anions is of paramount importance to ensure an excellent quality of drinkable water. Hence, considering electrostatic adsorption mechanisms, anions cannot be adsorbed easily by most of the negatively-charged natural clays. In order to solve this issue, positively-charged clays were tested as adsorbents for phosphate and fluoride in water treatement applications. This study compares the adsorption performances of synthetic layered double hydroxides (LDHs) and natural halloysite. The minerals were at first characterized by XRD, SEM and FTIR in order to highlight their chemical and mineralogical purity.
Regarding the adsorption tests, kinetics and isotherm experiments were carried out to evaluate both phosphate and fluoride performances. It has been found out that the phosphate removal was very efficient with halloysite and LDHs, with adsorption rates ranging from 262 to 423 mg/g, depending on the product mineralogy and chemical composition. Discussion on the adsorption mechanisms will also be presented and an outlook on the selection of adsorbent for industrial applications will be shown.

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AMMONIA REMOVAL FROM INDUSTRIAL WASTE WATER TREATMENT BY A SEQUENCED RENEWAL FLUIDIZED BED REACTOR

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The ammonium ($NH4^{+}$) in the wastewater indicates that the organic matter is not completely degraded. It can act as an indicator of water pollution. Ammonium can corrode pipes, cause bacterial revival or the development of odorous microorganisms.

Zeolite is a natural porous microporous mineral of green colour, composed of tetrahedral complexes of $(SiO_4)^{4-}$ and $(AlO_4)^{5-}$ and connected by an oxygen bridge. This mineral is increasingly studied for the treatment of water for its retention capacities (exchange and adsorption of cations), as a complementary solution to activated carbon (AC). For example, this mineral was used during the Chernobyl disaster to retain radioactive elements, limiting their spread in the environment.

In this case, the objective was to highlight the interest of using a natural zeolite, with a clinoptilolite ratio greater than 85%, for the adsorption of ammonium and metallic trace elements in an industrial effluent.

Thus, the performances of the zeolite were measured at a laboratory scale by doing tests in batch reactors and in innovative treatment facilities. The reactor is designed to be used in ascending water flow to fluidize the zeolite bed. The minimum fluidization speed is measured, as well as the rate of expansion of the bed and the contact time to have an optimal adsorption reaction.

This process has already proven its effectiveness with micrograin activated carbon for organic matter and organic micropollutant (pesticides/Drug residues) removal. The objective here is to highlight the ability to replace activated carbon with zeolite in a continuous fluidised bed reactor.

During the project, all the hydraulic feasibility studies were carried out, proving:

– The density of the zeolite, higher than AC micrograin, is not a showstopper. At the same water rise rate, the expansion of the zeolite bed is between 10 and 20%, while with AC we reach 30 to 40%

– the grain size of the zeolite is between 0.3 and 1.0 mm

– The residence time of 10 minutes in the reactor is sufficient to adsorb ammonium and trace elements

– The feasibility of using this type of material in this type of reactor.

In conclusion, micrograin zeolite is an interesting and feasible solution to treat industrial wastewater effluents in fluidized bed reactors, allowing flexibility in treatment rate, contact time and response to variation of concentration in the effluent.

Natural zeolite (clinoptilolite) from Imerys has a high adsorption capacity in ammonium and heavy metals and is therefore a chemical-free and sustainable solution for the treatment of industrial effluents.

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ADSORPTION PROPERTIES AND MEDICAL APPLICATION OF NATURAL CUBAN ZEOLITE

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The natural Cuban zeolite mainly used in our investigations resulted in a mixture of the medium-pore 10-membered ring zeolite clinoptilolite and the large-pore 12-membered ring zeolite mordenite. The fundamental research included particle size, mineralogical and chemical composition, as well as amine binding capacities (histamine and serotonin) of this mineral in some cases compared to a natural clinoptilolite from Mexico. The Cuban zeolite was applied both orally as contemporaneous drug for physiological processes within the gastrointestinal tract and topically for skin care treatment by a special paste formulation. The methods applied range from physical determinations like X-ray diffraction (XRD) over chemical analyses with inductively coupled plasma optical emission spectrometry (ICP-OES) and high-performance liquid chromatography (HPLC) up to blood examinations for different substances and characterization of clinical symptoms. All methods will be described in detail in the single papers which are listed in References. The Cuban zeolite exhibit higher BET surface areas and larger total pore volume in comparison to the Mexican clinoptilolite obviously due to their different mineralogical compositions. The histamine uptake capacity at corresponding particle size is significantly higher in the Cuban zeolite compared to the Mexican one. Furthermore, smaller particles adsorb more histamine than larger particles [1]. Histamine is of special interest because it performs pleiotropic effects in human beings like histamine intolerance, gastric acid production and influences multiple rare diseases. Serotonin (5-HT) is another important biogenic amine, produced within the gut and well known as the ‘hormone for fortune’ in the brain. The uptake and release experiments of 5-HT on zeolite were performed using its stable serotonin hydrochloride (5-HT-hc). The investigated zeolites (mordenite, clinoptilolite, Cuban zeolite) adsorbed 5-HT-hc at about 14 mg per gram zeolite without large differences between different samples but in the same range as histamine. Release studies of 5-HT-hc-loaded zeolite revealed that 5-HT-hc is strongly bound to zeolite independent of pH value and zeolite framework; only up to 12.7% was released into the water [2]. Excessive peripheral blood levels of 5-HT provoke amongst others severe diarrhoea as caused by neuroendocrine tumors (NET), usually known as “carcinoids”. Oral application of a natural Cuban zeolite formulation called Detoxsan® was able to reduce bowel movements of patients suffering from therapy-refractory diarrhea. The clinical results show that about 70% of patients benefit from taking it for reducing bowel movements from numerous defecations to normal level and thereby increasing significantly living quality [3]. Furthermore, natural Cuban zeolite for topical application on skin surface (Detoxsan® Paste) is based on petrolatum and contains additionally squalane as natural lipid component. This waterless formulation covers the skin surface, avoids water and oxygen supply as prerequisite for microbial growth of pathogens and acts as adsorbent for histamine and water. The skin damaged by intertrigo and mycosis could be visually restored completely during 10 and 15 days, respectively [4].

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CRYSTALLOCHEMICAL CONTROL ON THE HYDROGEN ISOTOPE EXCHANGE IN SMECTITES

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The hydrogen isotope ratio in clay minerals records their formation temperature and fluid H isotope composition during the mineral formation. A mineral resistant to post-formation isotope exchange can preserve its original composition whereas a mineral undergoing fast H exchange would lead to paleoenvironmental misinterpretations. On the other hand, the sensitivity of a mineral to post-formation H exchange allows determination of the extent of the post-formation changes, making the clay mineral a crystallographic site-specific probe of water-rock interactions over temperature gradient, i.e. in bentonite buffers.
Because of the presence of interlayer adsorbed water that instantaneously exchanges with environment and the nm-size crystallite dimensions, smectite is hypothesised to be the most prone to H isotope exchange in structural OH groups among all clay minerals. In this study, the H isotope exchange in smectites and their interstratified varieties was revisited using infrared spectroscopy (IR). IR is an efficient tool enabling in-situ and ex-situ observation of D/H exchange reaction based on OH and OD stretching bands as a proxy for H isotope exchange in nature. For various D/H exchange tests we used a set of smectites with various layer crystalochemical compositions and interlayer cations, and a few interstratified minerals with different illite-to-smectite ratios.
In any tested sample, no H isotope exchange within OH groups was observed at room temperature (~22°C), nor during short-term water saturation with relative humidity 60-80%, nor after a year in liquid D_2O water. Experiments conducted at 90°C under full D_2O vapour (not liquid) saturation for 12-16 months showed a strong control from the octahedral cation composition on H isotope exchange. Dioctahedral smectites with Fe^{3+} substitution for Al^{3+} (nontronite) exchanged most extensively (>20% D/H exchange), followed by the samples with both Mg^{2+} and Fe^{3+} substitution (montmorillonite), whereas those with nearly pure octahedral Al^{3+} (beidellite) exhibited negligible D/H exchange. Trioctahedral saponites did not show any exchange after 16 months. In interstratified illite-smectite, the exchange is controlled by the fraction of fixed illitic interlayers.
High temperature experiments were carried out in-situ using diffusion reflectance IR spectroscopy with gas flow at constant D_2O concentration at 150-300°C (below the temperature of dehydroxylation). Under these conditions, significant H isotope exchange was observed for all clay minerals within 60 minutes of exposure. The exchange is controlled by the extent of interlayer opening allowing interlayer D_2O diffusion, which is linked to the particular properties of interlayer cations.

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DEVELOPMENT OF RAW MATERIAL CONCEPTS FOR THE SUSTAINABLE SUPPLY OF THE CEMENT INDUSTRY WITH CALCINED CLAYS TO REDUCE CO2 EMISSIONS

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(1) Stephan Schmidt KG

In the course of decarbonisation, the cement industry is pursuing three routes. In addition to the capture of CO2 and its use (CCU) or its storage (CCS), a special focus is on the avoidance of CO2 emissions. Calcined clays play an important role here as a substitute for the cement clinker made from limestone. To meet the decarbonisation targets of the German cement industry, 6.8 to 7.5 million tonnes of clay will be needed by 2030 (Basten, 2022). In order to cover this very high demand for clays, which must be extracted in addition to the large tonnages for the ceramics industry, waste clays from treatment processes, such as filter cakes and clays from sludge ponds, are to be used in addition to quarrying from existing mining operations. However, these waste materials have the disadvantage that they are very variable in mineralogical-chemical composition in comparatively small quantities. Therefore, the operation of the calcination plants must be adjusted to these changing raw material conditions.
Stephan Schmidt KG operates 16 open-cast clay mining operations in the Westerwald/Germany. From these deposits, more than 100 clays were subjected to a screening process not only with regard to their basic suitability for calcination, but also with regard to a constant 20-year supply reliability of a calciner. In a first screening step, the carbonate content (< 5 mass-%), the sulphide concentration (< 1.5 mass-%) and the clay mineral/quartz ratio (> 50 %) were assessed. Clays that met these requirements were calcined at 750 °C and subjected to a test for pozzolanic properties. The Surana method (Surana and Joshi, 1990) was chosen to determine the pozzolanicity. By chemically treating the calcinates after Surana (solving with 0.5 molar sodium hydroxide solution and heating for 3 minutes), pozzolanic Si and Al ions are present. At a concentration > 80,000 ppm (Al+Si), suitability as a clinker substitute is ensured, comparable to the performance of blastfurnace slag and fly ash (Schulze and Rickert, 2019). The final step in the evaluation of calcined clays involves the testing of CEM I cements (activity index/EN 450-1; water demand/EN 196-3; compressive strength/EN 196-1), in which 25 % of the cement clinker phase is replaced by calcined clays.
As a result, 2 supply areas (Arbon, Sedan) were identified. While the raw material mixture from Arbon has a high smectite content, the Sedan mixture is kaolinitic-illitic dominated. Each site allows the delivery of 250,000 t clay/a (this corresponds to the production of 200000 t/a of calcinate) and the production in a flash calciner or rotaray kiln can be supplied over a term of at least 20 years with const. quality. These annual quantities of the two areas of origin will allow the continuous operation of two calcination plants.

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DEVELOPMENT OF A DISORDER STRUCTURAL MODEL FOR ILLITE-HYDROXY-INTERLAYERED SMECTITE (I-HIS) AND IT'S USE FOR THE QUANTIFICATION USING THE RIETVELD REFINEMENT TECHNIQUE

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The acidic weathering of soils leads to the degradation of essential soil properties such as soil fertility along with water or cation buffering capacity caused by Al^{3+} mobility and subsequent polymerization in the interlayer galleries of expandable clay minerals. This well-known Al^{3+}-intercalation is known as hydroxy-interlayering and minerals are classified as hydroxy-interlayered minerals (HIMs). Typically, these minerals have been only qualitatively described by X-ray diffraction because of their pronounced structural disordering, however, suitable structure models using Rietveld refinement technique have been developed recently (Dietel et al., 2019a,b). This approach also allows quantification of the mineral phases in soils based on physically meaningful calculations. The authors published first disorder structural models for hydroxy-interlayered smectite (HIS) as a first step to describe the phenomenon. Discrete smectite is usually only a minor component in soils compared to for example interstratified illite-smectite minerals. Such interstratified phases also contain smectitic interlayers and during acid alteration these "reaction volumes" are at least partially transformed to illite-hydroxy-interlayered smectite (I-HIS), which consists of micaceous (illitic) layers interstratified with hydroxy-interlayered smectitic layers (HIS) and expandable smectitic layers. The goal of the study was to develop disorder structural models for interstratified I-HIS with different typical Reichweite values (R0, R1, R3). Validation was performed using natural samples (R1, R3) ISCz-1 (CMS standard) and sárospatakite ("Füzérradvány illite"). Additionally, models were compared with calculated/simulated diffraction patterns (Reichweite R0) using an independent software (DIFFaX). The natural samples were experimentally treated with Al with I-HIS as reaction products of different degrees of hydroxy-interlayering. Calculated X-ray diffraction patterns (R0, DIFFaX) were tested on diffractograms without and with admixture of internal standard (corundum), in order to evaluate the quality of the fit and to check the quantification results. The presentation will give an overview about the model development, and it's use for natural soil samples.

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WHAT HAS CAUSED DIFFERENCES IN GAINS AND LOSSES OF EXCHANGEABLE CATIONS IN 'ALTERNATIVE BENTONITE BUFFER MATERIAL IN-SITU TESTS' (ABM-1, -2 AND -5) AFTER HEATING FROM 140 °C TO 250 °C?

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Bentonites are candidate materials for High-Level Radioactive Waste (HLRW) repositories and, therefore, investigated with respect to long-term stability. In-situ tests are conducted in rock laboratories such as the second phase (2012) of the 'Alternative Buffer Material test' (ABM) in Äspö, Sweden. Here different bentonite buffer materials with various exchangeable cation populations were packed vertically on each other with an iron tube as heater in the centre [1]. We report on changes of cation exchange data of the whole packages ABM-1, ABM-2, and ABM 5. Direct comparison of extracted exchangeable cation is a challenge because boundary conditions varied between the different packages. All three packages were:

(1) heated in different steps and to different peak temperatures.

(2) heated after water saturation (ABM-2 and -5) or directly from start (ABM-1).

(3) naturally saturated with water by typical fractures in the crystalline rock mass.

(4) additionally technically saturated with water using performated Ti tubes in different ways: ABM-1 started with an intensive water saturation system for each block at 4 different positions (120 holes) whereas only 4 holes for each 10 blocks (12 holes) were artificially water saturated in ABM-2 and in ABM-5 the water saturation system was not in operation.

(5) packed with the same bentonites plus two clay rocks plus cages with bentonite-granulate mixtures etc. (ABM-1 and -2) but with bentonites only in ABM-5.

(6) monitored for water pressure differences in the galleries above the experiments, and that system was used intensively for ABM-2 after pressure drops were detected. Such water pressure drops may be an indication for so-called boiling of water in the sand filter around the blocks. Here possibly water has left the system to the rock and was filled up again in cycles.

During heating groundwater entered the blocks for water saturation by diffusion from the rock side to the heater. Exchangeable cations were redistributed between the different (mostly bentonite) materials. In contrast to the former experiments ABM-1 and 2, however, in ABM-5 the average exchangeable Na^+ occupation of the reacted material (46 %) was much closer to the reference materials (49 %). Exchangeable Mg^{2+} loss was different from the exchangeable Na^+ trend and comparable to ABM-2, whereas exchangeable Ca^{2+} gains were lower at high temperatures. How does this fit together? The presentation will give an overview on possible reasons for these differences.

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CLAY AS MULLITE PRECURSOR AND ITS IMPORTANCE IN THE FIRING OF VITRIFIED CERAMICS

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In whiteware (porcelain, porcelain stoneware, vitreous china, etc.) clays have a recognized technological role, traditionally restricted to milling, shaping and drying operations, where clay minerals perform their function of slip stabilizer and plasticity provider. In fact, the action of clay minerals during firing is largely underestimated, being considered mere precursors of new crystalline and amorphous phases, especially mullite after kaolinite (or illite). Although several studies have concerned the kinetics of mullite formation and its microstructural aspects, little is known about the degree of mullitization and its repercussions on the sintering behavior of whiteware. To fill this gap, the quantitative determination of mullite in various porcelain stoneware tiles (XRPD-Rietveld) was performed as a function of the chemical composition of the batches (XRF-EDS) and their sintering behavior (optical thermodilatometry). The degree of mullitisation varies according to both the clay minerals and the overall chemical composition. This results in a gradient in the amount, composition, structure and physical properties of the liquid phase. Example is provided of how a mullite variation can affect some characteristics of the melt, such as the alumina saturation index, the degree of depolymerization, and the shear viscosity. These differences are reflected in the firing behavior, and in particular in the sintering kinetics, densification efficiency and dimensional stability at high temperature, which are improved by increasing mullitisation. The degree to which clay minerals give rise to mullite may explain why batches of similar chemical and mineralogical composition behave distinctly during firing.

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PREPARATION AND UTILIZATION OF FLY ASH – CLAY COMPOSITE SORBENTS FOR WATER TREATMENT

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A growing rate of industrial and anthropogenic activities on the one hand and increasing requirements for environmental protection on the other, have led to a finding and developing new methods for effective use of recycled and waste materials in decontamination technologies. Clays and other aluminosilicates including lower grade materials, opened new possibilities in adsorption technologies due to favourable physico-chemical and surface properties, environmental friendliness and reasonable price. Fly ash produced worldwide in large amounts as a product of combustion in heating and power plants represents a typical waste with promising properties, whose current utilization reaches only 25% of its global production.

The composite sorbents were prepared as the mixtures of high quality clays from Central European deposits (kaolin from West Bohemia containing more than 65% of kaolinite (SK), clinoptilolite with a purity of 85% from East Slovakia (CL)), and two fly ashes from Czech operations, differing in the type of fuel and combustion temperature. The prepared composites were tested for the adsorption of the toxic cations (Pb^{2+}) and anions (AsO_4^{3-}, CrO_4^{2-}) from model solutions at laboratory conditions. The initial concentration of 0.5 mmol L^{-1} simulated a heavily contaminated water system.

The use of composites with fly ash from biomass burning increased the sorbability of Pb^{2+} to SK from 10% to > 98%, and the sorbability of AsO_4^{3-} on CL by more than 15%. The composites containing coal ash demonstrated an increase in Pb^{2+} and AsO_4^{3-} sorbability up to 10% on both SK and CL. The effect of fly ash addition in clay sorbents depended on its chemical composition and homogeneity, but mostly on the specific surface area (S_{BET}), whereas the S_{BET} of biomass ash >> S_{BET} of coal ash.

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PD THICKNESS OPTIMIZATION ON SILICATE SHEETS FOR IMPROVING CATALYTIC ACTIVITY

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Maximizing surface-to-body ratio demands ever smaller metallic palladium (Pd) nanoparticles for catalytic applications. The quest for miniaturization is now reaching the single-atom limit. However, if the supported Pd is below a critical size, the p-d hybridization with the supporting material can detrimentally reduce the labile electrons that facilitate the catalytic reactions. Thus, the smallest attainable size, i.e., single-atom Pd, may not offer the best efficiency. Here, we demonstrate that Pd with at least 6 atomic layers (or thickness of ~ 1 nm) on the silicate sheets, synthesized via the partial exfoliation of a layered silicate, exhibits a metallic-like electronic property, yielding an excellent catalytic activity for dehydrogenating formic acid (a favorite hydrogen storage material) higher than both isotropic Pd nanoparticles and single-atom Pd.

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TIO2-LOADED NANOTUBULAR MATERIALS BASED ON KAOLIN GROUP MINERALS AS SPATIALLY CONFINED NANOREACTORS FOR PHOTODEGRADATION OF DEOXYNIVALENOL

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For a considerable time, TiO_2 has been widely acknowledged as one of the most promising photocatalysts. The mixture of its polymorphs, anatase and rutile, is particularly desirable due to their interplay. However, the high catalytic performance is likewise dependent on minimizing the semiconductor particles aggregation, thus exposing active sites and limiting charge carriers recombination. The loading of TiO_2 onto various supports may improve its dispersion and recyclability. Mesoporous nanotubular phyllosilicates have recently gained much attention due to their ability to serve as spatially confined nanoreactors to enhance the photodegradation of pollutants. Their use has a great potential for the decomposition of molecules that are difficult to adsorb, such as deoxynivalenol mycotoxin.

Our study employed a kaolinite-rich sample from Maria III deposit (Poland) as the source material for the synthesis of nanotubes through intercalation and grafting processes, which were described previously [1]. The obtained nanotubes (MN) and calcined ones (MNC), as well as untreated kaolinite (M), halloysite-containing sample from Polish Dunino deposit (HD) and halloysite purchased from Sigma-Aldrich (HS) were impregnated with TiO_2 via sol-gel technique. The applied procedure enabled the production of materials containing TiO_2 within the range of 13.4-22.3 wt.%. Raman spectroscopy revealed various anatase/rutile ratios depending on the mineral support. The samples' structure, texture, morphology, and light absorption capacity were characterized by XRD, FTIR, N_2 adsorption/desorption, UV-Vis DRS spectroscopy, SEM and TEM microscopy.

Due to the simplicity of the analysis, we conducted preliminary UV-induced photodegradation experiments (365 nm, 10 mW/cm^2) using dyes – methylene blue, safranin O and acid blue 129. The samples with the nanotubular support (excluding HD) performed significantly better compared to the platy kaolinite (M). The sample with MNC support achieved a high degradation rate, similar to the rate observed for the commercial P25 TiO_2 (Evonik). Taking into account the ratio of photodegradation efficiency to TiO_2 content, the materials with MNC and HS carriers showed a better photocatalytic effect than the P25. Radical trapping experiments indicated the dominating role of $\cdot OH$ and $\cdot O_2^-$ radicals in the photodegradation of methylene blue. Analogous photocatalytic experiments are currently being carried out for deoxynivalenol with the use of high-pressure liquid chromatography (HPLC) for the determination of its concentration.

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SYNTHESIS, CHARACTERIZATION AND APPLICATION OF ALGERIAN LOCAL CLAY-BASED MESOPOROUS MATERIALS FOR THE TREATMENT OF PHARMACEUTICAL EFFLUENT

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The Djebel Debbagh (Guelma) and the balconies of el Ghoufi (Batna) are part of the most important massive neritic platform Northeast Algeria. It is characterized by its high potential clay mining resources, especially kaolin (DD3) and palygorskite. A study was designed to assess the efficiency of treated and modified DD3 kaolin and palygorskite to mesoporous materials for treatment of pharmaceutical effluent. Indeed, the discharge of the pharmaceutical industry constitutes an enormous nuisance for the environment and for human health.
The mesoporous materials synthesized from DD3 kaolin and palygorskite were characterized by XRD, SEM imaging and EDS analysis. Optimisation of synthesis conditions of mesoporous material was performed and it appears that the pH and the amount of tribloc copolymer are the most important parameters affecting synthesis.
The hybrid process coagulation-floculation and adsorption on mesoporous material synthesized from DD3 kaolin or playgorskite of effluent treatment by several materials was carried out.
The efficiency of the hybrid process is determined by the reduction of the pollution indicator parameters (BOD, COD, colour, and turbidity) of the treated effluent. The overall data showed that the combined process led to an almost complete reduction in all physico-chemical parameters.
*This work is supported by the PRIMA program under grant agreement N°*2024-TRUST *project.*
Keywords: mesoporous material, DD3 kaolin, palygorskite, pharmaceutical effluent treatment, hybrid process (coagulation-floculation and adsorption).

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RESTORATION OF MOROCCAN HISTORICAL HERITAGE WITH A GEOPOLYMER BINDER

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The historical monuments of the Old Medina of Fez city in Morocco, were built from clays and sands available around. Nowadays, this historical heritage is restored using a cement-lime mortar that may cause irreversible damages to the monuments, as a result of efflorescence and the high rigidity of the cement [1]. To palliate these issues, geopolymer binders could be an alternative, indeed, these binders can be obtained using natural calcined clays. Consequently, the aim of this study is to develop a geopolymer coating, based on Moroccan raw materials for historical heritage restoration. To achieve this objective, different Moroccan sands and clays were collected nearby Fez city.

The experimental procedure consists on mixing the moroccan clay previously calcined at 700 °C with a potassium silicate solution, after that, the reactive mixture is applied on different substrates such lime stone (calcite), concrete and plaster by projection. The projection was done using a pressure of (3 bar), an application distance of 40 cm and a number of layers of two. Microstructural analysis and adhesion tests were performed on the applied coatings.

The characterisation of the clays show that it contain kaolinite, muscovite quartz and calcite. It was possible to obtain geopolymers from these calcined Moroccan clays, and to apply these materials as coatings. The adherence of the coatings varied from 1 to 9 MPa depending on the used substrate and its surface. The interactions between the geopolymer coating and the substrates are limited, manifested by a weak diffusion of the alkaline element of the order of 8 μm.

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FORMULATION OF A GEOPOLYMER GROUT FOR RADIOACTIVE WASTE DISPOSAL

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This study is a part of the project of high and intermediate level radioactive waste disposal (Cigéo project for Centre Industriel de stockage GEOlogique). The construction of the disposal facility will be conducted underground in the Callovo-Oxfordian argillite layer. This will lead to the excavation of millions of tons of argillites. To use and to recycle these large quantities of excavated argillites is one of the challenges of the Cigéo project. Among the materials developed from aluminosilicate sources, geopolymers can be a way to use the excavated argillites. One of the possible uses within the Cigéo project could be the formulation of a grout to be injected at the interface between the high-level radioactive waste vaults and the host rock. Geopolymers materials results from the activation of an aluminosilicate source, at ambient temperature, using an alkaline silicate solution. The requirements for the expected geopolymer grout are to display a viscosity ≤ 5 Pa.s, a working time of between 6 and 24 hours and a pH value ≥ 12 after setting. The aim of this work is to develop an injectable geopolymer grout and study its evolution with time, at 20°C and 80°C.
Different aluminosilicate sources were used, such as an industrial metakaolin and Callovo-Oxfordian argillite calcined at 650°C. Two potassium silicate solutions were used. Six formulations satisfying the above criteria were selected and characterized by structural and chemical analyses such as X-ray diffraction, Fourier transform infrared spectroscopy and thermogravimetric analysis.
The results show that, after setting, there is no evolution after few days at room temperature, while a curing period at higher temperature induced structural changes. At 80°C, there would be a different dissolution/reactivity of the aluminosilicate species, leading to a different structural network compared to room temperature preparation and curing. These more reactive species lead to the formation of a geopolymer network characterized by a different amorphous phase compared to the same materials stored at 20°C.

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SPATIALLY INDIRECT EXCITONS IN HOLLOW ALUMINOSILICATE AND ALUMINOGERMANATE NANOTUBES.

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Aluminosilicate (AlSi) IMO-NTs, structurally analogous to the naturally occurring imogolite mineral, have emerged as a potential and promising candidate for photocatalytic and co-photocatalytic water-splitting applications [1]. Being based entirely on cheap and abundant raw materials and easily synthesised at low temperatures with high compositional and monodispersity control, AlSi IMO-NTs represent a potentially viable and low-cost route to sustainable energy technologies. Central to their functionality is the permanent polarisation of the (1 nm thick) NT wall that promotes the separation of photogenerated electron-hole pairs on the external and internal NT surfaces. The AlSi IMO-NTs, therefore, potentially solve two long-standing issues within the field of photocatalysis: (i) Effective separation of charge carriers in photocatalytic materials, which is a critical obstacle that must be overcome to prevent rapid recombination processes leading to diminished photolysis rates, and (ii) promotion of charge carriers to the interface between the photocatalyst and the reactant molecules, which is a prerequisite for the charge transfer reactions that initiate photolysis. The development of an industrially viable photocatalyst has the potential to have a large impact on the solar energy sector.

DFT (and electrophoresis experiments) have revealed that the permanent polarization of the IMO-NT wall stems from their composition and structure. The NT wall curvature and surface functionality have been found to modulate the magnitude of the local dipole density across the wall (in an otherwise dipole-free system), potentially offering multiple routes for tailoring photocatalytic applications [1]. Theoretically, we have been able to begin to unravel the role of this dipole density for charge-transfer excitations and photocatalytic applications [1], but this has only been instigated utilising methods that have well-known and documented limitations: for example, the inability for DFT to model excited states, and for TD-DFT to accurately describe excitations (and associated excitonic relaxations) within crystalline solids.

The recent development and availability of low-scaling Bethe-Salpeter Equation (BSE) simulations within the Quantum ESPRESSO code [2], opens up the possibility to investigate excitonic excited states in chemically complex systems with a large number of atoms for the first time. In particular, we will report on the use of these BSE simulations to unravel the role of (i) intrinsic polarisation and surface functionalization in governing real-space separation of electron-hole pairs in an emerging class of photocatalytic materials based on Imogolite Nanotubes (IMO-NTs).

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SHAFT SEALING WITH THE SANDWICH SEALING SYSTEM - A LARGE SCALE EXPERIMENT AT THE MONT TERRI ROCK LABORATORY

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Shaft seals are part of the engineered barrier system (EBS) that belongs to the multi-barrier system for deep underground repositories of high-level radioactive waste. Shaft seals are designed to limit the fluid inflow in the early stage after closure of a radioactive waste repository and to delay a possible release of radionuclides from the repository at later stage. Current German concepts of shaft seals contain the hydraulic Sandwich sealing system as a component of the lower seal in the host rock. In contrast to conventional hydraulic seals of monolithic bentonite the Sandwich sealing system consists of sealing segments (DS) of bentonite and hydraulically conductive equipotential segments (ES) (Nüesch et al., 2002). Formation water that is penetrating the hydraulic seal via preferential flow paths is contained in the ES and evenly distributed over the cross section of the seal. Thus, a more homogeneous hydration and swelling of the DS is obtained.
In July 2019 a large-scale experiment was launched at the Mont Terri rock laboratory (MTRL) to demonstrate the feasibility of installation, to investigate the saturation process and to assess the sealing effectiveness. The in-situ experiment consists of two experimental shafts of 1.18 m diameter and 10 – 12.6 m depth in the sandy facies of the Opalinus Clay. The DS in both shafts are constructed of German Ca-bentonites from Bavaria (Calcigel) and Westerwald region (Secursol), respectively. Both Sandwich sealing systems are hydrated with Pearson water type A3. The in-situ experiment is accompanied by extensive laboratory work and numerical modelling.
The presentation will focus on selected aspects of the laboratory work, that comprises mineralogical analyses, swelling pressure tests, MiniSandwich experiments and semi-technical scale experiments. The variety of experiments on different scales and with different model geometries allow us to recognize and understand different scale-dependent and nonlinear effects on the hydro-mechanical-chemical properties and the system behaviour.

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The Sandwich pre-project and the Sandwich in-situ experiment were/are funded by the German Federal Ministry for Economic Affairs and Energy under contracts 02E11587 and 02E11799.

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REDOX PROCESSES AT THE CLAY MINERAL-WATER INTERFACE

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Reactions at the clay mineral-water interface significantly contribute to the biogeochemical cycling and environmental fate of contaminants, elements, and nutrients in soils and sediments and have even been connected to the advent of life on Earth. In addition to sorption/desorption and acid/base catalysis, redox reactions at clay mineral surfaces are key processes and the latter are enabled by the isomorphic substitution of the environmentally ubiquitous element iron into clay mineral octahedral and tetrahedral sheets. This talk will report on our work that has concentrated on developing a mechanistic understanding of electron transfer reactions to and from clay mineral iron and their quantitative description with the aim to better predict contaminant fate and remediation.

The particular focus will be on two intriguing aspects of interfacial clay mineral redox reactions: 1) the formation of transient, reactive mineral intermediates (RMIs) when aqueous ferrous iron reacts with clay mineral octahedral iron; and 2) the redox reactivity and fate of iron in tetrahedral sheets of clay mineral. To study the solids in the systems, we used a range of complementary techniques, including ^{57}Fe-Mössbauer spectroscopy, infrared spectroscopy (FT-IR), high-resolution transmission electron microscopic imaging and analysis (HR-TEM, EDS, SAED), and X-ray scattering analyses (XRD, pair distribution functions). To quantify the clay mineral iron redox reactivity, we used probe compounds or mediated electrochemistry.

Investigations of solid samples after exposure of clay minerals to aqueous iron demonstrate interfacial electron transfer from aqueous to clay mineral iron. Moreover, we observed 10-20 nm-sized RMI nanoparticles – made up of silicon and iron – that often occur embedded in the clay mineral matrix, implicating clay minerals as a source of silicon in addition to a sink for electrons. While short reaction times preserve the overall layer structure of the clay minerals, extended exposure (> 1 year) to ferrous iron leads to extensive clay mineral alterations, including decreased layer stacking, reduced mineral layer size, and mineral fringe bending, which are typical characteristics of freshly precipitated clay minerals. The absence of nanoparticles in these aged samples suggests the participation of these RMIs in the apparent transformation of the original clay minerals. Interestingly, chemical reduction (dithionite) and re-oxidation (hydrogen peroxide) of synthetic nontronites with variable amounts of tetrahedral iron (0-1/4) also resulted in alterations of the clay mineral. Several lines of evidence point to the convergence of the clay mineral tetrahedral iron content to the same low value (0.2/4) independent of the initial tetrahedral iron content. Although XRD results indicate that the overall clay mineral layer structure was preserved, evidence from TEM suggests decreased layer stacking and reduced mineral layer size, similar to what we observed after reaction with aqueous ferrous iron. Moreover, we found that iron released from clay mineral tetrahedral sheets was partly retained in the clay mineral interlayers and induced clay mineral aggregation into spherical superstructures. Despite these structural and morphological changes, the redox properties, determined electrochemically, were independent of both the initial and final tetrahedral iron content but differed between the native and re-oxidized minerals. Our data provide new fundamental process understanding of the role of the RMIs and tetrahedral iron in clay mineral transformation and for the (bio)geochemical cycling of iron.

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NAC CARRIERS BASED ON LAYERED DOUBLE HYDROXIDES OF ZINC, COPPER AND ALUMINUM

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The immobilization of N-acetyl-L-cysteine (NAC) drug into layered compounds through intercalation can be advantageous, since the architecture of these materials can provide increased physical-chemical stability, biocompatibility, bioavailability, besides the possibility of modified release [1]. NAC is a L-cysteine-derived amino acid applied as a mucolytic agent in treating paracetamol poisoning and in the control of the bacterial biofilms formation caused by *Xylella fastidious* [2]. However, NAC presents a very low bioavailability (from 4 to 10%), possibly due to the pro-oxidant characteristic of the plasma [2]. The aim of this work is to investigate the NAC intercalation into layered double hydroxides (LDHs) with zinc-copper-aluminum composition ($Zn_{(2-x)}Cu_xAl$-NAC, with x = 0.25, 0.5, 0.75 and 1). The metal cations were chosen considering their biological properties. $Zn_{(2-x)}Cu_xAl$-NAC was synthesized by the coprecipitation method and characterized by structural, spectroscopic, thermal, textural, and elemental chemical analysis. X-ray diffraction patterns presented d_{003} basal spacing of 19.3, 17.1, 18.2, and 16.3 Å, for materials with x = 0.25, 0.5, 0.75 and 1, respectively, suggesting a bilayer arrangement of the antioxidant NAC between the layers. The FTIR spectra of $Zn_{(2-x)}Cu_xAl$-NAC presented bands at 1575 (ν_{as} COO^-) and 1395 -1380 cm^{-1} (ν_s COO^-), 1628 (δ H_2O), 532 (ν Al-OH), and 418 cm^{-1} (δ O-M-O) [3]. The band assigned to S-H stretching is absent. Thermal analysis results for the samples showed the steps of dehydration, dehydroxylation (DTG peaks at 35-340 ºC), and decomposition of the organic species, which occurs with the release of fragments *m/z*= 44 (CO_2; DTG peaks at 150-830 ºC) and *m/z*= 64 (SO_2, DTG peaks at 350-830 ºC). The initial temperature of release of CO_2 molecules was 157 (x=1); 162 (x=0.75); 207 (x=0.5) and 262 °C (x=0.25). According to chemical elemental analysis, the loading capacities were 29.4%, 26.5%, 27.6% and 26.7% for x = 0.25, 0.5, 0.75 and 1, respectively. The results here reported demonstrate that $Zn_{(2-x)}Cu_xAl$-NAC hybrid material presents potential for application in the medicinal and agronomic fields. The results suggest that the greater the replacement of Cu^{2+} by Zn^{2+} in the matrix, the lower the initial temperature of release of CO_2 molecules, thus reducing the thermal stabilization.

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ROCKJOCKML: AN UPDATED VERSION OF ROCKJOCK FOR THE MODERN GEOLOGIST

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Quantitative phase analysis (QPA) of whole rocks and sediments using X-ray powder diffraction (XRPD) is a standard, workhorse technique for many types of geologists and soil scientists, and there are a number of methods for accomplishing this. Regardless of the method, however, the main source of analytical error in QPA is usually the likelihood of inexperienced analysts choosing inappropriate phases for modeling a sample XRPD pattern. The algorithms employed by standard XRPD analysis software to help the user choose phases to include typically involve simple peak-matching routines, which cannot mimic the sorts of background knowledge expert analysts use to make such decisions (e.g., the relative prevalence of different minerals, which minerals are likely to occur together, and the results of other analytical techniques).

RockJockML is a full-pattern summation QPA program for analyzing XRPD patterns of geological materials. It is based on the original RockJock program created by D.D. Eberl of the U.S. Geological Survey in Microsoft Excel, but updated to provide dramatically increased processing speed, an intuitive workflow, and a number of features designed to help the user more accurately pick phases for inclusion in the analysis. The program was created in the MATLAB language, but is deployable in a standalone version for Windows, Macintosh, and Linux operating systems without the need for a MATLAB license. It can be downloaded at http://geol.byu.edu/bickmorewiki/, where documentation and training materials can also be found.

Some of the methods available for phase selection in RockJockML are user driven, while others are automated using models generated by machine learning algorithms. The requirement of domain expertise, and the inability to apply a simple, straightforward algorithm to address the problem, is exactly the scenario where machine learning techniques are best applied. Machine learning algorithms generate models to perform complex tasks that would normally require human interaction. The initial release of RockJockML contains three machine learning algorithms, all of which find the best mixture without user intervention. The first algorithm is a forward method that selects minerals from most prevalent to least prevalent until a threshold is met. The second is a constrained optimization algorithm that automatically selects the best mixture of candidate minerals at once. Finally, we have implemented a genetic algorithm that utilizes random walks to determine the best combination of minerals.

We are in the process of creating a database of synthetic mineral patterns that can be utilized to train more advanced machine learning algorithms. We will briefly discuss these algorithms, as well as a plan to include chemistry data so that a user can determine if the phases chosen match bulk chemical analysis.

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CHARACTERISTICS OF A GLASS/COPPER/BENTONITE MODEL SYSTEM UNDER REPOSITORY CONDITIONS

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All states that engage in any kind of nuclear application must consider the management of radioactive waste and must secure safe-handling based on the level of radioactivity and the national/international regulations. There is a broad consensus that the accepted method of ensuring long term safety for high level radioactive waste (HLW) is the isolation in a deep geological repository (DGR), which will provide passive multibarrier isolation of radioactive materials. The vitrified HLW form in a copper canister is specifically designed for long term durability during storage and disposal [1,2]. The requirements for container lifetime and integrity depend on the DGR concept and the chosen geological medium.

The purpose of this research was to study the corrosion behavior of copper in a bentonite environment. We focus on the interface of two materials (copper in two forms and bulk borosilicate glass) in contact to B75 bentonite to obtain information on the chemical evolution in terms of alteration in solid phase composition at a detailed small scale (micron and sub-micron).

We built a scale model system where close to real conditions were provided (temperature, porewater). The main goal was to understand the characteristics, applicability, and stability of the whole system, from the physical/chemical properties of the glass and copper to the bentonite response in the repository. We have been conducted a glass/copper/bentonite experiment (setup) using synthetic porewater [3,4] for saturation. The corrosion potential was continuously measured (Cu wire vs Pt electrode in bentonite). The experimental setup was kept in an incubator at 80 °C. After 90-day exposure to the porewater, the setup was opened for post-mortem characterization. With SEM/EDX investigations we focused on the composition and nature of alteration products formed on the glass/copper and within the bentonite. Slight corrosion behavior appears on the Cu-plate, but no S species are detected in the corrosion product layer. No alteration layer has been found on the borosilicate glass samples, the elemental composition of the investigated material changes in rather small amounts. After the completion of the 12-week experiments the porewater solution was analyzed by ICP-OES/IC. The measured B, Ca, K and Na concentration increased, while the Mg, and Si concentration decreased. Concentrations of Cl^- and SO_4^{2-} ions as determined by ion chromatography in the final porewater are close to the starting concentrations, the increase was less than 10% for chloride but higher for sulfate.

Details of the phase characteristics and trends of the dissolution rates will be presented.

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VARIABILITY OF CHEMICAL WEATHERING CONDITIONS DEDUCED FROM MINERALOGY OF SEDIMENTARY CORES RETRIEVED FROM CRATER LAKES IN CENTRAL MEXICO

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Central Mexico represents a highly sensitive area for the study of climate variability as it lies beyond the northern limit of the Intertropical Convergence Zone (ICTZ) and at the southernmost limit of the area influenced by the North American Monsoon (NAM)[1]. NAM summer rainfall is modulated by El Nino Southern Oscillation (ENSO), with generally reduced/increased precipitation during El Niño/La Niña events[2]. Most paleoclimate studies on continental or marine (e.g. lacustrine sediments[3-4], speleothems[5], corals[6] and deep-sea sediments[7]) archives indicated stronger ENSO activity over the last 4 kyr than during the mid-Holocene but paleo-reconstructions give contradictory results on the variability of ENSO activity in terms of frequency and amplitude[5,8]. For the present study, three Holocene lacustrine sedimentary sequences were collected from Central Mexico along the Trans-Mexican Volcanic Belt. This area displays widespread crater lakes that are closed systems that in their sedimentary sequences potentially record climatic variability with relatively limited influence of human impact. The studied craters are small (0.3-0.6 km^2) with steep internal crater walls, i.e. conditions that favor a rapid response to rainfall-related runoff[9]. The mineralogical assemblages and their temporal evolution within the three lakes have been compared to better understand the main factors controlling the weathering conditions. Mineralogy being indicative of the degree of chemical weathering of the crater soil cover, it reflects the climate conditions within the closed watershed. By applying radiometric age-depth models, the mineralogical results will be compiled with regional meteorological measurements to identify any proxy as sensitive tracer of rainfall intensity. The new paleorecords will be compared with regional reconstructions[10-11] to evidence the common trends in ENSO temporal evolution and bring valuable insights into Holocene climate variability in the tropics, on a global scale.

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THE ROLE OF CLAY MINERALS IN MICROBIAL MN OXIDATION IN ROCK VARNISHES REVEALVED BY OBSERVATIONS AT THE NANO- AND ATOMIC SCALES

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Rock varnish is widely distributed on exposed rock surfaces on both Earth and Mars and is considered a potential location for the origin of life. In this study, we present systematic and detailed observations of rock varnishes from arid regions of China at the micro-, nano-, and atomic scales. Near-edge X-ray absorption fine structure (NEXAFS) analysis revealed a moderate negative correlation between the average oxidation state of Mn in rock varnishes and the crystallinity of illite, indicating that Mn oxidation is more likely to occur on larger, better-crystallized illite. Our results from electronic probe microanalysis (EPMA), high-resolution transmission electron microscopy (HRTEM), and atomic probe tomography (APT) further showed that illite provides nucleation sites for Mn oxidation. Fourier-transformed magnitudes of extended X-ray absorption fine structure (EXAFS) spectra of some rock varnish samples revealed high similarity to Mn_4Ca clusters in photosystem II, which was not observed in lower surface rock samples that received less solar irradiation (i.e. the shaded side of landforms). Additionally, scanning transmission electron microscopy equipped with electro energy loss spectra (STEM-EELS) and APT detected nanosized Mn clusters enriched in organic matter. We found intracrystalline and intercrystalline organic matter in close association with the Mn-Ca clusters, suggesting that such organic matter could be abiotic photosynthetic products of the illite-Mn_4Ca cluster association. This association has never been reported but may play a role similar to that of photosystem II in photosynthetic organisms.

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RED CLAYS AS ALTERNATIVE RAW MATERIALS FOR THE PORCELAIN STONEWARE TILES INDUSTRY: MINERALOGICAL AND TECHNOLOGICAL CHARACTERIZATION

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The ceramic tile industry requires annually a huge amount of raw materials. Clays represent the 40% of these raw materials, while feldspars and quartz sand represent almost the remaining 60%. It is thus straightforward how the supply chain of this materials may strongly impact on the economy of the European ceramic districts. Indeed, in Europe, the ceramic tile industry rely mainly on resources outside the European Union. In Italy, before 2022, a third of ball clays was imported from Donetsk basin, in Ukraine. The recent geopolitical upheaval poses serious questions on the supply chains for the ceramic production, stressing how the supply on alternative chain is strategic and vital for the ceramic sector. From a technological viewpoint, it would be desirable to find other raw materials with suitable properties, such as, e.g., a high plasticity, easy sinterability, and light color. In the Ukrainian clays, these favorable properties arise mainly from the mineralogical composition and grain size distribution. Thus, an accurate mineralogical and rheological analysis are of paramount importance in evaluating the exploitability of new raw materials.
The largest industrial district of the Italian ceramic tile production is located in the Sassuolo area. Starting from 90’s, the production converted into porcelain stoneware, with a shift from local resources to imported raw materials. However, in the current geopolitical scenario a partial return to local resources, alongside favoring the tendency toward a circular economy, can represent and option to reduce the import reliance. Regarding the characterization of raw material deposits located near Sassuolo district, the literature data were mainly obtained by qualitative mineralogical analysis coupled with chemical data, which provide a semi-quantitative mineralogical analysis, while and accurate quantitative phase analysis and detailed testing are missing.
In this work, we present the full characterization of two red clays deriving from quarries located near the Sassuolo ceramic district. These red clays are iron-rich (~7% Fe_2O_3), thus comporting well-known issues in the ceramic tiles production. The features of these samples were compared with those of a German ball clay containing rather high levels of iron (~3% Fe_2O_3). The employed analytical techniques are X-ray diffraction with Rietveld analysis, X-ray fluorescence, and thermogravimetric analyses. Moreover, we tested the effects of a partial substitution of Ukrainian ball clay body (used as benchmark) with the most suitable Italian red clay and the German ball clay into a standard batch for porcelain stoneware. The obtained bodies were fully characterized from milling to firing. The amount of the novel raw materials added to the batches were carefully chosen to evaluate the effect of the iron on the technological properties of the semifinished and finished products.
Results demonstrated that the substitution of the classic Ukrainian ball clays with the Italian and German clays do not introduce any bottleneck in the ceramic production. The addition of the German ball clay resulted in a slight increase of the sintering temperature (compared to the benchmark), possibly related to the higher quartz content of this raw material. Conversely, the addition of Italian red clay induced a reduction in the firing temperature (compared to the benchmark), possibly related to the higher content of iron as well as of feldspars. The most significant variations are in the color of the tiles, which results darker (compared to the benchmark) in all the tested bodies, for the presence of iron.

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CHARACTERIZATION AND TECHNOLOGICAL PERFORMANCES OF ZEOLITE-ENCAPSULATED ORGANIC UV FILTERS

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Zeolites are well-known to be particularly suitable for high-value technological applications based on ion exchange and selective adsorption of organic molecules. Besides the use of zeolites to remove organic pollutants from wastewater, in the last decades the attention was focused also on the realization of novel functional materials based on the encapsulation of organics (e.g. dyes, polymers) inside zeolites [1]. UV filters (UVfs) are organic or inorganic materials capable of blocking UV rays, and have become ubiquitous due to the adverse effects of UV rays on goods and human health. Unfortunately, organic UVfs easily undergo photodegradation, and several UVfs and co-formulants are often combined to enhance their stability and efficacy. In the last decades, the encapsulation of UV filters in diverse inorganic or organic matrixes demonstrated to be an effective stabilization strategy, e.g. [2], and the research and development of new UVfs is still ongoing.

We recently developed hybrid UVfs obtained by the encapsulation of the two organic UVfs octinoxate (OMC) and avobenzone (AVO) into zeolites with different topologies (MOR, FAU, MFI, and LTL) and Si/Al ratios [3]. We optimized the loading procedure and characterized the obtained hybrids, ZEOfilters, focusing on their UV filtering properties. The use of ZEOfilters should i) inhibit the UVf-skin and UVf-UVf interactions ; ii) reduce the content of UVf, stabilizers, and other co-formulants thanks to the enhanced filtering power and stability of the encapsulated UVfs. The optical properties of the obtained hybrids are strongly related to the UVf/zeolite combination. Potassium LTL and sodium 13X zeolites were found to be the most promising hosts for UVfs and were thus investigated more deeply. Then, as a proof of concept, LTL- and 13X-based ZEOfilters were formulated into simple cosmetic formulations. Recently [4], selected ZEOfilters were also investigated from a structural perspective, by high-resolution synchrotron X-ray powder diffraction, Fourier-transformed IR spectroscopy, and DFT modelling. In the LTL/OMC ZEOfilter, FT-IR highlighted a perturbation of the ν(C=O) mode of the OMC carbonyl group which was demonstrated, by structural refinement, to bond the extraframework K cations of LTL zeolite. This interaction may also secure the UVf molecule inside the zeolite structure thus preventing its release in the environment, but this hypothesis still needs to be validated. Meanwhile, DFT calculations are investigating the behaviour of ZEOfilters based on FAU-type zeolites, which showed strongly variable properties depending on Si/Al ratio and UVf.

The observed properties are promising for the future development and exploitation of ZEOfilters, which can be a more effective, safer, and eco-friendly alternative to traditional UVfs.

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SELECTIVE CO2 CAPTURE BY MICROPOROUS ORGANICALLY PILLARED LAYERED SILICATES (MOPS)

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Climate change is one of the greatest challenges of our time. Steadily rising CO_2 levels in the atmosphere are one of the main causes of global warming.[1] To counteract this, mitigation of CO_2 emissions is of utmost importance. The CCUS strategy (carbon capture utilization storage) includes the capture of CO_2 either at point sources or even directly from air.[2,3] A significant problem with most capture materials used today, like with amine scrubbing techniques, is the high energy consumption required for the regeneration of the materials due to the chemisorptive binding of CO_2, which makes this a costly technique.[3,4] In this context, microporous organically pillared layered silicates (MOPS) [5] represent a very promising class of materials in which the capture is based solely on physisorption and the energy input can thus be noticeably reduced.[6] The slit-shaped (ultra-)micropores in MOPS are obtained by intercalation of cationic (metal-)organic pillars between the silicate layers. The spatial arrangement of the pillars is based exclusively on undirected electrostatic interactions and the electrostatic attraction between the anionic silicate layer and the cationic interlayer species leads to a minimization of the layer spacing. By the choice of the pillar, slit height and width can thus be adjusted independently in sub-angstrom steps in a highly modular way. While the height of the pore is defined by the small elliptical axis of the pillar, the pore width can be defined by the tunable charge density of the layered silicate and the large elliptical axis of the pillar. Furthermore, chemical functionalization of the pore space is much more feasible since the pillars contribute directly to the internal surface area of the pore.[5-8] This allows MOPS to tune the selectivity and adsorption enthalpy independently. Here, we chose a flat-lying thin pillar, where consequently the selectivity is determined by the slit height (size exclusion principle), while the adsorption enthalpies are determined by the slit widths and potentially specific interactions with the pillar. With this diammonium-pillared MOPS, we observed superbly selective CO_2 capture based solely on physisorption. CO_2 was selectively captured from industrially relevant gas compositions (flue gas: CO_2/N_2 15/85; biogas: CO_2/CH_4 50/50; natural gas sweetening: CO_2/CH_4 5/95) even though the physical properties of the competing gases are very similar. The selectivity for CO_2 over CH_4 was ~7 and 400 for CO_2/CH_4 50/50 and CO_2/CH_4 5/95, respectively. A nearly perfect selectivity could be observed even over N_2, with N_2 uptake for typical flue gas composition being below the detection limit.[6]

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PORE WATER CHEMISTRY IN THE LOWER CONFINING UNITS OF THE OPALINUS CLAY FORMATION AT THE MONT TERRI ROCK LABORATORY

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In the framework of the HS (Hydrogeological Survey of the Mont Terri anticline) experiment performed at the Mont Terri Rock Laboratory (Switzerland), a new 60 m deep borehole BHS-1 was drilled into the lower adjacent aquifer of the Opalinus Clay with the aim of constraining the hydrogeological situation at Mon Terri. The borehole BHS-1 was drilled with water perpendicular to bedding through the Opalinus Clay and the lower confining units, Staffelegg Formation and Klettgau Formation (Early Jurassic and Late Triassic strata), from which no data were available so far. The borehole BHS-1 is located at the entrance of Ga98 north, the well head being located 320 m below surface in the southern limb of the Mont Terri anticline, below the Main Fault. Eleven core samples, belonging to six different lithostratigraphic units intersected during the drilling of borehole BHS-1, were collected, preserved from air contact inside aluminium foil bags at vacuum and analysed.

The objective of this work was to analyse the mineralogical, geochemical and physico-chemical properties of the rock samples, as well as to characterize the pore water chemical composition from each lithostratigraphic unit. This information will serve as additional input data for the existing 3D hydrogeological models and for better understanding the extent of carbonate aquifers and groundwater flow conditions around the Opalinus Clay Formation.

The mineralogical and geochemical analyses revealed the characteristics of the different units, showing variations in the organic carbon content, pyrite and clay mineralogy. The CEC ranged 67.4 to 246.1 meq/kg, being sodium the main exchangeable cation. The pore water was extracted by the squeezing technique at different pressures [1], depending on the water content of the samples, with values ranging between 4.8 to 10.7%. A chloride profile across the whole formations indicates a characteristic water and solute transport controlled by diffusion [2], decreasing the chloride content from the Opalinus Clay towards the lower adjacent formations, with values ranging from 0.31 M to 0.06 M. The average chloride accessible porosity was of 0.63.

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MICROSTRUCTURAL EVOLUTION OF LIGHTWEIGHT CEMENTED SOIL

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In the management of civil infrastructures, one of the main issues is to reuse the excavated soil as construction material, by improving its physical and mechanical properties. In this framework, the soil treatment is an efficient way to transform this kind of soils from waste into a resource and to guarantee the sustainability of civil works.
In the field of cement treated clays, Lightweight Cemented Soil (LWCS), i.e., a material prepared by the mix of natural soil, water and cement with air foam, is suitable for many geotechnical applications, thanks to a high workability of the mixture and good mechanical properties combined with a reduced unit volume weight [1]. The complex microstructure that characterises the material, i.e., a large pore system induced by foam immersed in a cemented porous matrix with inclusions of portlandite, suggests the needing of a multi-scale analysis to study the chemo-physical evolution and microstructural features of the system [2].
In this work, microstructural changes of LWCS over curing time have been investigated by means of Mercury Intrusion Porosimetry (MIP) and X-Ray micro-CT. Pore-size distributions of lightweight cemented samples were obtained at 24h, 7 days, 28 days and 60 days of curing. An increase in the cumulative intruded mercury volume is observed as air foam content increases, regardless of curing time. The modal pore size of cement-treated samples is not modified by the addition of air foam. Moreover, the results show an increase in small-diameter pore frequency with the progressive formation over time of hydrated phases characterised by nanometre-sized pores. However, this frequency is slightly affected by air foam addition for each curing time [2].
The use of X-Ray micro-CT is crucial for the analysis of the voids induced by foam, as this class of porosity has a mean diameter of about 300 μm, so it is outside the range investigable with MIP. Image analysis of X-Ray micro-CT scans, performed at 24h, 7 days, 28 days and 60 days, shows that voids induced by foam remain stable over curing time. Conversely, as curing time increases, the formation of shrinkage fractures due to the setting of cement and the consumption of the white and denser phase, i.e., the portlandite, consistent with the development of pozzolanic reactions, is clearly observed.

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INVESTIGATION AND CATALYTIC APPLICATIONS OF MAGNETIC HEMATITE NANOPARTICLES

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The past decade has attended a great deal of research into the catalytic reactivity of metal nanoparticles controlled by size, shape and composition. In these contests, the aim of researching a new eco friendly strategy entirely focused on green chemistry has received much attention and has become of prime interest. Several efforts were done to overcome the use of precious metals (Pt, Pd etc.) for the synthesis of catalysts. In fact, inexpensive metals, such as Ni, have been used for the synthesis of promising nano-catalysts [1] that were used for the reduction of basic organic compounds. [2] By using metal-nanoparticles, as catalysts, it has been possible to overcome several limits linked to the use of inexpensive materials; moreover is possibile to work under sustainable conditions and in respect of green chemistry principle. Here we report the results of synthesis and investigation of hematite nanoparticles (Hem_NPs) [3] obtained by controlled thermal treatment of polymer supported iron (III) complex (Fe-POL). The Fe-POL was synthesised under mild and green reaction conditions and analyzed by field emission scanning electron microscopy (SEM). The microporous grains which incorporate globular Fe-NPs was heated up to 400 °C, monitored every 25 °C by powder X-ray diffraction (PXRD) and thermogravimetric analyses. PXRD patterns showed the Hem_NPs formation, already after 300 °C with relevant diffraction effects at 400 °C. The Hem_NPs showed a magnetic behaviour and was deeply analysed by SEM-EDS, XPS, Raman and FTIR spectroscopy as well as by magnetic analysis, and then compared with the natural hematite sample. Differently from natural micrometric hematite, synthesised Hem_NPs turned out to be an efficient catalyst for the hydrogenation of nitroarenes in ethanol at 80 °C, by using hydrazine as reducing agent. Complete conversion of the substrate was obtained after 3 h, and the catalyst was recycled on nitroarenes and halonitroarenes (bromo-nitrobenzene)at least 7 and 5 times, with no drop of catalytic activity and selectivity. The magnetic properties of Hem_NPs make the catalyst an interesting and promising material for its easy recyclability.

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NEW HYBRID LAYERED DOUBLE HYDROXIDES/METAL COMPLEX/ENZYME EXPLORATORY SYSTEM: FROM CATALYSIS TO HYBRID CATALYSIS.

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Green chemistry aims to design and develop chemical products and processes that reduce the use of solvents, the number of by-products, and the number of synthesis steps, inspired from Nature. Here two strategies are considered to meet the objectives of green chemistry. The first is to use hybrid catalysis[1], combining enzymatic and chemical catalysts to lead to one-pot reaction cascades. The main scientific hurdle to be overcome concerns the compatibility of the conditions of the two catalytic reactions, acid pH and high temperature for the first reaction, neutral pH for the optimum activity of the biocatalysis. Heterogenization of both catalysts may solve this problem at the same time as it can facilitate recycling and purification of the catalysts. The challenge here is to select a support capable of catalyst immobilization and being resistant to the catalysis conditions. Thanks to their chemical flexibility, open 2D-framework and tunable surface properties, Layered Double Hydroxides (LDH) appear among the best candidates for the simultaneous confinement of molecular catalysts and macromolecular biocatalysts, acting as a barrier for the compatibilization of the chemoenzymatic system.

In this study, we explore the immobilization into LiAl and Zn_2Cr LDH of i) a gold catalyst, NHC-Au(I), which catalyzed the hydration of alkyne into alcohol[2] and ii) the Fructose-6-phosphate aldolase (FSA)[3] which catalyzed the aldol condensation into chiral monosaccharides (Fig.1). Chemical stability and catalytic activity of LDH-NHC-Au(I) and LDH-FSA were first investigated separately for various substrates, respectively a series of alkyne and the formaldehyde. In a second step we challenge the formulation of the ternary system LDH/NHC-Au(I)/FSA in the way to succeed the one pot one step hybrid catalysis of propargylic alcohol into erythrulose that must operate in acidic pH condition (pH 3.0). Various synthesis, post-treatment synthesis and biopolymer coating were tested to improve the acidity resistance of the LDH. [4]

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DESIGN OF NANOSTRUCTURED LAYERED DOUBLE HYDROXIDES USING METAL-ORGANIC FRAMEWORK MATERIALS AS SACRIFICIAL TEMPLATES

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The application of layered double hydroxides (LDH) in environmental remediation has been reported for more than two decades and is now well established [1]. However, LDH prepared by conventional methods are heavily stacked and have limited specific surface area, leading to a reduction in active sites [2]. Thanks to recent advances in synthetic methods, 3D layered and porous LDHs can be prepared [3], such as supramolecules, metal oxides and metal organic frameworks (MOFs) as sacrificial templates for LDHs [4]. MOFs are hybrid nano- and macro-structures based on transition metals that display different topologies and morphologies with enhanced surface properties and reactants [5]. The conversion of MOFs into LDHs provides a very novel and interesting strategic route for the preparation of LDHs with novel structures.
In this study, we first optimized and compared the preparation of iron-based MOF (MIL-88A) by hydrothermal-assisted and microwave-assisted precipitation to tune the size and shape of the particles. In the second step, MIL-88A was rapidly and efficiently converted to Ni-Fe LDH/MIL-88A by simultaneous local etching and co-precipitation reactions in a mixed solution under the screening of microwave conditions, and the original three-dimensional structure was maintained. The structural and morphological changes were monitored by X-ray diffraction, Raman and FTIR spectroscopy, electron microscopy (SEM, TEM), DLS and N_2 physisorption. LDH synthesized using conventional co-precipitation methods was used for comparison. This new LDH was further modified by calcination at 200°C, 300°C and 400°C to increase its specific surface area and reactivity. These materials demonstrate efficient catalytic activity via persulfate activation for the degradation of organic pollutants.

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NOVEL NIFE LDH CATALYSTS FOR THE DEGRADATION OF ORGANIC POLLUTANTS VIA PERSULFATE-BASED NONRADICAL OXIDATION

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Persistent organic pollutants (POPs), which are widely distributed in natural waters, are of global concern because of their high toxicity, carcinogenicity, bioaccumulation and potential threat to the aquatic environment [1]. Among the most studied POPs, bisphenol A (BPA), which has an aromatic structure, poses a significant risk to human health due to its difficulty in biodegradation and endocrine-disrupting effects [2]. Advanced oxidation processes (AOPs) are one of the most successful strategies for the complete degradation of emerging contaminants to harmless substances such as carbon dioxide and water [3]. Advanced sulfate-based oxidation processes (PS-AOP) have demonstrated their efficacy in degrading organic pollutants. Transition metals have shown successful and satisfactory efficiency in PS-AOPs due to high efficiency, ease of access and low cost effectiveness.

Iron and nickel layered double hydroxides (Fe-Ni LDH) containing two transition metals have been widely used as catalysts because of their high anion exchange capacity, adsorption properties and large specific surface area. The conversion of metal-organic framework-based materials into LDHs as sacrificial templates can preserve the original structure and lead to the formation of nanostructured mesoporous LDH macrostructures, thus promoting the degradation properties of LDH. Fe-Ni LDH using MIL-88A (LDH/MIL-88A) as a template was prepared and used as a catalyst for the degradation of bisphenol A and a large series of organics (Fig. 1) via persulfate activation. It was found that LDH was able to catalyze the degradation of BPA under both light and dark conditions, and that light had little effect on this process. And by comparing the catalytic degradation of LDH synthesized by conventional co-precipitation with MIL-88A, the efficiency of LDH/MIL-88A was much higher, and the best catalytic effect of LDO calcined at 300 degrees Celsius.

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CO2 CAPTURE BY HYDROXIDES INTERSTRATIFIED IN THE NANOLAYERED SPACE OF A CLAY MINERAL

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Due to the compact two-dimensional interlayer pore space and the high density of interlayer molecular adsorption sites, clay minerals are competitive adsorption materials for carbon dioxide capture. We have investigated the adsorption mechanisms of CO2 in dried and hydrated synthetic fluorohectorite clay using a combination of powder X-ray diffraction, gravimetric adsorption, spectroscopies and density functional theory simulations. Both dried and hydrated fluorohectorite show crystalline swelling and spectroscopic changes in response to CO2 exposure. These changes can be attributed to interactions with condensed hydroxide interlayer species, and swelling occurs solely in the interlayers where this condensed species is present. Furthermore, we have demonstrated that with a decreasing interlayer surface charge in a clay mineral, the adsorption capacity for CO2 increases, while the pressure threshold for adsorption and swelling in response to CO2 decreases. Synthetic fluorohectorite was investigated with three different layer charges varying from 0.3 to 0.7 per formula unit of Si4O10F2. We associate the mechanism for the higher CO2 adsorption with more accessible space and adsorption sites for CO2 within the interlayers. The low onset pressure for the lower-charge clay is attributed to weaker cohesion due to the attractive electrostatic forces between the layers. The excess adsorption capacity of the clay is measured to be 8.6, 6.5, and 4.5 wt % for the lowest, intermediate, and highest layer charges, respectively. Upon release of CO2, the highest-layer charge clay retains significantly more CO2. This pressure hysteresis is related to the same cohesion mechanism, where CO2 is first released from the edges of the particles thereby closing exit paths and trapping the molecules in the center of the clay particles.

[1] CO2 Capture by Nickel Hydroxide Interstratified in the Nanolayered Space of a Synthetic Clay Mineral Kristoffer W. Bø Hunvik, Patrick Loch, Leide P. Cavalcanti, Konstanse Kvalem Seljelid, Paul Monceyron Røren, Svemir Rudic, Dirk Wallacher, Alexsandro Kirch, Kenneth Dahl Knudsen, Caetano Rodrigues Miranda, Josef Breu, Heloisa N. Bordallo and Jon Otto Fossum Journal of Physical Chemistry C 124, 26222−26231 (2020)

[2] CO2 Adsorption Enhanced by Tuning the Layer Charge in a Clay Mineral Kristoffer W. Bø Hunvik, Patrick Loch, Dirk Wallacher, Alexsandro Kirch, Leide P. Cavalcanti, Martin Rieß, Matthias Daab, Vegard Josvanger, Sven Grätz, Fabiano Yokaichiya, Kenneth Dahl Knudsen, Caetano Rodrigues Miranda, Josef Breu, Jon Otto Fossum Langmuir 37, 14491 (2021)

[3] Influence of CO2 on Nanoconfined Water in a Clay Mineral Kristoffer W. Bø Hunvik, Rodrigo José da Silva Lima, Alexsandro Kirch, Patrick Loch, Paul Monceyron Røren, Martin Hoffmann Petersen, Svemir Rudić, Victoria García Sakai, Kenneth Dahl Knudsen, Caetano Rodrigues Miranda, Josef Breu, Jon Otto Fossum and Heloisa N. Bordallo Journal of Physysical Chemistry C 126, 17243 (2022)

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BRIGHT, NONIRIDESCENT STRUCTURAL COLORATION FROM CLAY MINERAL NANOSHEET SUSPENSIONS

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Structural colors originate by constructive interference following reflection and scattering of light from nano-structures with periodicity comparable to visible light wavelengths. We have demonstrated that bright noniridescence structural coloration can be easily and rapidly achieved from suspended two-dimensional nanosheets of a clay mineral. We showed that brightness is enormously improved by using double clay nanosheets, thus optimizing the clay refractive index that otherwise hampers structural coloration from such systems. Intralayer distances, and thus the structural colors, can be precisely and reproducibly controlled by clay concentration and ionic strength independently, and noniridescence is readily and effortlessly obtained in this system. Embedding such clay-designed nanosheets in recyclable solid matrices could provide tunable vivid coloration and mechanical strength and stability at the same time, thus opening a previously unknown venue for sustainable structural coloration. USAXS studies have provided us with information about the disorder responsible for the noniridescence in this system.

[1] Bright, noniridescent structural coloration from clay mineral nanosheet suspensions Paulo H. Michels-Brito, Volodymyr Dudko, Daniel Wagner, Paul Markus, Georg Papastavrou, Leander Michels, Josef Breu, Jon Otto Fossum Science Advances 8(4), DOI: 10.1126/sciadv.abl8147 (2022)

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WASTE-DERIVED LIGHTWEIGHT AGGREGATE OBTAINED BY MICROWAVE METHOD

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Continuous economic development in the world and improvement of living standards result in the generation of a huge amount of waste, which is a key problem for the natural environment, as well as human life and health. The general assumptions of the waste management strategy recommend preventing their generation and preferring to reuse them. This means the development of sustainable alternatives that can reuse different types of waste by turning them into secondary materials [1]. Among the typical waste, there are very often fly ashes after the energetic coal combustion or glass waste, the so-called glass cullet. Scientists are looking for new methods of waste valorisation, in particular in the buidling engineering sector – for example, for the production of lightweight aggregates. Currently, lightweight aggregates are obtained using naturally occurring clay minerals. This, combined with a high demand for energy – raw materials masses are most often sintered at high temperatures in furnaces – makes the whole process negatively affecting the environment. An alternative is microwave activation, which emits less hazardous gases [2] while reducing processing time [3].
The aim of the research is to produce a sustainable lightweight aggregate based not only on fly ashes, but also on other waste such as waste rock and glass cullet using microwave radiation. Four raw material masses were prepared, including a control aggregate containing fly ash, glass cullet and clay. The remaining 3 recipes contained waste rock (10, 20 and 30%) at the expense of fly ash. Aggregates were obtained by sintering previously granulated raw material masses using microwave radiation in 3 temperatures (1000, 1050, 1100°C). The materials were tested in terms of physicochemical (e.g. XRD, XRF, SEM) and mechanical (e.g. crushing strength, water absorption) parameters.The obtained results showed that the increase in the waste rock content in the aggregate changed its mineral composition, reducing the content of andesine. The sintering temperature had the opposite effect, regardless of the chemical composition of the raw material mass used to produce the aggregate. In addition, both the increase in temperature and waste rock content had a positive effect on the crushing strength (increase from 4.95 to 7.51 MPa).
The conducted research confirms the possibility of obtaining useful building materials (application in high-strength concretes, lightweight structural and non-structural concretes and lightweight mortars) as a result of microwave sintering of waste mixtures of appropriate composition. This, in turn, can bring ecological, environmental and technical benefits – less landfilled waste, lower energy costs and sintering time.
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THE USE OF CYCLODEXTRIN-MODIFIED ZEOLITES FOR THE REMOVAL OF TETRACYCLINE FROM AQUEOUS MEDIA

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Zeolite minerals are hydrated skeletal alumino-silicates of alkali elements, alkaline earth metals, composed of tetrahedrons connected by their corners via shared oxygen atoms. Due to their porous structure and unique properties, zeolites are widely used in environmental engineering, civil engineering, and agriculture [1]. They are frequently applied as efficient adsorbents for various types of environmental pollutants, especially in water treatment technologies for the removal of heavy metals, organics, radionuclides, or ammonium ions. Modification of zeolites with organic compounds is of increasing interest due to their significant potential in removing emerging pollutants from water. Tetracycline (TC) is among the wide-spectrum antibiotics, hard to remove in conventional biological treatment processes [2]. Hence, it is of utmost importance to search for effective methods to remove this type of emerging contaminants from water bodies.

In this work, zeolites from fly ash with three different structure types, NaX, NaA and NaP1, were modified with β-cyclodextrin (β-CD) and their adsorption efficacy towards TC have been studied. To assess the effect of modification on the zeolites, they were subjected to chemical, mineralogical and surface analyses using X-ray diffraction (XRD), thermogravimetry (TG), scanning electron microscope (SEM), N2 adsorption/desorption isotherm, Fourier transform infrared spectroscopy (FTIR), and X-ray photoelectron spectroscopy (XPS). The maximum adsorption capacity for NaX-CD, NaA-CD and NaP1-CD was around 48, 60, and 38 mg/g, respectively. It is much higher than capacities obtained for kaolinite mineral (4 mg/L) [3]. The fastest adsorption rate was observed for NaP1-CD, which achieved adsorption equilibria after 200 min, while for NaX-CD and NaA-CD it was established after around 24 hours. The kinetic data were best described by the Elovich model, followed by pseudo-second-order, while the Sips and Redlich-Peterson models were the most suitable to de-scribe the adsorption isotherms. Based on the adsorption data as well as FTIR and XPS results, TC adsorption efficacy is strongly related to the amount of CD attached to the mineral, and hydrogen bonding formation probably plays the major role between CDs and adsorbate. It is very likely that adsorption mechanisms are complex with dominating adsorption onto energetically homogeneous active sites which are CD cups, with the possibility of strong interactions between CD's hydroxyl groups and amine group present in TC. Zeolites from fly ash modified with CD exhibit good potential as alternative adsorbents in the water treatment technologies aimed at pharmaceuticals removal from the aquatic environments.

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APPLICATION OF ZEOLITES FOR THE PRODUCTION OF ASPHALT MIX BY THE IDEA OF SUSTAINABLE DEVELOPMENT

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Warm Mix Asphalt (WMA), as well as Hot Mix Asphalt (HMA), provide surface durability, comfort and safety for users. What is more, thanks to technological temperatures lowered by approximately 20-40°C, they are environmentally friendly and economical [1,2]. One of the WMA production methods is asphalt foaming through addition of zeolites. Thanks to gradual release of zeolite water, decrease in viscosity and improvement of workability are possible during mix asphalt production, placement and compaction [3,4]. WMA production involves the use of both synthetic and natural zeolites [5]. This work presents/shows the evaluation of the compactability of reference samples of mix asphalt and samples with the addition of zeolites – natural clinoptilolite and synthetic NaP1. Two methods of dosing the zeolites were applied: to the aggregate before the bitumen addition, in the amount of 0.4% of the mix asphalt mass, and directly to the heated bitumen in an amount of 5% of the asphalt weight. In order to improve the foaming effect zeolite material prior to the process of asphalt foaming were soaked with water. In the conducted compactibility tests in a gyratory compactor the compactibility factor, construction densification index (CDI) and traffic densification index (TDI) of the obtained mix asphalts were determined. Asphalt concrete mixture for surface course AC 11S was used as a reference material. The applied additive included: clinoptilolite natural zeolite and NaP1-type synthetic zeolite and obtained from flyash. In order to improve the “foaming effect“, zeolite materials were soaked with water (75% for NaP1 and 50% for clinoptilolite, which resulted from the maximal absorbability of these materials). The CDI and TDI values increased with decreasing compaction temperature in the reference mix asphalt. When zeolite dosed directly into asphalt was used, the CDI values ranged from 20.9 to 31.1 for zeolite NaP1 and from 42.4 to 57.0 for clinoptilolite, depending on the compaction temperature. It is possible to reduce the compaction temperature by 40°C when asphalt is directly foamed with zeolite NaP1 and by 20°C with clinoptilolite. The effect of lowering the compaction temperature depends on the type of zeolite. Based on the analysis of the research results obtained, it can be concluded that the amount and mode of zeolite water release depend on the type of zeolite structure, its textural properties and crystallochemical nature.
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EFFECTIVENESS OF ZEOLITE-BENTONITE PASTES IN SUPERFICIAL HEALING OF CRACKED CEMENT COMPOSITE SURFACE

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The operation of concrete structures is associated with the development of cracks, which can increase permeability and penetration of aggressive components. A preventive method may be surface application of pastes containing bacterial strains and components inducing carbonate precipitation.
The research objective was to evaluate the effect of the composition of pastes containing commercially available Na-bentonite (consisting of quartz, montmorillonite, illite, orthoclase and calcite) and NaX-type zeolite synthesized from fly ash on the intensity and depth of cracks surface healing. The study optimized the ratio between the clay mineral and zeolite, and the content of liquids by compressive strength analysis. Moreover, the impact of bacterial solution and the composition of cementation solution on compressive strength and the effect of the water-to-solids ratio on the penetration depth was evaluated. Finally, a study was conducted on the application effectiveness of pastes made of cementation solution along with raw and bacterial spore-impregnated materials. The proposed method was evaluated by analyzing the ratio and depth of crack surface repair.
Studies have shown that the addition of clay mineral is necessary to bind the paste, but its content above 30% may deteriorate the compressive strength. To ensure the right consistency of pastes the liquid-to-solids ratio should be greater than 1:1. Furthermore, the addition of ureolytic bacteria, both in the form of living cells and spores, had a positive effect on the intensity of carbonate precipitation and the concentration of cementing components can both promote and inhibit precipitation process. Nevertheless, the studied method of healing cracks is promising, but requires further investigation.

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CHARACTERIZATION OF SOIL MICROAGGREGATES AT THE MICROSCOPIC LEVEL USING MOLECULAR DYNAMICS

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Organo-mineral aggregates (OMAs) are the building blocks of soil microaggregates, forming a hierarchy of structures responsible for the unique features of each soil as well as its function in its respective ecosystems. Therefore, to understand and predict the behavior of soils, it is necessary to have a better understanding of the phenomena that take place at the microscopic scale.[1]

By using computational simulations, it is possible to explore molecular interactions in detail and gain insight into properties that are inaccessible from experiments. On the one hand , it is possible to generate representative models of the organic fraction of the soil based on the known elemental and organic composition of samples of humic substances.[2] On the other hand, it is possible to represent soil mineral interfaces by using models of surfaces of clay minerals such as kaolinite.[3]By simulating the models of OMAs under different electrostatic treatments, different regions of the microaggregates can be investigated, such as those within cavities as well as on the outermost part of the particles.[4]

Our results show that the behavior of adsorbed organic matter (OM) depends on its environment, leading to the formation of different structures. It was observed that OM is dispersed and strongly bound on the inner surfaces of the cavities, whereas on the outermost part, OM is weakly bound leading to the formation of supramolecular aggregates. This suggests differences in molecular affinity depending on the surrounding environment of microaggregates. Furthermore, this behavior explains the experimental differences observed in samples at the microscopic level. Thus, the used modeling methodology has the potential to provide an explanation for experimental observations based on microscopic phenomena and furthermore, to contribute to the debate about the way soil components are perceived and the processes that take place in it.

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3D-PRINTED GEOPOLYMERS FOR INNOVATIVE ENVIRONMENTAL APPLICATIONS

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Alkali-activated materials and geopolymers can generate environmental friendly products for several applications, including thermal and acoustic insulation, and as adsorbents for the treatment of polluted wastewater [1]. Solid wastes such as red mud, fly ash or slags, can be incorporated into these materials, ensuring interesting mechanical and physical characteristics, and thus obtaining new added-value products from waste [2,3]. Emerging technologies, such as additive manufacturing (AM), allow to obtain structures with high geometric complexity and low material waste. Waste-based geopolymeric pastes can be moulded by AM and the 3D-printed geopolymeric structures obtained are suitable for dyes or heavy metals removal, due to their high open porosity and adsorptive capacity [4].

In the present work, porous 3D-printed structures were produced using metakaolin and red mud (1:1) as aluminosilicate sources and used as membranes for the remediation of heavy metal-bearing wastewater. In continuous tests, using an up-flow column, these membranes presented very fast heavy metals removal: after 15 min of contact, 20 % of As, 25 % of Zn, 40 % of Ni and Cu and 60 % Cd were adsorbed into the geopolymer structure. These promising results demonstrate the potential of new waste-based membranes developed by AM to be used as an effective solution for environmental remediation.

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TEMPERATURE AND DRY DENSITY COUPLED EFFECTS ON HTO, 36CL, 85SR AND 133BA DIFFUSION THROUGH COMPACTED BENTONITE.

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Diffusion is the main mechanism for solute transport in compacted bentonite, which is the most important engineered barrier in radioactive waste disposals. Therefore, the determination of radionuclide diffusion coefficients, under a wide range of conditions, is crucial for assessing the long-term safety of these systems. In this study, the combined effects of temperature (from 25 to 80 ºC) and bentonite dry density (from 1.2 to 1.65 g/cm^3) on the apparent diffusion coefficient, D_a, was analysed, in a well characterised Ca-Mg clay (FEBEX bentonite), also accounting for the porewater (PW) chemistry under the different experimental conditions.

Apparent diffusion coefficients (D_a) for HTO, ^{36}Cl, ^{85}Sr and ^{133}Ba were determined in clay compacted at different dry densities (1.2; 1.4 and 1.65 g/cm^3) and at different temperatures (25; 40; 60 and 80°C). Previous sorption tests with Sr and Ba at different temperature were also carried out in PWs representative of the bentonite compacted at different dry densities.

For all the radionuclides, D_a increases with temperature and decreases with dry density, thus the highest measured D_a for each RN always corresponded to the highest temperature and the lowest dry density.

Under the same conditions of dry density and temperature D_a values increases in the following order Ba <Sr <Cl <HTO; with D_a for Ba (0.36-3.80)·10^{-11} m/s^2; for Sr (0.5-6.7)·10^{-11} m/s^2, for Cl (0.57-6.60)·10^{-10} m/s^2 and for HTO (0.17-1.00)·10^{-9} m/s^2.

The analysis of data with the Arrhenius' law allowed determining the activation energy, E_a, of the diffusion process. A larger interaction with the clay due to adsorption, which is reflected by lower D_a also causes larger E_a values.

The Stokes-Einstein equation reproduced the temperature behaviour of D_a, only for dry densities 1.4 g/cm^3. This limitation of the application of the Stokes-Einstein equation arises from the fact that the water structure in highly compacted clays is different from that of free water. A more precise determination of the porewater viscosity at different dry density and temperature may improve the match.

The method tested for determining D_a was the planar source method, which was shown to be very efficient for both the conservative (HTO and Cl) and sorbing elements (Sr and Ba).

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ADVANCES IN MORPHOLOGICAL AND TEXTURAL CHARACTERIZATION OF HALLOYSITE IN RELATION TO DISORDERED KAOLINITE.

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The relative accessibility of tubular forms of halloysite have potential advantages in new technologies. As it is recognized, halloysite exhibits an almost identical structure as kaolinite, with 1:1 dioctahedral layer stacked but it contains a layer of water molecules between two consecutive layers that is hydrogen bonded. Indeed, the transition of halloysite (10 Å) into halloysite (7 Å) is observed as a reduction of the basal spacing function of an irreversible dehydration process (Joussein et al., 2005; Hillier et al., 2016). Similarities to disordered kaolinite could indicate a continuous series of interstratified and intergrowth states, through intermediate terms between hydrated-dehydrated halloysite and disordered kaolinite, but García-Vicente et al., (2022) did not found evidence.

The objective of the present work was to investigate changes in structural and textural tubular halloysite in comparison with possible intermediate terms and disordered kaolinite. For this purpose, a characterization of 17 halloysite samples from different geological settings and 6 disordered kaolinites were studied. High resolution X-ray diffraction patterns were collected in Mo capillary using a X´Pert PRO MPD PANanalytical diffractometer and Transmission Electron Microscopy (TEM) images were obtained with JEOL JEM 1400. In order to examine morphologies of tubular halloysite and crystallographic relationships with disordered kaolinite, almost 2000 measures of tube dimensions, that is, values for tube length (L), inner diameter (d) and outer diameter (D) were carried out.

X-ray diffraction patterns of fully hydrated halloysite are located at 10.1 Å, while the basal reflection of halloysite (7 Å) fluctuates between 7.45 Å-7.20 Å, similar to those values of disordered kaolinite. Transition between halloysite (7 Å) and disordered kaolinite differs mainly in the broadness of the basal reflections, showing sharper and well-defined peaks in possible intermediate terms. Non-basal diffraction bands (*hkl*) progress from diffuse reflections in dehydrated halloysite towards well-defined peaks in intermediate and disordered kaolinite. TEM results display tubular halloysite morphology but, in some cases regular platy-like crystals appeared on the edges of the tubes. ´Hexagonal growth edges', has been documented by Dixon and Mckee (1974), are adapted in apparent crystallographic alignment at possible tube endings. Tube length (L), inner (d) and outer diameters (D) measures contributed to a size distribution constituting a lognormal curve. Tubular particles are of rather different sizes both in diameters and tube length, concretely higher observed outer diameters.

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CLAY MINERALS AS INGREDIENTS OF INK AND BIOINKS INTENDED FOR 3D PRINTING AND BIOPRINTING

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Three-dimensional printing (3DP) is an additive manufacturing technique that creates a physical three-dimensional piece from a digital computer design. One of the most important advantages of 3DP lies in its versatility, demonstrated by the wide variety of 3DP techniques currently available and the plethora of materials that can be used, to the possibility of adapting the dimensions and shape of the 3D construct just by changing the digital design to be printed. 3DP has influenced a significant number of areas. Regarding the pharmaceutical field, 3DP has opened a new door to the development of tailor-made dosage forms and medical devices (Desu et al., 2021). 3DP has even adapted to the idiosyncrasies of tissue engineering and regenerative medicine, enabling the production of anatomical models (acellular scaffolds) (Wang and Yang, 2021) and tailor-made 3D tissues and organs (cellular scaffolds) (Agarwal et al., 2020). In the last case, ink formulations are based on biocompatible and biodegradable polymers with high water content like gelatin, alginate, chitosan, fibrinogen, collagen, etc. However, their low mechanical resistance compromises their functionality and handling. At this point, there is a need for biocompatible ingredients to improve the limitations of the aforementioned polymeric ingredients. Among the potential candidates, inorganic materials like clay minerals (natural and synthetic) have proven their usefulness as mechanical reinforcement and rheology additives of different polymers (Ruiz-Hitzky et al., 2013). Moreover, they are naturally occurring materials with recognized biocompatibility and bioactivity, revealing them as optimal candidates for this cutting-edge technology. The pairing of “clay minerals” and “3DP” is a rather recent field of study. For the particular case of 3D bioprinting and tissue engineering, the number of publications dealing with clay minerals is still scarce but those already published highlight that these ingredients are useful as rheology modifiers, can favor cell adhesion/orientation and, mostly, as mechanical reinforcement (Garcia-Villen et al., 2021). Notwithstanding the aforementioned advantages, the use of inorganic materials as ingredients of inks and bioinks still has certain limitations that need to be addressed. Close collaboration between geochemists/mineralogists and experts in regenerative medicine could prove particularly fruitful in counteracting some of the current limitations in this field of study.

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ON THE NATURE OF INTERACTIONS BETWEEN HYDROPHOBIC ORGANIC COMPOUNDS AND CLAY MINERALS: CASE STUDY OF HEXACHLOROBENZENE AND MONTMORILLONITE

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Among many factors, the interactions between chemical pollutants and reactive mineral surfaces play a crucial role in the determination of their fate in the environment. In the present work the interactions of hexachlorobenzene (HCB) with the surface of a common clay mineral belonging to the smectite group montmorillonite (MNT) is studied by employing a geometry optimization machinery within the density functional theory framework. The MNT net surface charge, induced by isomorphic substitutions, is systematically varied and compensated by Ca^{2+} cations. Based on the calculated electron densities, conclusions are drawn revealing the nature of their mutual interactions, the related stability of such surface complexes as well as possible molecular arrangements. It becomes apparent that the dominant contribution to the stability of HCB-MNT complexes arises from the cation-π interactions between the HCB molecule and the nearest compensating Ca^{2+} cation [1] and thus besides the MNT net surface charge the type and size of the compensating cations are expected to play a crucial role in understanding the HCB adsorption on MNT [2]. This systematic study aims to contribute to a better mechanistic understanding of the interactions between hydrophobic organic compounds and reactive mineral surfaces. Results of calculations of a solvent effect on the HCB adsorption by using a polarizable continuum model for the solvent are presented.

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THE SORANO FORMATION (TUSCANY - ITALY): EARLY EVIDENCE AS GEORESOURCE FOR UNEXPLORED TECHNOLOGICAL APPLICATIONS

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The present research accounts for an deeply characterization of a pyroclastic formation from the volcanic district of northern Latium. The so-called Yellow Tuff, representing the Sorano Formation [1] of the Vulsini Volcanic District, deriving from syn- and post-depositional minerogenetic processes, has a zeolite content of more than 50% consisting of mainly chabazite and subordinate phillipsite [2]. This geological formation has already been widely exploited, mainly in the building sector, for the production of dimension stones. However, the large amount of waste material deriving from this activity may represent an interesting by-product to be used in different technological sectors. Such a waste, although potentially contaminated by the processing operations or by the wear and tear of industrial tools, retains all mineralogical and chemical features of the original rock.

The present research aims at investigating a possible reuse of this waste in some unexplored technological applications such as, a surface modification of zeolites to be used as carriers for non-steroidal anti-inflammatory drugs (NSAIDs) [3]. A deep mineralogical and chemical investigation on the rocks coming from two quarry sites, chosen for sampling, substantially confirmed literature data [1-2] endorsing the potential usability of raw materials.

After the determination of cation exchange capacity and external cation exchange capacity (CEC and ECEC) and surfactant sorption capacity, the starting geomaterial was surface functionalized using cetylpyridinium chloride (CP-Cl). Preliminary sorption tests allowed to verify the extent and the compactness of the formed micelle and to foresee the behavior of these composite material in the uptake of NSAIDs molecules (mainly ibuprofen and diclofenac). The effective functionalization was also inferred by the evaluation of the z-potential.

A mandatory quality check of the raw material is also required to determine the occurrence of undesired minerals and/or toxic elements, following the procedures dictated by international regulations. Anyway, the encouraging results obtained from early evidence strongly support the potential use of this zeolite-rich geomaterial in the pharmaceutical sector, once defined a preliminary basic protocol.

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EVOLUTION OF ELASTIC PROPERTIES OF THREE DIFFERENT CZECH KAOLINS DURING SINTERING MONITORED VIA IMPULSE EXCITATION

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The impulse excitation technique (IET) allows the determination of elastic properties, e.g. Young's modulus, as a function of temperature. It is a versatile tool not only for determining the temperature dependence of elastic properties of ceramics after firing but also for monitoring the evolution of these properties during firing of powder compacts *in situ*. In both cases the IET provides information on reversible phase transitions but in the latter case it provides additional information on irreversible phenomena, such as reactions and the evolution of the phase composition and microstructure. In this contribution, which is part of the project "Impulse excitation as an unconventional method for monitoring phase changes and microstructure evolution during thermal loading of materials" (grant no. GA22-225562S), funded by the Czech Science Foundation, the evolution of elastic properties is monitored for unaxially pressed powder compacts from three different types of Czech kaolins (Sedlec Ia / Sedlecký kaolin, SpEX / LB Minerals, KD50 / Kaolin Hlubany) from three important kaolin deposit regions in the Czech Republic with different geological genesis, granulometry and quartz content of the kaolins (Karlový Vary / wheathered granite / 61 % < 2 μm / 2 % quartz, Plzeň / wheatered arcose / 48 % < 2 μm / 10 % quartz, Podbořaný / wheatered orthogneiss or migmatite / 16 % < 2 μm / 20 % quartz). The monitoring of these properties provides information comparable with thermal analysis, and at the same time serves as an excellent guide for predicting the mechanical properties of ceramics produced from these kaolins. Bar-shaped specimens have been prepared from as-delivered floated kaolins by uniaxial pressing (40 MPa), and the evolution of their elastic properties has been compared during heating with a rate of 5 °C/min up to 1400 °C (with a dwell time of 5 min) and subsequent cooling. It is found that during heating the following processes are clearly discernible in the temperature dependence of Young's modulus: drying (70–130 °C), dehydroxylation to "metakaolin" (500–600 °C), formation of the defective Al-Si spinel-type phase with silica release (above 930–970 °C) and mullitization with silica release (above 1200–1320 °C), followed by the end of the densification stage, which reveals itself by a high-temperature plateau in which Young's moduli of the sintering ceramics have increased to values 44 GPa for Sedlec Ia, 33 GPa for SpEX and 24 GPa for KD50. During cooling, a further significant increase in Young's modulus appears, which is steepest at around 1270–1320 °C and then levels off, until at around 800 °C maximum values are attained (105, 90 and 38 GPa for Sedlec Ia, SpEX and KD50, respectively), which for Sedlec Ia and SpEX remain approximately constant and for KD50 slightly decrease (to 32 GPa) down to 200 °C. Below this temperature the material based on KD50 exhibits a strong decrease that is related to the phase transition from high- to low-temperature cristobalite. For materials from Sedlec Ia this feature below 200 °C is much weaker (because the quartz content is extremely low) and for materials from SpEX virtually absent (although the quartz content is much higher that in Sedlec Ia). This indicates that the quartz content alone is not the only factor controlling the development of cristobalite. Apart from the fact that the granulometry and the presence of other phases might play a role in the formation of cristobalite as well, it has to be noted that the quartz in KD50 is residual quartz from orthogneiss or migmatite, which has been been exposed to elevated pressure during rock metamorphosis, and it is well known from the production of silica bricks that mechanically pre-stressed quartz is more prone to the reconstructive transformation into cristobalite (and tridymite) than unstressed quartz. On the other hand, the quartz in KD50 is secondary quartz that has developed during the wheathering of (essentially quartz-free) arcose in a soft clay matrix, and it seems that this completely unstressed quartz, which usually forms idiomorphous crystals or polycrystal aggregates, is less prone to the reconstructive transformation into cristobalite.

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ORGANO-CLAYS MODIFIED WITH WASTE-DERIVED COLLAGEN HYDROLYSATE FOR HEAVY METALS CAPTURE

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Heavy metals (HMs) bioaccumulation in soil has become a serious issue, since they can be adsorbed by crops, and enter the food chain causing adverse health effects to humans and natural organisms. One of the preferential diffusion routes of HMs is represented by animal manure[1,2]. Indeed, heavy metals in animal diet may be present as contaminants or as essential nutrients[1]. Several strategies can be used to prevent the spread of HMs, from monitoring the concentrations of HMs added to animal feed to deal with treatment of animal manure to prevent HMs contamination. In this context, clay is one of the most well-known materials for the treatment of pollutants, due to its peculiar structure that allows for the capture of various contaminants, such as cations, organic molecules, and biomolecules[2,3]. In previous works[4], a commercial linear hexamine (L6), was used as chelating agent to improve metal capture. However, to move towards a circular economy approach an attempt to replace the L6 with a waste-derived material has been done. Therefore, in this study, the expandable Ca-montmorillonite (STx) was modified with a collagen hydrolysate (supplied by Ilsa group), obtained by the treatment of the leather tanning process byproduct. The modified clay STx-HY was thus tested as sorbent for Cu capture, i.e. one of the main ionic contaminants in pig manure[1]. STx-HY synthesis was performed via a solid/liquid adsorption approach previously developed[3], where mild conditions and water solutions are applied. The HY content in ST-HY was evaluated by Chemical Oxygen Demand (COD), while inductively coupled plasma-optical emission spectroscopy (ICP-OES) was applied to determine captured Cu. Considering STx modification, it was found that a plateau, corresponding to a HY to a loading of 0.56mmol $_{HY}$/g $_{STX,}$ was reached. HY immobilization seems to occur in two-steps, apparently involving intercalation, as suggested by the progressive shift of the d_{001} towards lower angles, as well as a surface adsorption process. Upon contacting the Cu solution with ST-HY a change in the sorbent color, from yellowish-cream to blue was observed, which became more intense on increasing Cu capture. For a HY loading of 0.56 mmol$_{HY}$/g$_{STx}$, a maximum Cu capture of 0.35 mmol$_{Cu}$/g$_{STx\text{-}HY}$ was measured, to be compared with 0.12 mmol$_{Cu}$/g$_{STx}$ found for pristine clay, and 0.17 mmol$_{Cu}$/g$_{STx\text{-}L6}$ for a L6 content of 0.40 mmol$_{L6}$/g$_{STx}$. The presence of different amino acids in the collagen hydrolysate, resulting in a larger number of -NH_2 groups may account for the enhanced Cu capture observed in STx-HY.

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USE OF ADSORBO® CLAY-BASED MATERIAL FOR THE CONTROLLED RELEASE OF LYSOZYME FOR FEED ADDITIVES

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The immobilization of biomolecules with antimicrobial properties, alternative to antibiotics, on solid carriers is a burning topic in several fields of application, such as food and feed production[1]. Indeed, one of the challenges of biomolecules administration is to avoid gastric passage degradation. Clays and zeolite minerals could represent an innovative carrier strategy due to their outstanding properties in adsorption capability[2]. In this work, Adsorbo® (supplied by Biomicron s.r.l),a commercial feed additive for zootechnics application, which is a mixture of bentonite (B), sepiolite (S), and a commercial zeolite (Phil75®, PH), was tested as potential carrier for egg white lysozyme (LY), being the latter representative of a bioactive molecule , both in terms of MW (14.3 KDa) and antibacterial activity. The synthesis of the hybrid organic-inorganic materials was carried out with an environmentally friendly method based on a solid/liquid adsorption process in mild conditions and water environment. The better operating conditions for an effective and complete LY adsorption were studied in terms of LY concentration (0.25-3 mg/mL), reaction time (10-90 min), and pH (2-11.3). Both in case of initial LY concentration and reaction time, a plateau was achieved for initial LY content of 1.5 mg/mL and 30 min of reaction time. In these conditions a LY loading on Adsorbo® carrier of 31 mg_{LY}/ g $_{AD}$ was obtained; i.e the LY loading required for the application[3]. The pH effect was studied, at pH 4, i.e. the natural pH of LY solution here applied, at pH=11.3, the LY Isoelectric point, and pH=2, far below of it[4]. No pH effect was found, and a constant LY loading in the range 31-33 mg_{LY}/g_{AD} was obtained. As already reported, the final application of the prepared hybrid materials is to exert a possible controlled release in the intestine of weaning pigs; therefore, understanding the LY-AD interaction is of paramount importance to investigate the binding mechanism and the structural stability[1]. For this reason, the hybrid materials were fully characterized by means of physicochemical techniques such as XRD, FT-IR, TG-DTG and SEM-EDX analysis, suggesting that AD-LY interactions result in the combination of several contributions, such as surface functional sites and interlayer ions exchange. Finally, release tests were performed at three different pH = 3, 5 and 7 to simulate pH condition of stomach and intestine of weaning pigs. In the range considered range, a LY controlled release seems to occur in one hour. LY release at pH=3 was 0.05 mg_{LY}/g_{AD}, lower than 0.14 mg_{LY}/ g $_{AD}$ found at at pH=7 Accordingly, all these evidence suggest for the presence of a protection effect exerted by the carrier, Adsorbo in this case, towards lysozyme.

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WETTABILITY OF CLAY SURFACES AND ITS IMPLICATION ON THE STATUS OF WATER IN UNSATURATED POROUS MEDIA

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Clays have been investigated extensively under saturated circumstances, but investigations in unsaturated media are still uncommon. Nevertheless, partially saturated transient situations occur when storing high-level radioactive waste in deep geological formations, both during the operational period of the storage areas and after the closure phase due to heat impact and the production of H2 gas from radiolysis. Understanding the physical and chemical processes at the origin of the liquid/gas surface tension and the contact angle at the solid/liquid/gas interface within unsaturated nanoporous clayed materials is necessary to provide a multiscale vision of the mechanisms of water and solute diffusion, from the scale of the clay layer to that of the stacking of clay particles under various conditions of partial water saturation. Understanding how clay mineral crystallochemistry and the makeup of charge-compensating cations affect surface wettability is particularly crucial.

The advantage of molecular simulations is that they provide an in-depth look at the atomic-level physicochemistry of these systems, but they also depend on the reliability of the force field used to characterize interatomic interactions. In this study, we conduct contact angle experiments on cleaved clay surfaces with various crystallographic structures and counter-ions at solid/water/air and solid/oil/water interfaces [1-2]. Clays were selected based on their negative charge placement (tetrahedral layer or octahedral layer) and their hydroxyde or fluorine concentration. The molecular dynamic simulations of a water drop on clay surfaces using the regularly used forcefield ClayFF and the currently being developed polarisable forcefield PIM (Polarizable Ion Model) [3] are compared to the experimental contact angles.

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INVESTIGATION OF THE INFLUENCE OF THE FIRING ATMOSPHERE ONTO THE THERMAL TRANSFORMATION OF IRON-RICH KAOLINS

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Sustainable development and ecological transition have been at the center of many issues over the years. The ceramics industry needs to follow environmental developments towards a “competitive low-carbon economy by 2050”. Environmental issues related to water, natural resources and waste must be considered; emissions and energy consumption must be reduced [1].
Clays, more precisely phyllosilicates, are generally of natural origin and can be found all over the world. In particular kaolins are widely used to manufacture materials for traditional and advanced functional applications. These kaolins are mainly constitute with kaolinite mineral ($Al_2Si_2O_5(OH)_4$). Kaolinite is a 1:1: clay mineral where the unit sheet results from the superimposition of an octahedral layer and a tetrahedral layer [2]. The understanding of the transformations and interactions of kaolinites with secondary phases is a key point to control the physical and chemical properties of related materials. In the case of ceramics, their production involves multiple steps, among which, sintering is a critical step to achieve the desired final properties of the designed product.
Kaolins are included in the formulation of silicates ceramics whereby the firing step is performed within “natural gas” kilns at industrial scale. In order to match the “European Green Deal”, whose objective is to achieve carbon neutrality by 2050. Alternatives for thermal treatment, such as the use of biogas, green hydrogen or electricity furnaces should be considered. These changes in the sintering environment can significantly affect the transformation kinetics by changing the surrounding atmosphere and heat transfer patterns. Therefore, the challenge of the present study is to understand the effects of such modifications, especially on the physical and chemical transformations together with the performance of kaolin-based ceramics regarding the presence of iron compounds.
One model clay was chosen for this study: a kaolin known as “CR” provided by Imerys company. A deep study of biogas and green hydrogen allowed identifying some key parameters for sintering, namely the partial dioxygen pressure. Accordingly, to the Ellingham diagram, the influence of impurities such as iron oxide is studied. To this end, controlled additions of iron oxide were performed up to 10 wt.%. The thermal behavior of these kaolinitic compounds is investigated under different thermal cycles under controlled atmosphere. In situ DTA/TG and ex situ XRD and SEM analyses were performed to implement the knowledge in line with the phase transformations and interactions of kaolinite with iron oxide. In general, the presence of nanosized iron oxides, tends to promote the earlier mullite crystallization.

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UTILIZATION OF ALKALI-ACTIVATED METAKAOLIN-BASED GEOPOLYMERIZATION: IMMOBILIZATION OF THE EXCHANGEABLE LEAD IN TAILING

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Geopolymerization is a reaction of aluminosilicate occurred under the alkali or acid activator, in which silicon-oxygen tetrahedrons ([SiO_4]) and aluminum-oxygen tetrahedron ([AlO_4]) monomers depolymerize from the aluminosilicate and reorganize into the new disorderly three-dimensional network structure. Based on the geopolymerization, the cations could be isolated into the network or attracted to balance the negative charge of structure caused by the Al in four-fold coordination. This results in the geopolymers, the product of geopolymerization, performing the quality of immobilizing the toxic metal cations from the industrial solid waste. However, most research focused on the chemical environment of metals in final geopolymer products and given metals have an equal impact on the environment. This is not conducive to the risk control of metals in tailings and the development of immobilization methods.

Tessier Procedure is a classical method to examine trace metals in sediments and soil. It separates the chemical forms of metals into basically five different fractions which include exchangeable, bound to carbonates, bound to iron and manganese oxides, bound to organic matter, and residual. It provides a precise way to analyze the potential environmental threats of metals in tailings, especially in the aquatic environment, which is similar to the tailings storage encountering leaching.

In this work, we used alkali-activated metakaolin-based geopolymerization to immobilize the lead (Pb)-mine tailings. The Tessier Procedure was combined with X-ray diffraction (XRD), field emission scanning electron microscope (FE-SEM), and X-ray photoelectron spectroscopy analysis (XPS) to explore the mechanism of immobilization. The results indicated that the 7 d and 28 d compressive strength of geopolymers reached 11.86 MPa and 15.12 MPa respectively even with the addition of 70 wt.% tailing. Both the tailings and geopolymer with 50 wt.%, 60 wt.%, 70 wt.%, 80 wt.%, and 90 wt.% tailings performed low leaching loss of Pb, which were less than 0.025 ppm in water after 18 h. However, comparing the content of exchangeable Pb between tailings and geopolymers, it decreased from 0.231 ppm to below 0.134 ppm. At the same time, there are only tiny changes in the content of Pb bounding to carbonates, and bounding to iron and manganese oxides. The chemical environment changes were also detected in XPS analysis, the binding energy of Pb^{4f} shifted to the low direction after the geopolymerization. Without the generation of new mineral phases performed in XRD results, the immobilization of Pb is caused by the transformation of exchangeable Pb. At the beginning of geopolymerization, the tailings released the exchangeable Pb to attend to the polycondensation. The Pb cations with large radium were fixed in the aluminosilicate network and the other fractions with unreacted Pb could be encapsulated by the new aluminosilicate, which means alkali-activated metakaolin-based geopolymerization is an efficient way to stabilization of exchangeable Pb in tailings.

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SCROLLING OF NANOSHEETS BY ADSORPTION OF STILBAZOLIUM DYES

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We have observed that exfoliated nanosheets prepared by exfoliation of inorganic layered crystals in the colloids are not strictly flat but rounded, undulated, or folded in many cases [1]. This morphological deformation was supposed to be caused by the intercalation of organic cations (exfoliating reagents) in the process of exfoliation of the niobate nanosheets. In this study, we observed in situ the deformation of the nanosheets in the process of adsorption of stilbazolium dyes on exfoliated niobate (NB) or fluorohectorite (FHT) in colloidal dispersion using an optical microscope. Scrolling of the nanosheet was observed during the adsorption by the addition of stilbazolium dye equipped with a long alkyl chain to the dispersion of NB or FHT.

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2D NANOHYBRID PHOTOCATALYSTS FROM CLAY TEMPLATES

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Thickness and anisotropy of nanoscale materials has been shown to strongly influence photophysical properties. While different exfoliation strategies for 2D materials have been proposed in this direction, many cause damage or chemical modifications, and control over size and aggregation can be problematic. In this talk, methods for templating the synthesis of semiconductors using nanoscopic clays which are anisotropic in both shape and surface charge is presented as a means to achieve 1D and 2D nanomaterial hybrids. The colloidal growth of semiconductors such as MoS_2[1], In_2S_3, [2,5], $ZnIn_2S_4$ [3], and BiOI [4] leads to nanohybrids with promising enhancements in catalytic and photophysical properties. Furthermore, it can provide routes to engineer the growth of specific crystalline facets, which can also enhance the uniformity of the internal electric field perpendicular to the basal surface, in certain materials [4]. In addition to providing increased aqueous dispersibility, the resulting thin growth of semiconductors and the isolation of these 2D layers from one another via the clay template allows improved photophysical and optoelectronic properties. Improved quantum efficiencies and interfacial charge transfer leads to improvements as aqueous-phase photocatalysts. The improved photocatalytic properties, dual functionality, and emergent outcomes show the promise of such materials for the energy transition.

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POTENTIAL OF CARBON DIOXIDE REMOVAL INTEGRATED WITH PASSIVE TREATMENT OF ACID MINE DRAINAGE BY ENHANCED ROCK WEATHERING

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The Negative Emission Technologies (NETs) that are popular nowadays to fulfill the net-zero (2050) target of neutralizing the atmospheric carbon dioxide according to the Paris Agreement on 2015. Enhanced Rock Weathering (ERW) is one of the NETs, which is accelerating the natural weathering rate of rock by means of crushing or grinding for Carbon Dioxide Removal (CDR). According to Beerling et. al., (2020), the application of basalt ERW on cropland can obtain for co-benefits, CDR by carbonate mineralization and supplying the necessary nutrients for plants back to the soil. However, the mechanism of ERW in such neutral environments is much slower than in acidic environments like Acid Mine Drainage (AMD) and take more energy for example the powdering. Therefore, we considered the use of AMD from abandoned mines as an alternative site for ERW. On the other hand, the toxicity of AMDs is causing major social problems, and the recent treatment methodologies are costly and need frequent maintenance. Furthermore, from the net-zero emission perspective, the use of CaO base materials in treatment processes, emit CO_2 gas back to the atmosphere and it need to stop using in the future.

Here, we are conducting a feasibility test with AMD formed at the Shojingawa abandoned mine in Hokkaido, Japan, where pH is around 2.8. Therefore, we can unambiguously expect a high rate of basalt weathering with the aspiration of co-benefits of treating the AMD, and carbonate mineralization. Our previous research indicates that natural attenuation of arsenic in the AMD can be available when the pH is raised to more than 3.2 with the formation of Schwertmannite by coprecipitation. In this study, 1-D geochemical reaction and transport modeling was conducted to determine how basalt could be placed to rise the pH to 3.2 or higher. Furthermore, we also estimated how much CO_2 mineralization would be possible. The modelling results showed that the pH could be increased by the dissolution of over a hundred tons of grinded basaltic rock but in comparison to the AMD channel size, such a massive volume is not applicable. Therefore, we are also planning to spread basalt powder to the forest area near the AMD channel by expecting for the leaching water. From the above preliminary calculations, we may attain the co-benefits by applying basalt ERW to passive treatment of AMD from the Shojingawa abandoned mine with high amount of CDR at the ocean.

Keywords: *Negative Emission Technologies, Enhanced Rock Weathering, Carbon Dioxide Removal, Acid Mine Drainage, Basalt.*

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DEVELOPMENT OF PBS-NATURAL FYBERS-MONTMORILLONITE CLAY BIOCOMPOSITE FOR AGRICULTURE APPLICATIONS

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PBS hybrid biocomposites based on clay and natural fibers (wood sawdust from Brazilian trees and canabrava fiber) were developed for application in the manufacture of tubes used in planting seedlings for agriculture to reduce the generation of plastic waste. The PBS hybrid biocomposites were produced using two natural fibers and/or montmorillonite clay wood sawdust and canabrava. Additionally, the influence of lignin incorporation was evaluated. The PBS is bio-based with an MFR of 22 g/10min (at 190ºC and 2.16kg). Wood sawdust (mean diameter of 0.686 mm) is a residue from lumber companies that work with Brazilian trees, such as Massaranduba, Copaiba, and Argelin. The Canabrava plant (*Gynerium sagittatum*) is frequently used by local communities to manufacture baskets and handicrafts in Brazil. The PBS-clay biocomposites were prepared with up to 10 wt% of clay in their composition. The canabrava fiber was ground to be mixed with PBS containing between 10-40% of the threads. The materials were dried at 70ºC for 3 hours. The bio-composites were obtained by melt blending using a twin screw extruder (D=16 mm and L/D=40) in compositions from 10 to 40% of fibers with or without lignin to evaluate its effect on melt flow rate. Good melt flow results and mechanical properties were obtained when PBS was mixed with up to 30% wood sawdust and 10% lignin and the mix of canabrava fiber and clay. As expected, adding wood sawdust fiber and canabrava reduces the viscosity of the melt. Still, adding lignin has a lubricating effect during processing, increasing the melt flow, which is interesting for the injection process. Furthermore, thermal stability was improved by adding clay to the PBS matrix. The composites were characterized by mechanical tests, scanning electron microscopy, thermogravimetric analysis, and differential scanning calorimetry. Finally, a combination of PBS and montmorillonite clay, as well as PBS and natural fibers produced hybrid composites with improved performances for injection molding tubes for seedlings in agriculture.

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SELF-ASSEMBLY OF IMOGOLITE NANOTUBES UNDER ACOUSTIC LEVITATION

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Self-assembly of liquid crystals is of key relevance for the design of materials with enhanced electrical, electrochemical or optical properties [1]. Evaporation induced self-assembly (EISA) on various solid substrate has already received a lot of attention providing an easy way to produce nano-assemblies [2]. However, the method suffers from the influence of solid-liquid interface which provide a non-uniform dispersion known as the "coffee-ring" effect [3]. In this context, acoustic levitation appears as a genuine way to self-assemble liquid crystals in a substrate-less environment and to provide 3D assembly compare to the 2D film obtained with solid substrate [4]. Among others liquid crystals, 1D "rod-like" liquid crystals enable to investigate anisotropic self-assembly with large aspect ratio particles. Imogolite double-walled nanotubes (Ge-DWINTs) appears as a perfect candidate as their aspect ratio can be easily tuned by synthesis [5],[6]. In particular, these nanotubes form stable colloidal dispersions that may also exhibit a rich liquid-crystalline phase behavior at low concentration before the gel state [5],[7].

EISA were carried out by acoustic levitation on Ge-DWINTs dispersions prepared at different volume fraction (f) and different aspect ratios (5, 65, 295). We compared it with EISA on a hydrophilic substrate (glass) and hydrophobic substrate (Teflon/FC40). Along the evaporation process on a hydrophilic substrate, it appears that the organization of nanotubes is trapped in their initial liquid-crystalline/isotropic phase whether the evaporation rate is fast (room temperature) or slow (humid atmosphere). Under levitation, EISA provide 3D dry droplet whose shape, either like a "pancake" or spherical, is a function of nanotubes aspect ratio and independent of the initial volume fraction. The dry droplets show birefringence even when the initial suspension was in the isotropic phase promising a rich organization of the resulting materials.

Further small-angle X-ray scattering (SAXS) experiments will show the role of the initial volume fraction and the Ge-DWINT aspect ratio on the self-assembly and on the preferential direction of the nanotubes in a spherical confinement. Moreover, the study of different evaporation stages enables us to provide a complete exploration of the phase diagram of Ge-DWINT at high volume fraction, which is hardly obtained using osmotic stress concentration methods.

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MICROSCOPIC PORE STRUCTURE AND MACROSCOPIC FLUID FLOW-CHEMICAL TRANSPORT IN CLAY-RICH GEOLOGICAL MEDIA

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Slow diffusion in fine-grained and clay-rich geological media is relied on, or complicated in, these mudrocks being critically involved in energy geosciences studies. However, low-permeability mudrocks whose pores are poorly interconnected (a topological attribute of pore structure) are known to have anomalous flow and diffusion properties that strongly impact long-term performance of a repository or unconventional reservoir.[1-2] From the perspectives of pore structure in conjunction with multiple and complementary approaches to examining a range of sample sizes under different observational scales, we find that the poor pore connectivity is prevalent in low-permeability mudrocks that is related to geological processes (e.g., compaction, diagenesis, and thermal maturation). For example, the deep and organic matter-rich mudrocks have a much smaller effective porosity than the total porosity (as a result of poor pore connectivity) and associated diffusion coefficient, and the effective porosity and diffusion coefficients are also dependent upon the sample sizes used in the measurement. Similarly, most of the pore space in the shallow mudrocks is also controlled by pore-throat diameters in the 5-50 nm range of intergranular pore types from its fine-grained nature, but with an overall good pore connectivity. However, the nm-sized pore space (physically pore-network architecture) and strong sorption capacities (chemical retention from clay minerals) of both shallow and deep mudrocks lead to the synergistic retention of cationic radionuclides and their utilities as effective host rocks and barrier materials. Our unique approaches of studying how the micro-scale pore structure affect macro-scale fluid flow, diffusion and retention, and chemical transport produce improved mechanistic understanding, and realistic quantification, of diffusion and retention of typical radionuclides in clay-rich geological media, with the overall results leading to scientifically-based understanding of enhanced isolation (from both diffusion and retention) of radionuclides and improved confidence on the long-term performance of geological repository.[3]

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STRYTAN (ICELAND), A SHALLOW-SEA HYDROTHERMAL ALKALINE FIELD. WHAT CAN BE FOUND THERE?

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Iceland's location on the Mid-Atlantic Ridge results in intense hydrothermal activity, both on land and in the surrounding waters. On the North coast, there is a shallow hydrothermal field discharging waters at moderate temperature (~70°C), high pH (pH ~10) and low mineralization in the Eyjafjordur fjord. There are several discharge zones, but only in one of them several hydrothermal chimneys have grown in the form of sharp cones, rising from the seafloor several tens of meters, to a depth between 15 and 60 m. This is the Strýtan Hydrothermal Field.

The discovery in 2001 of the Lost City hydrothermal field (Kelley et al., 2001), formed by calcium carbonate towers, revealed the existence of alkaline hydrothermal fields. While typical hydrothermal vents are acidic and rich in sulfides, alkaline vents are characterized by their alkaline (basic) pH and their high concentration of hydrogen gas. Subsequently, some other examples have been found.

Alkaline vents are found in various locations on the ocean floor, particularly in areas associated with slow-spreading ridges. Some of the most well-known alkaline vents are located in the Lost City Hydrothermal Field, which is situated on the Mid-Atlantic Ridge in the Atlantic Ocean. Other alkaline vents have been discovered in the Okinawa Trough in the Pacific Ocean, the Rainbow hydrothermal field in the Atlantic Ocean, the Loki's Castle hydrothermal vent field in the Arctic Ocean, and Prony Hydrothermal Field in New Caledonia (Monnin et al, 2014).

Strýtan is a unique enclave in the world. It consists of magnesium silicate towers, partly of very low crystallinity, and saponite-type phyllosilicates. There is no other with this mineralogy. Their formation is associated with chemical (e.g., pH, Na^+, SiO_2) and thermal gradients. The great interest they have recently aroused is due to the analogy of these shallow-sea environments with some of those of the primitive Earth in which life could have emerged.

Although alkaline vents are less common than typical hydrothermal vents, they are significant because they create a exceptional chemical environment that can support the growth of unique microbial communities. The relationship between alkaline hydrothermal vents and the emergence of life is an area of active research and debate. Some scientists believe that the first living organisms may have evolved in these environments, where the alkaline fluid would have provided a stable and consistent environment for early life forms to develop.

In this contribution we will try to present in detail the Strýtan mineralogy, microstructure and to deepen in the conditions that gave rise to the precipitation and transformation of the phases that compose these formidable structures. This research was funded by FEDER/Junta de Andalucía-Consejería de Economía y Conocimiento (PY20_01389) "a way of making Europe".

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ACID-BASE SURFACE TITRATION OF PALYGORSKITE AQUEOUS SUSPENSIONS

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Interactions of palygorskite with aqueous solutions are largely determined by the surface structure and crystal chemistry of the particles. The electrostatic interactions among charged dangling atoms at the crystal edges (surface sites) and aqueous ions and molecules develop a distorted layer of solvent surrounding the particles, called the palygorskite/solution interface, which can be envisioned as an electric double layer. This is the scenario where reactions of hydrolysis, adsorption and precipitation occur. It is also origin of interparticle electrostatic interactions that produce colloidal behavior and rheological applications. There is limited information on the surface chemistry of palygorskite. The crystallographic analysis of the structure shows three main surfaces where several cations are exposed. The surface groups may exhibit different reactivity due to pH conditions, developing a surface charge of a permanent nature (isomorphic substitutions) or pH-dependent (amphoteric or basic sites).

Potentiometric surface titrations of aqueous palygorskite suspensions provide titration curves that contain information on the bulk sample: the surface charge under several pH conditions, the effect of ionic strength and the point of zero charge (PZC). Furthermore, models of the electric double layer can be applied to the interface to derive information on the reactivity of the surface groups: the type of reactive surface sites, the surface speciation (amphoteric, basic) and surface ionization constants (pKai) and potentials.

Potentiometric titrations of palygorskite suspensions were performed over a wide range of pH (3-11) to measure proton adsorption/desorption as a function of pH, ionic strength (0.1, 0.01, 0.001 M KCl) at room temperature (~25°C). One gram of palygorskite was suspended in 50 mL of an inert electrolyte solution of KCl, and 4 mL of KOH 0.1 M solution was added to attain an initial pH of ~11. Titrations were conducted with an automatic titrator, and 0.1 M HCl was used as the titrant solution. Solutions were bubbled with N2 gas to purge CO2. The pH electrode was calibrated at the temperature of interest with buffer solutions of pH 7, 4 and 9.2. Suspensions were continuously stirred, and N2 gas was pumped directly into the suspensions during titrations to purge the solutions of CO2. Titrant solutions were added after pH stabilization, presumed to exist when the pH changed approximately less than 0.01 unit per minute.

Titration curves showed inflection points associated with surface protonation/deprotonation of Si and octahedral cations. The surface charge at different pH values was obtained by proton balance, after correction of dissolution and background effects.

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RELATIONSHIP BETWEEN PETROGRAPHIC TEXTURE AND SWELLING PROPERTY IN CEMENTED BENTONITE ORES

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In the geological disposal of high-level radioactive waste, bentonite will be used as a buffer material because of its high swelling property and low permeability. Alteration of bentonite may degrade the buffering performance. One of the possible alterations is cementation of bentonite, in which secondary minerals precipitate in the pores and adhere to coexisting minerals. This may cause the reduction of swelling pressure [1,2]. However, fundamental mechanism of reducing swelling pressure due to cementation has not been well understood. To understand the mechanism, it is essential to identify the cementitious materials and observe the changes in microstructure associated with cementation.

In this study, the microstructural observation and swelling tests were conducted on several bentonite ores collected from Tsukinuno Mine in Yamagata Prefecture, Japan, as natural analog of cementation, and the relationship between petrographic texture and swelling pressure was discussed. Thin sections of bentonite ores were prepared by dry polishing technique to observe flat surfaces in micro scales. Scanning electron microscopy (SEM) demonstrated the widespread distribution of authigenic, a few microns silica in the matrix of montmorillonite. Transmission electron microscopy (TEM) revealed that the micro silica minerals (commonly quartz and less commonly amorphous silica) adhered to the edge of montmorillonite grains. These observations suggest that the adherence of these cementitious materials to montmorillonite prevents water access to the interlayer of montmorillonite and swelling, resulting in a decrease in swelling pressure. While these microstructures were observed commonly in all samples collected from several bentonite beds, the relative abundance of montmorillonite and micro silica minerals varied among different beds. It is possible that the swelling pressure in the cemented bentonite is affected by the relative abundance of montmorillonite and cementitious materials, not only the amount of montmorillonite content.

This study was performed as part of “The project for validating near-field system assessment methodology in geological disposal (JFY2022, JPJ007597) ”.

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PRECISE DESIGN OF THE LAYERED SURFACTANT CRYSTALS FOR TAILORED SYNTHESIS OF GADOLINIUM-DOPED CERIA NANOSHEETS

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Ceria (cerium oxide) has attracted significant attention as an electrolyte and catalyst due to its high oxygen ion conductivity and excellent redox capability. In particular, molecularly thin ceria nanosheets are expected to show superior ionic conductivity due to their abundant oxygen vacancies and enhanced in-plane ionic conductivity on their surface[1][2][3]. Moreover, doping rare earth elements should lead to improving the functionality of ceria nanosheets; however, controlled doping into ceria nanosheets has yet to be achieved. Here, we present a rational approach for the tailored synthesis of gadolinium-doped ceria nanosheets using designable layered surfactant crystals. We synthesized solid surfactants containing both cerium and gadolinium ions by adding a mixed aqueous solution of cerium nitrate and gadolinium nitrate into a solution of sodium octadecyl sulfate. The formation of the lamellar structure and chain packing of synthesized solid surfactants were confirmed by XRD. In addition, ICP measurement revealed that the content of gadolinium in the interlayer of solid surfactants was proportional to the preparation ratio of cerium and gadolinium. Then, the obtained surfactant crystals were exposed to humid ammonia vapor to promote the hydrolysis and condensation of cerium and gadolinium ions, leading to the formation of gadolinium-doped ceria. Finally, the nanosheets colloidal solution was obtained by immersing the surfactant crystals containing gadolinium-doped ceria into formamide. As a typical example, the nanosheets synthesized with a preparation ratio of Ce:Gd=0.7:0.3 were characterized. The AFM image showed that the nanosheets had 3 nm thickness with a lateral size of 30 μm. The TEM image of the obtained samples showed the formation of the nanosheet, and the obtained nanosheets were composed of small-sized (>3 nm) nanoparticles. The SAED pattern also showed a ring pattern, indicating a polycrystalline fluorite structure. EDS analysis revealed that the nanosheets contain both cerium and gadolinium, and their molar ratio corresponds to the composition of the solid surfactants. These results indicate the successful synthesis of gadolinium-doped ceria nanosheets by using solid surfactant crystals.

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NATURAL ZEOLITE ENRICHED WITH ASCORBIC ACID FOR REDUCING THE RISK OF LATE AND LONG-TERM EFFECTS OF VIRAL AND BACTERIAL INFECTIONS

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Natural zeolite with high clinoptilolite content (>85 %) could be considered monomineral rock composed of clinoptilolite (Cpt). Clinoptilolite crystals have well-formed plate-like habitus and specific monoclinal symmetry. In individual rock samples, at the border between zeolite and mordenite field, Prof. Boyan Aleksiev (discoverer of industrial fields of natural zeolite in NE Rhodope Mountain) has observed well-formed spherolites of zeolite . Besides clinoptilolite, the zeolite rock contains small quantities of feldspar, cristobalite, and montmorillonite. Clinoptilolite has unique properties of ion exchange, adsorption, catalytic processes, and molecular sieve. It is an inorganic mineral with prominent biological effect that is important for the normal metabolic processes in the human body.

When getting into the stomach after *per os* administration, Cpt interacts with hydrochloric acid (HCl), ion exchange of K^+ and Na^+, binds to H^+ and gets protonated. Released K^+ and Na^+ ions get to the duodenum, bind to the insoluble bile acids and convert them into colloid-soluble alkali salts. The process of bile and cholesterol excretion gets activated. Good conditions are brought about for formation of complex aggregates of lecithin, cholesterol, cholesterol ester, lysolecithin, and glycoproteins. In the presence of water spheric cholesterol micelles are formed – cholesterol spheroids (Chol Sph). The equilibrium reaction between cholesterol and lecithin (the left side of the equation) and the resulting cholesterol ester and lysolecithin (the right side of the equation) are catalyzed by the same enzyme acyltransferase (AT) [1,2]:

cholesterol + lecithin <=> cholesterol ester + lysolecithin

The interaction between cholesterol and lecithin is one of the basic biochemical reactions of great significance for the normal function of cells, tissues, and organs [1].

By means of CholSph the cholesterol ester transfers cholesterol to the cell membranes, and to the brain. During the hydrolytic decomposition of lecithin (comprised in the CholSph structure), choline is excreted and it crosses the blood-brain barrier and participates in the biochemical reactions of acetylcholine synthesis (one of the main mediators of nerve impulses).

Depending on the metabolic processes going in the organism, CholSph compose of high-density lipoproteins [spheroids of “good” cholesterol (CholSph “good” cholesterol) – have radial growth, a centrally positioned pore, and are able to reproduce and of spheroids associated with cholesterol, and lipoproteins with low density – spheroids of ”bad” cholesterol (CholSph “bad” cholesterol).

Bacterial and viral infections cause structure amendments and destruction of Chol Sph.

Metabolic processes in the human organism are regulated for operation of reduction-oxidation (redox) reactions that define the function and system biopotential (for the different biosystems, at pH 7 this potential is from -0,670 E° Volt to +0,820 E° Volt).

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STRONTIUM ISOTOPE SIGNATURE OF HUMAN URINARY STONES FROM SOUTH ITALY: PRELIMINARY RESULTS

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This study aims at characterizing the strontium isotope signature ($^{87}Sr/^{86}Sr$) of 22 human urinary stones collected from patients admitted between 2018 and 2020 at the Department of Urology of the San Pio Hospital (Benevento, Italy), in addition to having already been deeply characterized and classified from a morphological and mineralogical point of view [1,2].
Sample preparation and isotope analysis were carried out in an ISO6 – ISO5 clean room at the Department of Earth Sciences, Environment and Resources of University of Naples Federico II. About 0.05 g of each sample were dissolved with Suprapur grade reagents (0.25 mL HNO_3 (65%) + 1.5 mL HF (40%)) in PTE vials on a hot plate at 110 °C under a laminar flow hood overnight. Each sample was then placed in an ultrasonic bath for 8 minutes and dried at 110 °C. Organic matter was removed with 3 cycles of alternating 0.1 mL HNO_3 (65%) and H_2O_2 (30%). The procedure continued by adding 0.75 mL of HNO_3 (65%) and dried on hot plate at 110 °C, followed by adding 2 mL 6M HCl and placed on hot plate at 110 °C under a laminar flow hood overnight. Finally, samples were taken up in 1 mL 2.5M HCl and centrifuged at 4500 rpm for 10 minutes. Strontium was chromatographically separated from the liquid matrix using quartz columns filled with 2 mL of cation exchange resin Dowex AG 50 W X-8 (200-400 mesh) following the protocol described in Arienzo et al. [3]. $^{87}Sr/^{86}Sr$ ratios were then determined by thermal ionization mass spectrometry (TIMS).
The study samples were composed of 7 calcium oxalate stones (both weddellite and whewellite), 12 purines (mainly uric acids and one ammonium urate mixed with calcium oxalates), 3 phosphate stones (one brushite and two carbonated apatite mixed with calcium oxalates) showing Sr-isotope ratios ranging from 0.70761 for one of the uric acid samples to 0.70997 for one of the calcium oxalate stones.
Further investigations are currently being undertaken to evaluate the potential relationship existing between these pathological biomineralization and regional environmental matrices such as bedrock, groundwaters, food, soils and plants.

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TEMPERA PAINTS PROBED ON THE MOLECULAR SCALE : EXAMPLE OF RED AND GREEN EARTHS WITH YOLK

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In contrast to the oil painting technique which supplanted it at the end of the 15th century, *tempera* painting [1], practiced on wood panels, walls or canvas has received little attention on the physico-chemical scale. This painting technique, which has been practiced since Antiquity, is characterised by pigments applied in a water-based binding-medium, often egg-yolk. In order to understand the properties and appeal of this mixture on a molecular scale, we reproduced 15th century recipes which a Tuscan painter Cennino Cennini had consigned to paper, using egg-yolk and two clay-based pigment, green earth (*terra verde) or red earth*. Rheological properties were investigated. Thanks to the synergy between the yolk of egg and the pigment, the spreading and covering properties of the paint are enhanced due to a better internal cohesion of the pigments in the presence of the binder. The formation of a network between the proteins of the egg-yolk, the water molecules and the clay particles of the pigment which renders the mixture more viscoelastic was by low field NMR. The drying of these tempera paints was subsequently monitored for the first time, showing an initial stage of water evaporation followed by long term chemical processes.
This study at the very boundary of materials science and art history contributes to a better understanding of the materials chosen by painters, with the prospect of enhancing the conservation and restoration of works executed with this technique.

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USE OF TUNISIAN CLAY IN THALASSOTHERAPY

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The use of clays for cosmetic and medicinal applications has been known since Antiquity. The use of Mesopotamia clay has been proven, using sludge for mummification of corpses. Cleopatra, Queen of Egypt, had used the mud of the Dead Sea for her aesthetic treatments.

The Romans were the first to recommend mud baths for therapeutic purposes as evidenced by thermal baths everywhere in Tunisia.

In Tunisia, the history of thermal waters dates back more than two thousand years. It experienced a great boom in Roman times (44-43 before JC) during which the use of hot waters was a cult, an art of healing, an art of living.

Tunisia has very important thermal potential. More than 80 thermo-mineral events of meteoric origin, spring from north to south of Tunisia, 50 hot thermal sources of which have been identified with the necessary chemical composition allowing them to be exploited for thermal cures responding to different therapies. Most of these sources have been the subject of traditional thermal exploitation since Roman times.

These thermal waters, the temperature of which exceeds 45 ° C will be mixed with local clays that meet the requirements of use such as peloid. The use of clays on the human body leads to relief of the tissues and then muscles of the human body.

Tunisia is among countries with a big destination for Thalasso Therapy with 60 thalassotherapy centers welcoming tens of thousands of spa guests per year.

We looked for Tunisian clays which have slow cooling, easy to handle and pleasant in contact with the skin giving the most complete relaxation possible to make a good peloid.

Essays with Tunisian Smectitic clays and Kaolinitic illitic clays were carried out and have given very satisfactory results.

This leads us to generalize these tests to other remote regions of the country to try to enhance the remote thermal resources (inside the country) with local clays.

Attention should also be paid to the possibility of maturing Tunisian clays with algae and sea water.

Thermalism with its components constitutes, like any other economic activity, a very important vector of development for the sector of tourism, regional development and alternative medicine.

Humanity must therefore be encouraged to consume more thermal medicine to spend fewer drug.

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EVALUATION OF ZEOLITE APPLICABILITY AS CARRIER MATERIAL FOR BIO-HEALING AGENTS IN SELF-HEALING CONCRETE

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The use of zeolites in civil engineering materials is constantly gaining interest to researchers. Among many applications, one of the new paths is the application of zeolites as carrier materials for bio-healing agents in self-healing concrete.

In this research, the possibility of using NaP1 zeolite to produce a healing agent by impregnating it with a strain of *Bacillus subtilis* bacteria was investigated. Firstly, the zeolite was characterized, e.g., in terms of chemical composition, physical properties (bulk density, water absorption), and the ability to adsorb bacterial cells. Then, the viability of bacteria immobilized on the material was determined using two impregnation methods, taking into account the storage of the material under reduced temperature conditions. Finally, the bio-healing agent and raw zeolite (as a control sample) were added to cementitious mortars to determine their impact on strength parameters and their recoverability, and healing ability of artificially induced cracks.

The potential of using zeolite NaP1 as a carrier for bacteria was confirmed by the adsorption capacity of bacterial cells, which was greater than 70%. However, the high water absorption of the material indicated the need to consider its volumetric contribution in the cement mixture. The viability of bacteria on vacuum-impregnated zeolite obtained higher values than for material impregnated by immersion. Nevertheless, after 28 days of storage, the number of spores decreased compared to the initial preparation for both impregnation methods (by 36% for immersion and 14% for the vacuum method). The addition of bio-healing agents did not significantly affect the composite's strength, but during treatment in a healing solution, it increased self-healing abilities by filling the crack to at least 85%. In summary, the study indicates that zeolite with the NaP1 structure type can be effectively used as a carrier material for a biological healing agent in cementitious composites.

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VISIBLE LIGHT-INDUCED DEGRADATION OF DYES BY LAYERED DOUBLE HYDROXIDES SUPPORTED ON CLAY MINERALS: THE SYNERGISTIC EFFECT OF ADSORPTION-PHOTOCATALYSIS

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Photocatalysis and adsorption are widely used methods for water purification that are usually applied separately. Both of these processes are controlled by the surface of the used solid-state materials which leads to integrated interactions that may enhance the efficiency of pollutant removal. Yet, most of the known photocatalysts have low adsorption capacity, which prevents this synergistic effect. Layered double hydroxides (LDH) are well-known, positively charged adsorbents that can be also used as photocatalysts. With the use of proper divalent and trivalent metal ions, synthesized LDHs show visible light activity for the photodegradation of organic pollutants. The performance of LDH materials is however limited by the recombination of photogenerated charge carriers, their chemical stability, and low dispersion in water. Using negatively charged clays as supports for LDH may minimize mentioned drawbacks, as well as enhance the removal and degradation of anionic pollutants. Hence, the purpose of this study was to synthesize LDH photocatalysts on clay minerals and compare their efficiencies in the removal of organic compounds.

LDH phases (Zn/Cr, Ni/Cr, Cu/Cr, and Co/Cr) were obtained by the co-precipitation method with the M^{II}:M^{III} ratio set to 2:1. The LDH-clay composites were synthesized by the co-precipitation of Zn/Cr LDH in the presence of each clay mineral (kaolinite, halloysite, and montmorillonite). Three different contents of clays were used in the syntheses: 20%, 33%, and 50% wt. In the photocatalytic experiments, two organic dyes were used: cationic methylene blue (MB) and anionic acid blue 129 (AB). The aqueous solutions containing dye and photocatalyst were exposed to visible light (150 W LED lamp, approximate light intensity of 120 000 Lx). Prior to that 30 minutes of adsorption in the dark was performed. Analogous control experiments were conducted in the dark. Removal of the dyes was monitored using UV-Vis spectrophotometry.

The obtained LDH and LDH-clay materials were analyzed by X-ray powder diffraction, which confirmed the formation of layered structures. With the use of diffuse-reflectance UV-Vis spectroscopy, it was possible to state that all of the synthesized LDH photocatalysts are active in the visible light region. All of the materials' spectra showed strong absorption bands in the 300-750 nm region. For all of the LDH phases the MB adsorption was negligible, while the photodegradation (after 1 h) was most efficient for the Zn/Cr phase – over 20% concentration decrease. Removal of the AB dye was more efficient for all of the LDH phases, still, the Zn/Cr material was characterized by the best performance – with a concentration decrease of 30%, in which 12% p.p. was adsorption. Therefore, the Zn/Cr material was used for further studies. As for composites, halloysite and kaolinite supports did not enhance the removal of both AB and MB dyes. The decrease of AB was less than 10% (with less than 6% p.p. adsorption) and the decrease of MB was less than 6% (with less than 3% p.p. adsorption). The Zn/Cr LDH supported on montmorillonite was the most effective composite and the best performance of the material was observed with a clay content of 50% wt. This material led to a 79% and 73% decrease in MB and AB concentration, respectively. Under these conditions, the pure adsorption for both dyes reached 53-58% p.p.

In conclusion, the Zn/Cr LDH-smectite composite exhibits promising results in the synergistic adsorption-photocatalytic removal of organic dyes. Further studies of the material are currently being carried out.

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HYDRATION HYSTERESIS OF SMECTITE-DNA COMPLEX

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The analysis of environmental DNA has revolutionised the fields of paleoenvironmental reconstructions [1], evolutionary inference [2] and biodiversity monitoring [3]. DNA is an unstable polymer [4] so the mechanisms and conditions at which the millennial stabilization is achieved are unclear. Adsorption and intercalation of DNA in smectite interlayers is a promising route for its long-term stabilization and storage. Using smectites with various layer charges, we measured the adsorption capacity for DNA using UV spectroscopy and intercalation capacity using X-ray diffraction. We found that while the smectite adsorption capacity is large, the DNA intercalation decreases as smectite charge increases. No intercalation was observed $\geq$1.2 charge per $O_{20}(OH)_4$.

The stability and preservation of DNA is affected by its hydration, *i.e.* hydrated DNA is easier to chemically degrade compared to dehydrated DNA. To probe the hydration properties of smectite-DNA complex, we conducted X-ray diffraction experiments under controlled humidity conditions using smectites with a range of layer charge, various solution composition and lengths of DNA polymer. We noticed that the volume of adsorbed water by smectite-DNA complex is different if the complex is dehydrated or hydrated to an equivalent relative humidity. The hysteresis between dehydration and hydration pathways is significantly larger for a smectite-DNA complex than for a smectite without DNA. In addition, the hysteresis increases with layer charge and it is controlled by pH, ionic strength and DNA length. Combined, our results suggest that the hydration of adsorbed and intercalated DNA, *i.e.* its preservation potential, is a function of both the mineral substrate and the environmental conditions.

We demonstrate that DNA intercalation in smectites is likely an important strategy for DNA preservation. We show that the hydration state of smectite-DNA complex is controlled by environmental factors suggesting that the knowledge of postdepositional conditions is important for assessing the preservation potential of environmental DNA, particularly in environments such as soils where the continuous fluctuations in humidity impact the recalcitrance of organic compounds.

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ATOMIC LEVEL DESCRIPTION OF PHOSPHATE SORPTION AND DESORPTION BY LAYERED DOUBLE HYDROXIDES (LDH) INVESTIGATED BY SOLID-STATE NMR

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Recovery and reuse of phosphorus (P) is important as industrial phosphate production is based on non-renewable resources [1]. Among the different strategies, sorption has got attention as regulations for phosphorus have become more rigorous and the approach is also promising for the reuse of P [1]. Layered double hydroxides (LDH, general formula $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2][A^{n-}]_{x/n}\cdot yH_2O$) are good candidates for phosphate sorption due to their high ion-exchange properties [2].

While LDH high phosphate affinity has been extensively studied [2], important properties in relation to reusability, *e.g.*, sorption behavior, stability, and P desorption are fairly unexplored. Thus, MgAl-LDH-Cl were synthesized, and a series of P sorption/desorption experiments were caried out to investigate its behavior. To understand P sorption, sorption isotherm and kinetics were carried out in phosphate solutions, while for desorption different anions and concentrations were used in kinetic-like experiments. The solids were characterized by bulk (powder X-ray diffraction, PXRD) as well as at the atomic level by infrared spectroscopy (FTIR), and solid-state ^{1}H, ^{27}Al, ^{31}P and ^{35}Cl NMR spectroscopy (SSNMR).

Following phosphate sorption, the Cl^- was exchanged with HPO_4^{2-} as indicated by the shift of (003) peak from 7.7 to 9.0 Å in the PXRD diffractograms. Moreover, PXRD showed that LDH reflections were preserved but loss in peak intensity and its broadening could indicate formation of (amorphous) impurities. Indeed, ^{31}P MAS NMR (22.3 T, 30 kHz) showed characteristic peaks of aluminum and magnesium phosphates (Al-P and Mg-P, respectively) indicating (partial) dissolution of the LDH.

Intercalated phase (in PXRD) was formed just with 5 min of contact time in a time-dependent ex-situ study of the P sorption at the same P concentration. Moreover, ^{31}P MAS NMR also indicated the formation of Al-P and Mg-P within the same time-range. On the other hand, exposure of the LDH to lower P concentrations did not form impurities and no shift of the (003) reflection was observed. Those results indicate that the P sorption pathway by LDH is highly dependent on phosphate concentration.

Different anions have been used for P desorption by a second anion-exchange process [3] and a detailed understanding of the process is lacking. Thus, P-saturated MgAl-LDH were regenerated after submitting them to different anions (NaCl, NaOH, $NaHCO_3$) in different concentrations. Both the anion and concentration influenced the release percentages, *e.g.,* 50 % for OH^- at 5 molar equivalents in comparison to 27 % for Cl^-. Again, multi-nuclei SSNMR provided a good description of the exchange/regeneration process, including efficiency and LDH stability.

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STUDY OF SYNTHESIS ROUTE AND INDUCED MORPHOLOGIES INFLUENCE ON PHOSPHATE CONTROLLED RELEASE BY LAYERED DOUBLE HYDROXIDES AND THEIR INTERACTIONS

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Phosphorus (P), which is anessential nutrients for plant growth, is considered a critical resource by the European Union due to limited availability of phosphate mineral. Orthophosphate are disseminated in large excess as a soluble fertilizer in soils to avoid plant deficiencies. Lixiviation of this anion is responsible for the eutrophication of freshwater bodies. This is why, beyond its recovery for the remediation of water reservoirs, the recycling of phosphate is of great importance.

The development of slow-release fertilizers (SRF) without polymer coating that degrades in the soil and need a quite expensive process, can produce sacrificial fertilizers such as struvite $NH_4MgPO_4 \cdot 6H_2O$ and its analogues (K, Na…). whose dissolution is slower as compared to a soluble fertilizer[1,2]. From a non-sacrificial support point of view, Layered Double Hydroxides (LDH) displaying anionic exchange properties, possess a strong affinity for phosphate anions, which allow to consider them for both recovery and reuse of P[3,4].

The versatility of LDH in terms of composition, morphologies, and synthesis ways offers a large panel of phases with different structural and morphological properties.

In this study, phosphate intercalated MgAl- LDH phases prepared using different synthesis routes were characterized in detail by a multi technique approach (XRD, SSNMR, FTIR, microscopy) to explore the influence of the morphology and particle size on phosphate adsorption and release. Phosphate release kinetics and matrix dissolution will be presented. In order to accurately describe the release mechanisms, characterizations of the solid phases before and after release was performed. All the results obtained will be detailled in this presentation showing different mechanisms of phosphate adsorption and desorption depending on synthesis route.

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MINERALOGICAL CHARACTERIZATION AND ORAL BIOACCESSIBILITY OF GUYANE GEOPHAGIC PEMBA

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The consumption of white clay (njang pemba) among the Businenge of western Guyana is a practice known to the medical profession and the local population, but poorly understood in its cultural globality, and widely controversial today in Guyana. Pemba are theoretically white clay balls made by hand. The use of pemba is essentially female, often associated with pregnancy, i.e., a pathological behavior (pica). However, the oral consumption of pemba seems to be inseparable from other practices, (i) assumed to be the association between geophagy (as an appetite suppressant, as a protective mechanism against plant toxins, parasites and other pathogens…) and food insecurity, or (ii) external, closely associated with ancestral spirits and marronage territories. However, from a strictly sanitary point of view, the ingestion of pemba could lead to risks related to oral exposition to metals or metalloids (according to their bioaccessibility), but also to potential highly available forms of Fe and Al.

The aim of this work is to increase our understanding of geophagy risks or benefits by a careful characterization of the physical, chemical, and mineralogical properties of 15 samples of ingested pemba clay representative of various local practices. The bioaccessibility of metal(loid)s such as Al, Fe, As, Pb, Ni, V, Zn and Cr is also studied in this pemba samples.

For this, the samples were characterized mineralogically (XRD, FTIR), chemically for the majors and traces elements (XRF) and in term of speciation by XAS at Soleil synchrotron (France) at the Al K-edge (E0=1559 eV) from LUCIA beamline, and Pb LIII-edge (E0=13035eV) and As K-edge (E_0=11.875eV) on DIFFABS beamline. As expected, the granulometry of the samples is predominantly clayey. The chemical and mineralogical investigation clearly evidence the main kaolinite nature (with a little bit of halloysite for some samples) of pemba whatever the practical used. Some impurities are present composed by fine quartz, gibbsite or hematite for some samples evidenced by qXRD. This point is interesting considering that the local populations rely only on empirical knowledge for the use of these materials. Note that the crystallinity of kaolinite changes from one sample to other from XRD (Hi index) and FTIR. The XANES Al K-edge is in accordance with it. The concentrations of trace elements is low on average 150 mg/kg for Cr, 151 mg/kg for V, 30 mg/kg for Ni, 15 mg/kg for Cu, 50 mg/kg for Zn, 43 mg/kg for Pb and about 2 mg/kg for As (only for 3 samples in this case). Note that some experiments by XAS (As and Pb) evidence the different speciation of elements between the pemba samples.

The gastric and gastrointestinal bioaccessibilities determined according to BARGE protocol are low for all the considered elements. The elements the more bioaccessible are Al followed by Fe and Zn.

A discussion about the link between mineralogical speciation and oral bioaccessibility will be proposed to better highlight the potential risks or benefits in relation with pemba geophagy in western Guyana.

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INVESTIGATING THE LAYER CHARGE AND CATION EXCHANGE CAPACITY ALTERATIONS IN THE ALTERNATE BUFFER MATERIALS (ABM) EXPERIMENTS: WHAT WE KNOW THUS FAR?

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Several different bentonites, of interest for use as buffer materials in the storage of nuclear waste, underwent layer charge (LC) and cation exchange capacity (CEC) analysis to track alteration of the bentonites over a thermal gradient during their emplacement in the underground, long-term (up to 7 years), thermal-water-rock interaction experiment in Äspö, Sweden.

The LC of the smectitic component of bentonite controls properties integral to the performance of a bentonite for safe nuclear waste storage and include: adsorption, expandability, and CEC. As the CEC of a bentonite is influenced by its LC, a combined analysis of the LC and CEC datasets has provided an enhanced understanding of alterations that occurred in these bentonites.

Methodology included the new, quick and efficient spectroscopic method, "O-D method", for LC determination of materials with wettable, smectitic surfaces, providing reproducibility <0.010 e^- per smectite formula unit. The "O-D method" facilitated the identification of subtle LC changes in ~175 of the thermally reacted samples and non-reacted reference materials. The established Cu-trien method was used to obtain CEC results for the same samples.

A common trend emerged between the LC and CEC results for the bentonites from the high-temperature ABM5 experiment: when temperature increased towards the heater, both the LC and CEC values decreased. We suggest that – while the smectite content and expandability remain constant – smectite's LC controls bulk rock CEC, by partial fixation of interlayer cations occurring on the smectite surface with the increase of temperature over an extended time. In ABM5, higher temperatures of ~250°C were achieved and corresponded with higher LC changes when compared to ABM2, where the highest temperature was only ~140°C. ABM2 showed contrasting LC and CEC results to ABM5, as some samples displayed a LC increase directly at the heater contact. This indicates that advanced crystal-chemical changes in the smectite structure may be occurring. As ABM2 was subjected to a significantly longer reaction time than ABM5, this points to the possibility that kinetics may impact the long-term stability of some bentonites. A further correlation was observed between the degree of LC changes in a particular bentonite and that of the LC of the original unreacted reference material. This correlation indicates that bentonites which initially possessed a relatively higher LC underwent a greater degree of LC alterations within the ABM packages.

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INFLUENCE OF HEATING RATE ON FRESH AND HARDENED PROPERTIES FO GEOPOLYMERS FROM LATERITE SOIL

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Geopolymer appears as alternative of portland cement and the characteristics are linked to the type of aluminosilicate materials used for the synthesis. The present work investigated the influence of heating rate on some properties of geopolymer like setting time, flexural strength, water absorption, porosity and bulk density. The collected laterite were heated at 600 °C with under diverse heating rate (1.5, 2.5, 5.0, 7.5, and 10 °C/min) and activated with an alkaline solution. The obtained results revealed that the values of flexural strength increased when applied heating rate from 1.5 to 5.0 °C and then decreased from 7.5 to 10 °C. The highest performance (10 MPa) was achieved on sample made with powder heated with 5.0 °C/min. Same formulation exhibited lower porosity and water absoprtion with densified strcuture. While the heating rate above 5.0 °C/min prolonged the setting time from 4h to 6h. The consolidated specimens could be used in engineering building.

Keywords : Laterite, Alkaline solution, Mechanical property, Porosity, Microstructure

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FUNCTIONAL CLAY-BASED FILM CONSISTING OF LIGNIN, A PLANT AROMATIC POLYMER

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In this presentation, we present about functional clay-based film consisting of lignin, a plant aromatic polymer. Lignin is particularly promising for composite functional materials production, as its physical and chemical properties are uniquely adapted to the structural, defensive, and water transport functions in plants. However, the lignin in functional materials production has usually been chemically reacted during the extraction process, which modifies its native properties.

In this study, the lignin was obtained by simultaneous enzymatic saccharification and comminution (SESC) of plants, a novel method for extraction of plant biomass without deterioration of lignin and environmental road on extraction process [1]. Here, the clay-based films consisting of lignin were prepared by an environmentally friendly process, *i.e.,* no need of hazardous petroleum-derived chemicals until whole procedure. Simple mixing of water-dispersed components and drying the casted mixture give a transparent film. The obtained film exhibits various novel functions such as excellent UV absorbability, non-flammability, and moisture/gas permeability [2]. The optical properties and gas permeability of the films could be tuned by the components and phase separation structure of the clay minerals and lignin derivatives [3].

The film production from clay and lignin would not only encourage the utilization of mineral and plant components as high-value industrial materials (*e.g.*, non-flammable UV protection agricultural films) but also reduce the environmental load of extracting limited petroleum-based resources. Ultimately, the replacement of petroleum-based resources with natural resources is expected to establish a novel field of the agricultural industry.

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NATURAL AND ACID ACTIVATED CLAYS AS HETEROGENEOUS CATALYSTS – APPLICATION EXAMPLES

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(1) BYK Additives Ltd.

To achieve a greener, more sustainable future, processes and reagents in the chemical industry must be reassessed. One approach to the challenge is to look at the past catalyst technologies that have fallen out of favour in recent years. Montmorillonite clay-based catalysts have been used for many years as clean, sustainable, cost-effective solid Lewis or Brønsted acid catalysts. The ionising effect of the negatively charged montmorillonite clay surfaces generate Hammett acidities of up to -3 [1]. With acid treatment, the number and potency of the acid sites increases and Hammet acidities of -8 can be achieved. Based on these properties BYK have developed a range of clay-based catalysts, FULCAT®, for use in such key chemical reactions as Friedel-Crafts alkylation, siloxane equilibration and oleochemical processing.

High performance aminic antioxidants based on diphenyl amines (DPA) are growing in popularity, partly due to the regulatory issues associated with phenolic based antioxidants. We will present high performance liquid chromatography (HPLC) data describing how FULCAT® catalysts outperform alternative solid catalysts and show good recyclability. The final FULCAT® catalysed products were optically clear, free of toxic catalyst residues and substituted at the preferred para-position[2].

Siloxane equilibration polymerisation of cyclic siloxanes is used to produce silicone fluids, functional silicone fluids and silicone surfactants. Using simple viscosity measurements, it will be demonstrated that FULCAT-22 S® combines low sulphur, required for functional silicone fluid and surfactant production, with excellent catalytic performance.

Oleochemicals are an important and growing sector of the chemical industry. For example, in the oleochemical industry, both acid and natural clays have been used as Diels-Alder cycloaddition catalysts in the production of dimer acids from tall oil[3]. As well as demonstrating excellent catalytic performance in dimer acid production, this talk will discuss how FULCAT® clay-based catalysts can also be used as heterogeneous esterification and alcohol dehydration catalysts, for the production of such oleochemicals as fatty acid esters and dehydrated castor oil.

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DETECTION AND QUANTIFICATION OF LOW LEVELS OF CARBONATE MINERAL SPECIES USING THERMOGRAVIMETRIC-MASS SPECTROMETRY TO VALIDATE CO2 DRAWDOWN VIA ENHANCED ROCK WEATHERING.

Simon Kemp* (1), Amy Lewis (2), Jeremy Rushton (1)

(1) British Geological Survey, (2) Undo Carbon Ltd

Enhanced rock weathering (ERW) is a promising technology being actively investigated to ameliorate anthropogenic climate change. ERW accelerates atmospheric carbon dioxide (CO_2) drawdown in agricultural soils following the addition of crushed, silicate rocks. The application of basalt, an abundant silicate rock, has widely been proposed for ERW. In order to measure and model the efficacy of ERW, it is critical to fully characterise the mineralogical composition of the basaltic materials being deployed in laboratory to catchment scale experiments.

As previously demonstrated on analogous basaltic rock and soil materials on Mars, thermal analytical methods such as coupled thermogravimetric analysis-mass spectrometry (TGA-MS), provide a potentially rapid, effective technique to identify and also quantify the carbonate mineral species present in ERW basalts and their weathering products.

Our study of six different basaltic materials used in ERW experiments, from widely different geological and geographical settings, suggests that TGA weight losses can provide useful information on the low-levels of carbonate minerals present. Furthermore, carbonate mineral identification and quantification derived from the accompanying MS-detected CO_2 evolution and corroborated by SEM-EDS mapping, is capable of detecting even lower concentrations with detection limits below 100 ppm for calcite. TGA-MS therefore offers significant advantages over the traditionally-applied inorganic carbon analyses.

Carbonate mineral weight losses encountered during TGA, and their accompanying CO_2-evolutions have previously been ascribed to relatively small, defined temperature ranges. However, crucially, this study has revealed the concentration-dependent, large-scale variation in the mass spectrometric peak CO_2-evolution for a range of carbonate minerals. A knowledge of such parameters is imperative for the accurate interpretation of basalt TGA-MS output, the characterisation of these materials and assessment of ERW technologies.

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ENGINEERED UK CLAYS FOR THE PRODUCTION OF LOW-CARBON CEMENTS

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To maximise the benefits of calcined clay cements, we need to unlock the full potential of a range of regionally available clay resources. The majority of research has previously focused on kaolinitic clays, as kaolinite is known to be the most reactive of the commonly occurring clay minerals, once activated. In the United Kingdom (UK), as well as other countries/regions, the majority of clay resources are formed of common clays, typically containing a combination of smectite, illite, chlorite and kaolinite. Non-kaolinitic clay minerals can exhibit noticeably different physical characteristics, composition, and dissolution kinetics, meaning that the knowledge base developed for kaolinitic clays cannot simply be transferred to the more complex, common clays found in the UK. The “Engineered UK clays for production of low-carbon cements” project takes a mineralogy-driven approach to the design of calcined clay cements. This project seeks to establish the composition-processing-performance relationships for UK clay resources, in order to develop predictive power around how to best process and use them in calcined clay cements. It will investigate existing clay resources which are already exploited (e.g. cement quarries, brick clay quarries) as well as material streams which are not currently valorised (e.g. quarry overburden, excavation waste). In addition to calcination in a rotary kiln, it will also explore alternative activation routes (e.g., flash calcination, mechano-chemical activation) to capture the most value from UK clay resources. We will present findings from the initial characterisation and screening stage, and provide initial indications as to which geological formations and material streams are most promising for calcined clay production in the UK.

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THE OCCURRENCE AND MICROSTRUCTURE OF SECONDARY MINERALS FOUND IN "ACTIVE" HYPERALKALINE ENVIRONMENT

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(1) Hokkaido University, (2) Central Research Institute of Electric Power Industry, (3) Radioactive Waster Management Funding and Research Center

In the geological disposal of HLW and TRU waste, alteration of engineered barrier materials by hyperalkaline leachate from the cement has been concerned. Studies using geological or archaeological analogues are important to verify mineral dissolution-precipitation reactions in long-term alkaline environments, and “active” sites where the water involved in the reaction is still accessible are particularly valuable. Active interaction has been observed in Narra District, in central Palawan where alluvial fan deposits spreading on gentle slopes of serpentinite basement. Several trench or drill hole samplings were performed to investigate the interaction between ultramafic sediments and the hyperalkaline groundwater (pH ~11, Ca-OH type) which seeps from the trench walls and drill holes [1]. The deposition of sediment was determined to have continued from 15000 to 2560 yrs BP based on ^{14}C dating, and the depositional environment is considered to change from seawater – brackish to freshwater over time [2]. Several types of F-M-S-Hs (Iron-Magnesium Silicate Hydrates) have been reported as secondary minerals [3]. Here we report on the occurrence and microstructure of F-M-S-Hs, to elucidate the relationship between primary minerals and newly formed F-M-S-Hs, including F-M-S-Hs with exceptionally high Ca/Si ratios compared to our previous studies.,

The solid samples were examined by electron microscopy techniques (SEM-EDX. EPMA, FIB-SEM and (S)TEM,) and powder XRD. Major secondary minerals were F-M-S-Hs; they were similar to Fe-Mg-bearing smectites, such as saponite or nontronite, though they showed slightly less expandability after ethylene-glycol solvation. The cavities of the sediments were infilled with Fe-rich F-M-S-H, which shows a composition similar to Fe-saponite or nontronite, but with incomplete tetrahedral sites and excess Ca as interlayer cations. STEM analysis suggested that a part of this excess Ca is located in the structure of the F-M-S-H. Mg-rich F-M-S-H was also found around the fractures and rims of serpentine and Opx. TEM observations demonstrated the formation of saponite-like layers aligned with serpentine layers. The two types of F-M-S-Hs have a continuous composition, which may reflect the degree of influence of Mg-rich primary minerals. In addition, younger sediments contained C-S-H (14Å-tobermorite) accompanying with calcite shells or forming a mixture with Fe-rich F-M-S-H. Mineral saturation indices support the formation of saponite in the current alkaline groundwater and nontronite in the past brackish environments. The formation of zeolites, which are common products in alkaline alteration experiments, were not confirmed and not supported by saturation indices.

This study was carried out as a part of R&D supporting program titled “Advanced technology development for geological disposal of TRU waste (2021-2022 FY) under contract with the Ministry of Economy, Trade and Industry (METI), Japan (Grant Number: JPJ007597).

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APPLICATION OF STEELMAKING SLAG FOR NEGATIVE EMISSION BY ENHANCED WEATHERING

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(1) Hokkaido University

Negative emission technologies (NETs) for carbon dioxide (CO_2) capture are in the early stages of development, and one promising approach is enhanced weathering, a low-cost, land-free alternative that utilises the natural chemical weathering of rocks and industrial wastes rich in calcium (Ca) to store atmospheric CO_2 permanently. While mafic rocks such as basalt have been studied extensively as effective candidates for enhanced weathering, industrial wastes such as steelmaking slag and fly ash have received less attention (Myers and Nakagaki, 2020; Sandalow et al., 2021). Here, we used steelmaking slag, a by-product of the steelmaking process that can be utilised as an alternative and effective material owing to its high reactivity and abundance of dissolvable calcium oxide, commonly known as free-lime. Additionally, the mineral weathering rate is typically accelerated under acidic conditions, and acid mine drainage (AMD) is strongly acidic, making it an ideal site for enhanced weathering. As a result, this study simulates the use of steelmaking slag for enhanced weathering employing column experiments and geochemical reactive transport modelling (using The Geochemist's Workbench 17.0). The column experiments were conducted utilising finely crushed steelmaking slag and different pH input solutions. The output solutions and solid samples were subsequently analysed to investigate the effects of reactions occurring during the experiment. Furthermore, the effectiveness of steelmaking slag in removing CO_2 over the period of a year was evaluated by comparing the modelling results under different conditions, including different sites and materials.

The results of the column experiments indicated a high concentration of Ca and alkalinity in the output solutions due to the rapid dissolution of portlandite. The geochemical reactive transport model predicted that the dissolution of steelmaking slag in AMD would be considerably enhanced, leading to the removal of large amounts of CO_2 after mixing with seawater. The dissolution rate in AMD was unambiguously faster than in agricultural land due to the pH difference between the reactive fluids in the AMD and agricultural land. The modelling findings also revealed that the quantity of CO_2 removal per tonne of material for AMD did not differ considerably between basalt and steelmaking slag since nearly all reactive minerals could be rapidly dissolved in AMD. In contrast, steelmaking slag removed significantly greater amounts of CO_2 annually than basalt, principally due to the kinetics of the minerals contributing to the formation of carbonate mineralisation. However, due to the high equilibrium pH of portlandite in the slag, the use of steelmaking slag on agricultural land should be handled with precaution. Therefore, the present study demonstrated the potential of enhanced steelmaking slag weathering in AMD as a very effective approach for CO_2 capture that outperforms the use of basalt.

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SYNTHESES AND CHARACTERIZATION OF CLAY-POLYMER NANOCOMPOSITES CONTAINING TETRAMETHYLBENZIDINE FOR DETECTION OF HAZARDOUS ORGANIC COMPOUNDS

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Chromism is a phenomenon in which the color of a substance changes reversibly due to external stimuli such as thermochromism, a phenomenon in which the color changes with temperature, and photochromism, in which light of a specific wavelength causes color change. Solvatochromism and vapochromism are the phenomena in which the color of substances changes by chemical substances in solvents and in vapor, respectively. These materials are expected to be used as the chemical sensors to detect and visualize the hazardous substances in water and air. Especially, the vapochromic materials are expected to detect volatile organic compounds (VOCs), which are present not only in factories and other work spaces but also in offices and living environments and cause the sick building syndrome. Several vapochromic materials have been reported but most of them are complexes of minor metals such as platinum, which is expensive and not suitable for mass production. Therefore, cheaper and more readily available materials are desirable.
We have previously reported vapochromism of materials derived from a simple organic compound, 3,3′,5,5′-tetramethylbenzidine (TMB), and tetrasilisicfluormica, which is an environmentally harmonious clay mineral. In this report, we investigated chromism of a hybrid material consisting of a hydrophilic polymer P(NIPAAm), several clay minerals, and TMB to improve the formability from the previously reported one and focused on the detection of organic materials not only in the gas phase but also in the aqueous phase. The synthesized samples showed colors yellow-green in dry condition, green upon exposure to water vapor and blue-green upon exposure to acetonitrile vapor. On the other hand, it showed no color change for the vapor of alcohols or nonpolar organics. These results suggest that this material is effective for detecting acetonitrile in the environment. In the presentation, we will also report the color change of the material in the aqueous phase involving organic matter.

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ADSORPTION OF 226RA AND BA BY ILLITE AND MONTMORILLONITE

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Argillaceous rocks are considered suitable for the construction of deep geological waste repositories for high-level radioactive waste in several waste management programs e.g. in Switzerland, Belgium, or France. To account for the retardation properties of clay minerals in these host rocks in safety studies, thermodynamic models capable of predicting the retention of radionuclides over a wide range of physico-chemical conditions are crucial. Illite, smectite and illite/smectite mixed layers are relevant constituents of many argillaceous host rocks. In addition, bentonites are envisaged as engineered barriers in underground waste disposal concepts. Montmorillonite, the major constituent of bentonite (up to 90 wt.-%) is an important sink for potentially released radionuclides.

Adsorption data for ^{226}Ra onto illite and montmorillonite are sparse in the open literature. Because of this knowledge gap, the adsorption and diffusion of ^{226}Ra in clay minerals are assumed to behave similar as Ba, based on chemical analogy. In order to verify this hypothesis and improve the quantitative understanding of the adsorption of ^{226}Ra by 2:1 clay minerals, a combined adsorption and modelling study was carried out. Parallel adsorption experiments were carried out onto the homo-ionic Na forms of montmorillonite (SWy-2, Wyoming, USA) and illite (IdP-2; Illite de Puy, Le Puy-en-Velay, France) in diluted systems and compared to the adsorption of Ba under the same conditions. ^{226}Ra and Ba adsorption edges in the pH range 5 to 10 at different ionic strengths (0.01 – 0.3 M NaCl) and an isotherm (pH 7, 10^{-9} M < [Ra, Ba] > 10^{-2} M) were carried out on Na-SWy and Na-IdP. The 2-site Protolysis Non Electrostatic Surface Complexation and Cation Exchange adsorption model (2SPNE SC/CE) developed for montmorillonite [1] and illite [2] reproduces the experimental data for both elements well.

For montmorillonite, the selectivity coefficients (K_c) for Ba^{2+}-Na^+ and $^{226}Ra^{2+}$-Na^+ exchange are in good agreement at low ionic strength (log K_c = 0.70 – 0.84), whereas at high ionic strength, the K_c (Ba-Na) is slightly higher (log K_c of 0.90 (0.3 M) vs 0.70 (≤ 0.02 M)). In contrast, the K_c (Ra-Na) exhibits a clear dependency on ionic strength, with log K_c values of 0.7, 1.14 and 1.34 at NaCl background concentrations of 0.01/0.02 M, 0.14 M and 0.3 M, respectively.

For illite the Ba adsorption at trace concentration was higher and an additional high selectivity site was needed to model the Ba data. The Ra pH edges at varying ionic strengths consistently reveal a higher ^{226}Ra selectivity of illite compared to Ba. The ^{226}Ra pH edges are well described by an adjusted 2SPNE SC/CE model for illite. Additional ^{226}Ra-Ba adsorption experiments with Ba intended as a carrier for ^{226}Ra again showed a higher affinity of ^{226}Ra. The distinct differences in the behaviour of ^{226}Ra compared to Ba can only be described by a more complex model, which includes two additional high affinity sites for ^{226}Ra. These sites are characterized by a low capacity and high selectivity for ^{226}Ra. These may be sub-sites of the Ba high affinity sites, leading to a partial competition between Ba and ^{226}Ra. The results presented here indicate that Ba can be used as a good analogue for ^{226}Ra regarding the adsorption on montmorillonite at ionic strengths < 0.1 M and pH < 8 but deviates in its behaviour at higher ionic strength. Different from ^{226}Ra the adsorption on montmorillonite, Ba cannot be considered a very good analogue for ^{226}Ra on illite, and a more complex adsorption model is required to quantify Ra adsorption on this clay mineral.

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INTERCALATION CAPACITY OF HALLOYSITE-(7Å) FOR NMF

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Halloysite can be detected in the presence of kaolinite by its fast intercalation causing interlayer expansion [1]. Quantification would require prior knowledge of the intercalation capacity of the individual minerals present. Several kaolinites are only partially accessible to e.g. N-methylformamide (NMF) [2]. To the best of our knowledge, the corresponding behavior of halloysite is poorly investigated.

A systematic experimental investigation of the NMF intercalation capacity of halloysite-(7Å) was conducted by high resolution thermogravimetric analysis (HiRes-TGA), mid-infrared, XRD and in situ Near-infrared (NIR) spectroscopy monitoring.

Cylindrical and polygonal halloysites from the Dragon mine (Utah, USA) [3] exhibited different intecalation capacities for NMF: at infinite time of exposure, intercalation was quantitative in the former (2NMF molecules per $Si_2Al_2O_5(OH)_4$) but only about 65% in the latter. In all cases, intercalation was accompanied by the ordering of halloysite layers, as seen by the narrowing of the inner 2νOH band.

A sample of mixed cylindrical-polygonal form from the same locality (85% intercalation capacity) was subjected to step-wise heating from 50°C to 300°C. The unheated sample contained the so-called 'hole' H_2O, $xH_2O \cdot Si_2Al_2O_5(OH)_4$ with infrared bands at 3550 and 1650 cm^{-1}. Heat treatment induced the progressive decrease of x from 0.37 (50°C) to 0.06 (300°C).

Slurries of the heat-treated halloysite with NMF (1:1 wt) were left to intercalate at 30°C with synchronous NIR monitoring. The intercalation kinetics of the original sample were fast and exponential, but turned to a delayed sigmoidal known also from kaolinite after heat treatment above 250°C. The final uptake was gradually decreased from ~85% to less than 40% (300°C).

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FROM MACRO TO MICRO: ADVANCED AND EXPERIMENTAL METHODS FOR THE ANALYSIS OF FINISHING TECHNIQUES AND POST-FIRING TREATMENTS ON ANCIENT CERAMICS

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The study of the decoration on a pot's surface is essential in gaining insight into the pot's function and aesthetic quality. At the same time, the multi-analytical study of the coatings, the finishing techniques, and the decorative patterns, all allow a deep understanding into the potter's technological know-how.

This presentation focuses on polychrome decorated pottery from the site of Mahtoutabad in southeastern Iran (Madjidzadeh, 2002; Madjidzadeh & Pittman, 2008; Desset et al., 2013; Vidale & Desset, 2013). This ceramic class is characterized by brown linear motives on buff surface, but often two or three colors decorate the same pot (brown-hue, red/brown, black, white colours). Its production is dated back to the late 5th/early 4th mil. BCE until the 3rd mil. BCE and is attested in contemporary sites in Iran and possibly in Pakistan (Vidale & Desset, 2013).

The early dating, the large-scale, specialized, and long-lasting production of this pottery, as well as its changes into the mid-4th mil. BCE— so-called Aliabad ware—, raise important questions about the potters' ability of producing this exceptional style.

The ongoing macroscopic investigation of Mahtoutabad's pottery provides valuable information. However, this project takes a step beyond the typological documentation and explores the technological characteristics of this assemblage. The aims of this study are multiple: i) to clarify the conditions under which the polychromy is achieved (firing atmosphere, raw materials, specific techniques); ii) to detect possible technological changes in the production throughout the site's lifespan; and iii) to address questions regarding the production organization, the potters' skills, the degree of specialization, and the technological choices, as well as to validate them through an experimental approach.

To achieve these, a multi-disciplinary, three-staged approach will be followed integrating: a) macroscopic examination of the material, b) application of analytical techniques (ceramic petrography, XRPD, μ-XRD, μ-XRF, SEM-EDS, XRF), and c) experimental reproduction of pots and their coatings.

This work presents the preliminary results of an ongoing MSCA PhD project (Grant Agrreement no. 101034319) and offers an opportunity to discuss the operational sequence of the polychrome decorated pottery from Mahtoutabad, throughout its lifespan. The results provide also a first glance at the role of this production within the social context of southeastern Iran in the 4th-3rd mil. BCE.

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ZEOLITES IN AGRICULTURE: OVIPOSITION DETERRENT EFFECT OF GREEK ANALCIMIC ZEOLITE ROCK AGAINST THE OLIVE FRUIT FLY BACTROCERA OLEAE

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In recent years, inert dusts, and particularly zeolites, are increasingly being used in agriculture, and specifically in pest control, as natural, non-toxic, ecologically advantageous and affordable materials. The most common phases of the zeolite mineral group are clinoptilolite, mordenite, analcime, phillipsite and heulandite. Analcime exhibits a complex and compact structure, compared to other zeolites. The main physical properties of analcime are: 18% porosity, high heat stability, 454 meq/100g ion exchange capacity. [1] A representative sample (anaS) from zeolite-rich sediments of Karlovassi-Marathokampos basin of Samos Island, Greece, was mineralogically and chemically characterized for oviposition-deterrent effect against one of the most serious pests of olive fruit, namely *Bactrocera oleae* (Diptera: Tephritidae) [2]. The analysis of the mineralogical composition was performed using X-ray diffraction method, while whore-rock chemical analysis was performed using X-ray fluorescence. The morphological and chemical characteristics of the contained analcime crystals by SEM-EDS were also studied. To determine the sorption ability the sample was treated according to the AMAS method. Regarding the effectiveness of the zeolite rock against the olive fruit fly *B. oleae*, we used our studied sample with a grain-size distribution <63μm, after procession. The laboratory colony of *B. oleae* was established with adults emerged from infested olives collected in Kassandra, Chalkidiki, northern Greece. Sample anaS consists of 54 wt% analcime (zeolite) and can be characterized as analcimic zeolitic tuff. It is free of fibrous zeolites and fibrous minerals. The sorption ability measured 285 meq/100g. An aqueous dilute suspension of the analcimic zeolitic tuff applied on the surface of olive fruit, and subsequently determined its oviposition deterrent effect for the olive fly. The studied anaS sample had a significant oviposition deterrent effect and resulted in a significant reduction in the number of the eggs laid on olives, 2, 4, 6 and 8 days after the application. The reduction, and therefore the inhibitory effect on oviposition of the olive fruit fly, was significantly lower than in the control (olives treated with water). This deterrent effect seems to be attributed to the creation of a thin layer (hymen) of the analcimic zeolite rock on the surface of the fruits. In conclusion, anaS analcimic zeolitic tuff from zeolite-rich sediments of Karlovassi-Marathokampos basin in Samos Island, Greece, had a significant oviposition deterrent effect against one of the biggest crop enemies of olive trees, the olive fruit fly *Bactrocera oleae*. To the best of our knowledge, this is the first time that an analcimic zeolitic tuff has been used for agricultural use, and specifically as pest control. Future laboratory and field research is required in order to verify the present results and improve the effectiveness of zeolites for the control of the olive fruit fly, and other pests.

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SOME OBSERVATIONS ON XRPD DATA OF SAMPLES OF HYDRATED AND DEHYDRATED HALLOYSITE

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Most mineralogical information about halloysite concerns the mineral in its essentially dehydrated, so called, 7Å form. This is almost certainly a result of the well-known ease that the interlayer H_2O molecules of the 10Å, hydrated form, are lost from the structure. For example, even short exposure of a sample to the ambient laboratory atmosphere can result in the loss of the labile interlayer H_2O molecules. There is, however, consensus that the *du novo* form of halloysite in nature is the hydrated 10Å form. As such, it is essential to gather more information on this primary hydrated form, along with other states, if, for example, we are to better understand aspects like how and why halloysite forms. This study has examined several cylindrical and prismatic tubular halloysite samples, in various states of hydration/dehydration, primarily using a variety of X-ray powder diffraction (XRPD) data and attempts to model these data. One of the questions addressed includes the character of any interstratification between hydrated and dehydrated layers and the layer spacings (thickness) involved. A further question is the nature of layer stacking arrangements in the hydrated forms and the relationship to those seen in dehydrated specimens and their development at temperatures above 200°C. These and related aspects, mainly from the perspective of XRPD data, will be addressed in this presentation.

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ESTIMATION OF ISOTHERMS/RETENTION CURVES FOR NATURAL BENTONITES BASED ON MINERALOGICAL INFORMATION

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At the moment, basically all designs for radioactive waste repositories in crystalline rocks or claystones rely on compacted bentonite as a geotechnical barrier. Such barriers are conceived to protect the waste canisters against corrosion due to contact with groundwater and against spreading of radionuclides in case of a canister breach. The re-saturation dynamics as well as the state of the fully saturated bentonite are important aspects that define the achievable protection by buffer and backfill.

The behaviour of bentonite during re-saturation is complex, though, and a time span in the order of decades is expected to be required for reaching full saturation. Under these circumstances, numerical models to predict the re-saturation process are called for. However, such models depend strongly on a constitutive relation that relates water content and relative humidity (isotherm) or, equivalently, suction and water saturation (retention curve). As bentonite is a natural product, the shape of these isotherms varies with each individual specimen. Characterisation of a specific bentonite with respect to isotherms is therefore a prerequisite for predicting the buffer performance by numerical modelling. If determined by classical methods with a sufficient data density [1], though, such measurements take much time.

It is well-known that the shape of the isotherms depends strongly on the interlayer cations. They are decidedly different for Na^{+}– and Ca^{2+}-cations [2], which is a consequence of the different ion charge. In natural bentonites, however, monovalent and divalent cations can be found at any ratio. Rather obviously, also the montmorillonite content of a bentonite has an impact on the isotherm [3].

The assumption thus stands to reason that the shape of any isotherm can be derived as the weighted sum of isotherms for pure sodium and for pure calcium montmorillonite acknowledging the ration of mono- and divalent cations as well as the montmorillonite content of the bentonite in question. This hypothesis has been tested using a well-documented set of 13 natural bentonites [4,5,6]. The complete hysteretic loop of adsorption and desorption isotherm was measured and compared to the theoretical shape. The resulting reasonable fit for all samples indicates that a good estimate of the isotherms for any bentonite can quickly be derived from mineralogical data which may avoid long and costly direct measurements.

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CATION EXCHANGE CAPACITY- AN ALTERNATIVE METHOD TO INVESTIGATE THE GEOLOGICAL BARRIER OF LANDFILLS?

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

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

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

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IDENTIFICATION AND CHARACTERIZATION OF ANTIBACTERIAL PROPERTIES OF CLAYS

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Contamination and associated infections caused by pathogenic microorganisms have long been recognized as a serious threat to the quality of human health care. With the rapid spread of antimicrobial resistance due to overuse of antibiotics[1], there has been a growing interest in developing novel antibacterial agents. Certain clay minerals, such as kaolinite, talc, smectites (montmorillonite, saponite, and hectorite), palygorskite, and sepiolite, were discussed by researchers as possible alternative treatments due to their high specific surface area, optimum rheological characteristics, high adsorption and cation exchange capacity[2,3]. The chemical interaction of clay minerals with bacteria, on the other hand, has received less focus.

The primary objective of our project is to establish the potentialities of various types of clay with regard to an eventual antibacterial activity. Different mechanisms such as the generation of reactive oxygen species through Fenton reaction, or the release of bactericide ions, will be studied. Different sources of smectite were selected worldwide, based on their mineralogical composition, natural iron load, or extent of impurity such as manganese oxide or pyrite. The clays were first characterized in terms mineralogy and elemental composition. Some modified clays were also prepared, by exchanging the interlamellar cation with iron at different oxidation states.

Preliminary results showed a 50% degradation of an organic fluorescent probe (rhodamine RhB) by montmorillonite after such iron loading, and up to 90% when this was followed by the iron reduction. This suggests amplification of the Fenton reaction induced by the reactivity of Fe(II).

Our hypothesized mechanism to consolidate, is that some electrostatic interactions between negatively charged clay minerals surfaces and cationic end of the amine are responsible for the clay minerals' substantial uptake of RhB[4]. Then, the rhodamine molecule is broken down by the cleavage of its ethyl groups, followed by the destruction of its carboxyl and amino groups to form small molecular substances that will be mineralized into CO_2, H_2O, NO_3^- and NH_4^{+5}. Iron-loaded clays produced an oxidative stress that led to the production of reactive oxygen species (ROS) including HO• and O2-•. These ROS will be examined so as to identify their potential role in the deterioration of RhB.

This poster will present the main objectives and the first results obtained of a starting PhD thesis.

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CR/NI ELECTROPLATING SLUDGE AS A COLOURING AGENT FOR STONEWARE PASTES

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Nowadays, the scientific community has been working on the industrial wastes valorisation to assure production processes more sustainable and efficient considering economic and environmental aspects. In the structural ceramic sector several papers were published, testing the incorporation of distinct wastes, such as galvanizing sludge, and glass waste, among others. However, no work involving the use of waste as tinting agent in utilitarian and decorative ceramics was found.

This work aims to develop a coloured stoneware paste using the paste shavings and, as a colouring agent, a hazardous waste – the Cr/Ni electroplating sludge (ES) that will be immobilized in the ceramic matrix. The ES was used as received and after calcination. The addition of 1 and 3 wt.% have a very small influence in the properties of the samples in terms of weight loss, shrinkage, water absorption and density. The use of 3 wt.% calcined ES improved the flexural strength (≈ 28%) of the products. A brownish colour was obtained, opening the possibility of using the ES as a partial substitute for the commercial pigments.

Keywords: electroplating sludge, stoneware ceramics, colouring, pigments.

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CONCENTRATION AND DISTRIBUTION OF CRITICAL METALS IN LOWER CRETACEOUS LATERITES FROM THE IBERIAN RANGE (NE IBERIA)

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Chemical weathering processes that occur on the Earth's surface form iron and aluminium-rich residues, such as laterites and bauxites. During these processes, immobile elements such as critical metals (REE, Sc, V, Co, Ga, Sr, Nb, Hf, Ta and W) may be concentrated. Recently, remarkable attention has been paid to laterites and bauxites as potential source of these elements considered critical to industry.

In this study, we compare the concentration and distribution of major and critical elements in lateritic levels included in four Lower Cretaceous profiles located in the Iberian Range (NE Iberia). These profiles have variable thickness (3-23 m) and were previously characterised from a mineralogical and sedimentological point of view [1]. The laterites consist of 2 to 3.5 m-thick clayey levels with abundant ferruginous pisoids. The lower levels present red colours (RC), whereas the middle and upper levels are ochre and violet (OVC). They are composed of kaolinite, illitic phases, smectite, quartz, hematite, goethite and minor proportions of orthoclase, ilmenite, rutile, anatase and diaspore. An upward decrease in kaolinite content in the profiles, coinciding with a decrease of quartz and illitic phases and the presence of smectite reflect a decrease in the chemical weathering intensity related to a change from warm and humid to cooler and drier conditions [1].

Geochemical analyses of 26 lateritic samples and 5 pisoids normalized to the Upper Continental Crust (UCC) indicates that the laterites are enriched in Al, Fe, Mn and Ti, especially the lower levels. The ferruginous pisoids are also enriched in P. This trend, along with the decrease in the calculated CIA values in all the profiles towards the top, confirm the decrease in chemical weathering intensity previously detected.

The critical elements concentration is higher in the lower levels of the profiles (RC:549.07 ppm) and the pisoids (622.99 ppm) than in the upper levels (OVC: 293.01 ppm). Regarding the REE, both the laterites and the pisoids are enriched in LREE (RC:298.37 ppm; OVC:161.23 ppm; pisoids: 223.01 ppm) and depleted in HREE (RC:46.77 ppm; OVC:23.99 ppm; pisoids:39.20 ppm).

The $(La/Sm)_c$ average values (RC:4.95; OVC:3.91; pisoids:3.76) and the $(Gd/Yb)_c$ average values (RC:1.50; OVC:1.71; pisoids:2.40) show that the lower part of the profiles exhibit higher fractionation of LREE than the upper levels and the pisoids, whereas the pisoids exhibit higher fractionation of HREE. This indicates that the HREE are less mobile than the LREE during weathering.

In the lateritic samples, the critical metals present a good correlation with Al_2O_3, Fe_2O_3 and TiO_2, whereas in the pisoids, this correlation is also adequate for Zr and acceptable for P_2O_5. Among the REE, LREE have better correlation with Y and HREE exhibit better correlation with Th. These results show, therefore, that lateritic processes favour the concentration of critical elements and that these elements are associated to certain mineral phases, such as clay minerals (kaolinite, smectite or illitic phases) and Fe and Ti oxides (hematite, goethite, anatase or rutile). Nevertheless, more intense chemical weathering could trigger the depletion in certain elements, as occurred in nearby Lower Cretaceous karst bauxites [2-3].

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CLIMATIC CHANGES RECORDED IN CLAYED SEDIMENTS FROM COASTAL SUCCESSIONS OF THE GALVE SUBBASIN (UPPER JURASSIC, NE IBERIA)

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Clay minerals assemblages of sedimentary successions can be powerful palaeoclimatic and palaeoenvironmental proxies. This work focuses on the application of clay minerals as paleoclimate indicators in the upper Kimmeridgian-lower Tithonian Cedrillas Formation (Galve subbasin, NE Iberia), to confirm previous interpretation of the existence of alternating arid and humid periods controlling the changes in the coastal systems recorded in this unit [1]. This formation consists of four 30–80 m thick sequences (S1–S4) bounded by widespread (subbasin scale) discontinuities. S1 and S2 record a reciprocal sedimentation, being the lower part (arid period) characterized by coastal plain-lagoon carbonates and the upper part (humid period) dominated by wave dominated deltas. S3 still records the imprint of arid (mixed siliciclastic-carbonate coastal plain-lagoon) to humid conditions (wave-dominated delta). Nevertheless, extensional tectonics controlled the increase in siliciclastic input in S3, and development of mixed sedimentation and fault activity in S4 [1].
A detailed mineralogical analysis of 20 selected samples of coastal plain-marginal lagoon muddy facies (grey marls and red mudstones) has been carried out to evaluate the proposed climatic control. The mineralogy of the whole sample and the <2 μm fraction was determined by X-ray diffraction and the arid/humid index (illite+chlorite vs. kaolinite+smectite) has been calculated.
The mineralogy of whole samples includes clay minerals (13-51%), quartz (9-48%) and calcite (6-47%), and minor proportions of dolomite, k-feldspar, plagioclase, siderite and hematite. In the clay fraction (<2 μm), illite (28-85%), kaolinite (5-52%), and chlorite (5-29%) are present in all the samples. Sepiolite and palygorskite (6-35%) and smectite (<9%) are present only in some samples.
Most of the clay minerals are probably detrital in origin, being transported from the continent to the coastal plain-lagoon by rivers and/or wind. The sepiolite and palygorskite could be detrital or authigenic, formed in aqueous environments. The clay minerals underwent minimal modifications during transport and diagenesis, as indicates the preservation of kaolinite and smectite (unstable minerals in early stages of diagenesis). This is coherent with the relative low burial depth of the studied unit (c. 1 km).
The analysis of clay minerals confirms that the carbonate-siliciclastic alternation in S1–S3 where in turn with arid (dominated by illite and chlorite) and humid conditions (dominated by kaolinite and smectite) and that the imprint of extensional tectonics at the upper part of S3 and in S4 did not completely obliterate the climate signal. In addition, the clay mineralogy suggests that the humid periods were coeval with warm conditions.
These results show thus that clay minerals can be powerful palaeoclimatic proxies in transitional environments, reinforcing the climatic information obtained from sedimentological data.

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DETERMINATION OF LAYER CHARGE DENSITY BY ALKYLAMMONIUM IONS: A COMBINED EXPERIMENTAL AND THEORETICAL ASSESSMENT OF THE METHOD

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Layer charge deficit is a key crystal-chemical parameter for the classification and nomenclature of 2:1 phyllosilicates that also controls some of their fundamental properties such as cation exchange capacity, expandability, water content, or rheology. Significant efforts were thus devoted to determine this parameter either from smectite/vermiculite chemical composition (the structural formula method) or experimentally using the alkylammonium method, that theoretically allows the determination of the mean layer charge density and of its distribution. Comparison of atomistic simulations with X-ray diffraction data supported the robustness of the experimental approach, allowed describing the organization of interlayer alkylammonium cations, and provided insights into the molecular-level interactions responsible for the changes in layer-to-layer distances as a function of interlayer alkyl chain length.

In the present study density functional theory (DFT) and classical molecular dynamics (MD) simulations are compared to experimental X-ray diffraction data for a series of synthetic saponites with layer charge ranging from medium-charge smectite to medium-charge vermiculite. Consistency of computed and measured layer-to-layer distances confirms the ability of computational approaches to accurately predict the organization of alkylammonium cations in smectite interlayers. Thermalization of DFT-optimized structure models through MD simulations allows probing possible alternative interlayer configurations allowed by thermal expansion, such as the electrostatically-favored location of ammonium heads above/below Al-substituted tetrahedra. X-ray diffraction results showed that layer-to-layer distances intermediate between those corresponding to the stable interlayer configurations described initially (h1, h2, etc) result from the interstratification of these stable configurations although similar distances may be computed for a single interlayer configuration.

The overall consistency of computational and experimental results confirms further the ability of the alkylammonium method to accurately determine a mean value of layer charge density consistent with smectite structural formula when using the revised equations proposed by Laird et al. (1989). The validity of the method appears however limited to smectite-group minerals [layer charge density ranging from ~0.5 to ≤1.2 per $O_{20}(OH)_4$] most likely owing to the coexistence of both stable “layered” and paraffin-like interlayer configurations for higher values of layer charge. In addition, this consistency challenges the ability of the method to quantitatively describe distributions of layer charge in expandable phyllosilicates even when using the complete series of alkylammonium cations thus promoting the use of a reduced number of alkyl chain lengths.

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ION EXCHANGE PROPERTIES OF VERMICULITE CHARACTERIZED BY SORPTION EQUILIBRIA WITH MAJOR CATIONS

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Clay minerals are abundant in geological formations and soils. Their chemical retention properties give them an important role in the behaviour of contaminants in soils. Among phyllosilicates, vermiculite is recognised as one of the main sorbents of caesium. To predict the bioavailability of such radionuclide in soils, knowledge of its sorption/desorption capability in soil-water systems is crucial. Nevertheless, cation adsorption/desorption depends on competition with surrounding cations in solution, especially major cations (H^+, Na^+, Ca^{2+}, Mg^{2+} and K^+). By characterising the retention properties of vermiculite by an ion exchange model, major cation exchange properties need to be determined to accurately describe the caesium behaviour in soil, in interaction with a multi-cation solutions. Major cation exchange data on vermiculite are only partially available to date.
In the present study, ion exchange properties of vermiculite are described by using the multi-site ion exchanger model [1] to determine the exchange site capacities and the selectivity coefficients ($H+/M^{m+}$) of four major cations (Na^+, Ca^{2+}, Mg^{2+} and K^+) found in natural waters. The exchange capacities of three major sorption sites have been previously determined experimentally on Ca-vermiculite, based on saturation curves, considering H^+ as reference cation [2]. Here, pH-dependent saturation curves are carried out on a 5-10 µm size fraction of homoionic Ca or Na vermiculite in $CaCl_2$ ($4\ 10^{-2}$ mol.L^{-1}) and NaCl ($2\ 10^{-2}$ mol.L^{-1}) solutions respectively, over a large pH range (3-11). pH-dependent adsorption isotherms of Ca and Na are performed using ^{45}Ca and ^{22}Na isotopes as tracers. The selectivity coefficients ($H+/M^{m+}$) are then determined by adjusting the ion exchange equations on experimental curves. As radioisotopes of K and Mg being not available, the saturation curves of K and Mg are obtained by exchange of Na/K and Na/Mg over a large pH range. The concentrations of Mg and K at equilibrium are analysed by ion chromatography. Adsorption isotherms of K and Mg associated with the Na desorption isotherms make it possible to constrain the model to determine the selectivity coefficients.
Previously, it has been shown that high-selective and low-capacity sites control Cs uptake at concentrations below 10^{-8}-10^{-7} mol.L^{-1} for both Ca-illite and Ca-vermiculite [2]. The Na^+, Mg^{2+} and K^+ selectivity coefficients for this minor site are determined on concentration isotherms at fixed pH. A Na concentration isotherm is acquired by exchange with Ca^{2+} on Ca-vermiculite in $CaCl_2$ solution with Na concentration ranged between 10^{-8} and 10^{-2} mol.L^{-1}. Isotherm concentrations of K and Mg are acquired by exchange with Na on Na-vermiculite in NaCl solution with K or Mg concentrations ranged between 10^{-6} and 10^{-2} mol.L^{-1}. K and Mg in solution at equilibrium are analysed by ICP AES.
The exchange capacity values of the three main sorption sites obtained for the four cations are compared with each other. The robustness of sorption sites capacities – which are an intrinsic property of the mineral – and selectivity coefficients determined for each cation is finally tested by modeling previous results obtained on the caesium adsorption data in multi-cation solutions on vermiculite [3].

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FORMULATION OF KAOLIN AND HALLOYSITE-BASED TEXTURED CERAMICS: INVESTIGATION OF MECHANICAL AND DIELECTRIC PROPERTIES OF UPON SINTERING

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The development of textured products will be of great interest in terms of application for several fields, ranging from wide diffusion ceramics and electroceramics to bioceramics and reactive ceramics as the ones used in filtration and catalysis. Phyllosilicates are natural readily available material and offer the advantage of exhibiting particles with specific shape and anisotropy and therefore, may already include a first level of textured microstructure when using tape casting to shape kaolin-based ceramics. Furthermore, the use of halloysite and kaolin as starting powders has a significant influence on the sintering behavior and related mechanical properties of as-obtained textured ceramics. In comparison to kaolinites that exhibit platelet-like particles, halloysite is a natural nano-sized tubular clay mineral that has many potentially important uses in different industrial fields. This work will focus the characterization of rheological, structural and mechanical properties of kaolin-halloysite samples before and after sintering at specific temperatures. Indeed two commercial kaolins noted as KCS and KRG were used together with a halloysite (H) provided by Imerys Company. Correlation may be highlighted according to the respective densification state (sintering at 1300 and 1400°C) and microstructures of the studied samples. In addition, addition of zirconia, alumina or zinc oxide were performed up to 50 mass% the as-obtained products were sintered up to 1400°C and the relative properties changes were investigated and correlated to the sintering behavior. Zirconia and alumina, tended to improve the occurrence of zircon and mullite respectively. Nevertheless, the densification state need to be improved by sintering at temperature higher than 1400°C, due to the refractoriness of zirconia and alumina compared to kaolins. Besides, the improvement of dielectric properties of phyllosilicates ceramics sintered at different temperatures has been investigated. Dielectric constant (ε'), dielectric loss tangent ($\tan \delta$) and loss factor (ε'') were very sensity to the glassy phase content and the occurrence of multiple crystalline phases upon sintering. The best conditions for dielectric properties were obtained with kaolin-alumina samples, while the best mechanical properties were reached while mixing KRG with H.

Key words: kaolinite, halloysite, rheology, textured ceramics, mechanical resistance, dielectric properties, microstructure

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SYNTHESIS AND CHARACTERISATION OF FE-RICH CLAY MINERALS WITH DIFFERENT FE(II)/FE(III) CONTENTS FOR THE UNDERSTANDING OF THE REDOX CONDITIONS AT THE BENTONITE-CANISTER INTERFACE

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Corrosion of the canister in deep geological storage is one of the most important risks threatening the clay barrier system, which can cause the reduction of iron (Fe) in the clay structure. The oxidation state of iron (Fe) in the crystal structures of smectite clay minerals has been found to be a critically important factor underlying the behavior of the clay. In this context, the synthesis and characterization of synthetic and natural nontronites and other Fe-rich smectites with different Fe(II)/Fe(III) ratio are important for the analysis of the possible alterations of the clay mineral structure, affecting the properties of the bentonite barrier, as well as the redox effects affecting radionuclide retention in clays.

In this study, an experimental approach is carried out based on the combination of known procedures with the aim of synthesizing and characterizing synthetic and natural nontronites with different Fe(II)/Fe(III) content for the study of the U, Tc and Se sorption on clay minerals. Fe(II)/Fe(III) nontronites were synthesized according to the procedure of Decarreu et al. (2008) [1] and Baron (2016) [2] from a co-precipitated silico-metallic gel. 500 mg of the powdered starting gel was placed in contact with 30 mL of deionized water. The pH was adjusted from 11 to 12.5 by adding drops of 1M NaOH at 25ºC. Then, nontronites were synthesized at 150ºC under equilibrium vapor pressure during 15-30 days. The solids were characterized by XRD and Far-, Mid- and Near-infrared spectroscopy.

At second stage, NAu-2 nontronite (Uley Mine, Australia) was purchased from the CMS Source [3]. A batch of purified NAu-2 was fully oxidized to Fe (III) at octahedral sites following the methodology described by Jackson et al. (1985) [4]. Also, a batch of purified NAu-2 was partially reduced to Fe(II) nontronite with dithionite/citrate bicarbonate following the methodology described in Stucki et al. (1984) [5]. The structure and properties of both NAu-2 nontronite clay minerals were characterized by XRD, Far-, Mid- and Near-infrared spectroscopy, TEM, BET and Mössbauer techniques, and determined their BET and CEC properties.

XRD patterns and MIR spectra of the obtained clay samples, exhibit reflections and absorption bands characteristic of nontronites. These samples are similar to analogous naturally formed minerals without so much variability in their chemical and mineralogical composition. This is useful to improve our understanding of redox effects affecting radionuclide retention in clays.

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RHEOLOGICAL CHARACTERIZATION OF METAKAOLIN-BASED GEOPOLYMER SUSPENSIONS: EFFECTS OF SOLID CONTENT, TEMPERATURE, CURING TIME, AND DEFLOCCULANT CONCENTRATION STUDIED VIA DOE APPROACH

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This study investigates the effects of solid/liquid content, temperature, curing time, and deflocculant concentration on the rheological parameters of metakaolin-based geopolymer pastes activated by NaOH, using a statistical design of experiment (DOE) approach.
The results showed that the solid content was the most significant parameter, affecting viscosity, shear behaviour, and yield stress [1]. The industrial grade sodium polyacrylate additive had a limited effect on viscosity and yield stress. Interestingly, increasing temperature resulted in an increase in viscosity due to the acceleration of geopolymerization reactions, contrary to the classical rheological influence reported in the literature. The rheological parameters were found to be sensitive to the chemical changes during curing, making them a potent tool for monitoring the microstructural evolution of geopolymer network [2]. Characterization of the rheological behaviour at various shear rates allowed for early detection of changes in chemical and physical properties during curing. The DOE approach was used to identify statistically significant interactions between independent variables and exclude irrelevant ones. The combination of rheology and DOE offers a powerful tool for microstructural characterization of geopolymers during early stages of curing.

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DETERMINATION OF TEXTURE CHARACTERISTICS OF CLAY MINERALS

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Porous substances occur in many areas of chemical technology, most often as catalysts, membranes, adsorbents. Clay minerals can also be considered porous materials and therefore the knowledge of textural properties is one of the important characteristics of these materials. Clay materials are divided into several groups, which differ in their structure and also have different textural properties. Therefore, the knowledge of the basic textural characteristics of these substances, such as the shape, width, pores volume and classification, porosity, specific surface area (S_{BET}), true and apparent density, as well as the appropriate methods for their determination is necessary for the processing and use of clay materials. The methods for examining porous materials vary according to the size of the pores. The adsorption methods are preferably used for micro and mesoporous materials, while the Hg-porosimetry for macroporous materials. The methods of studying the solids structure are mostly based on adsorption phenomenon. The goal of all adsorption theories is to predict the amount of adsorbate needed to covering the sorbent surface with the monolayer of gas molecules and to determine the area required to the adsorption of one molecule of adsorbate. From the number of theories the "BET" isotherm is currently used to the S_{BET} calculation. As the example of clays characterization for the determination of structural characteristics of kaolinite, bentonite, montmorillonite and rehydroxylated kaolinites the adsorption methods are used. The adsorption isotherms were measured on an ASAP 2020 and 3Flex surface analysers (Micromeritics, Norcross, GA, USA) using the gas sorption technique (N_2 at 77 K). These adsorption isotherms were fitted according the Brunauer-Emmett-Teller (S_{BET}) method and t-plot method ($S_{t\text{-}plot}$) for specific surface area, the micropore volume by the t-plot method and the pore-size distribution by the Barrett-Joyner-Halenda (BJH) method and Density Functional Theory (DFT) method. In addition, the scanning adsorption isotherms of all the mentioned samples were measured. The scanning isotherms provide important information about the pore network geometry including its connectivity and pore size distribution, which cannot be revealed from the main adsorption and desorption isotherms.
In this study, the results concerning complex clay textural analysis were obtained. Although there is a wide variety of methods applicable to the clay texture characterization, each method has the limitations, which must be finally taken into account when evaluating the results.

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INFLUENCE OF INDIGO-HYDROXYL INTERACTIONS ON THE PROPERTIES OF SEPIOLITE-BASED MAYA BLUE PIGMENTS

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Maya blue is a stable greenish-blue pigment that was widely used in the ancient Mayan region. It is now known as an indigo-palygorskite or -sepiolite hybrid pigment. However, the color-causing and stabilization mechanism of Maya blue remain unclear. In this study, the interactions between different hydroxyl groups of sepiolite and indigo, as well as their effects on the color and stability of Maya blue pigments, were investigated. Sepiolite materials were heated at 160, 360, 610, and 880°C to remove zeolitic water, the first coordinated water, the second coordinated water, and structural hydroxyls. A series of Maya blue simulants were prepared by heating the mixture of indigo and sepiolite materials at 180°C. Reflectance spectroscopy and the CIE 1976 color space were employed to characterize the color properties and color differences of hybrid pigments. Chemical resistance to concentrated HNO_3 and dimethyl sulfoxide (DMSO) and the photostability under visible light were evaluated. Microporosity analysis and Fourier transform infrared spectroscopy were applied to investigate the indigo-sepiolite interaction. Coordinated water was essential for the greenish-blue color and outstanding stability of Maya blue, while zeolitic water and structural hydroxyls did not affect the pigments' properties. Indigo molecules were confirmed to be inserted into sepiolite channels, where they formed hydrogen bonds with coordinated water at one side. The role of structural hydroxyls was minor in the formation of Maya blue.

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RHEOLOGICAL BEHAVIOR OF BIOORGANOCLAY IN OIL-BASED DRILLING FLUID

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The rapid growth of oil demand and the gradual depletion of shallow hydrocarbons have drawn more attention to deep reservoirs and unconventional oil and gas reservoirs such as shale gas. Oil-based drilling fluids exhibit superior performance than water-based drilling fluids in unconventional oil and gas exploitation due to their low friction and excellent stability at high temperatures and pressures. The application of organic montmorillonite as oil-based drilling fluid additive to control rheological behavior has long been a subject of research.

Inspired by zinc soaps in paints, an organic montmorillonite (OMt) modified with zinc ions and lecithin was synthesized and dispersed in vegetable oil and mineral oil for the preparation of oil-based drilling fluids. Their rheological properties were investigated and linked to structural information obtained by XRD and TEM.

The rheological behavior and viscoelasticity of drilling fluids were assessed and different rheological models were compared. The OMt exhibits more outstanding rheological properties in vegetable oil than in mineral oil. The vegetable oil-based drilling fluid behaved as a non-Newtonian fluid, exhibiting shear thinning properties at temperatures below 120°C. It was observed that the thixotropy of vegetable oil-based drilling fluid increased as the temperature increased from 60 to 120 °C, followed by a decrease as the temperature raised from 120 to 180 °C. Viscoelasticity test results show that mineral oil-based drilling fluid always exhibits liquid-like behavior, while vegetable oil-based drilling fluid display solid-like behavior at temperatures below 120°C. As the temperature further increases, both vegetable oil-based drilling fluid and mineral oil-based drilling fluid show a transition from non-Newtonian fluid to Newtonian fluids due to the degradation of the surfactant in the organoclay. The XRD and TEM results demonstrate that the exfoliation of OMt is the key phenomenon to explain the increased thixotropy of vegetable oil-based drilling fluid, but too high temperature will lead to the degradation of organoclay, which in turn leads to poor rheology. The properties of oil-based drilling fluids are significantly affected by base oil and temperature. The prepared OMt presents a potential for use as an additive in the vegetable oil-based drilling fluid.

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SYNTHESIS AND CHARACTERIZATION OF TRIOCTAHEDRAL SMECTITE WITH LOW LAYER CHARGE

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Smectites are widely used in many technical applications and are important components of soils. A definition gap exists between the uncharged non-swellable pyrophyllite and talc ($x = 0$) and the low charged swellable clay minerals (smectites) with $0.2 \leq x \leq 0.6$. Furthermore, no reliable measurement method exists for $x < 0.2$. A recent theoretical study on the hydration of smectites (Emmerich et al. 2018) based on the density functional theory (DFT) indicates the existence of stable dioctahedral 2:1 layer silicates with $x < 0.2$ and substitutions either in the tetrahedral or octahedral sheet that are swellable. Therefore, the aim of this work is to synthesize low charged smectites.

The Na_2O-MgO-Al_2O_3-SiO_2-H_2O system was subjected to a reaction to synthesize trioctahedral smectite at 200 □ for 72 h, using stoichiometric compositions corresponding to ideal layer charges $x \approx 0.1$, 0.125, and 0.18. X-ray diffraction (XRD) analysis revealed successful synthesis of trioctahedral smectite with small particle size, and the particle size was confirmed by atomic force microscopy (AFM) measurements. The cation exchange capacity (CEC) values indicated low charge within the envisaged range. According to the principles of the alkylammonium method (AAM) (Lagaly, 1981), under ideal conditions, when the layer charge value is less than 0.2, long-chain alkylammonium ions will only form a monolayer structure (with a basal spacing <17.7 Å) after intercalation into the smectite layer. This was confirmed by measurement of the d001 value of the synthetic smectite, and is consistent with the results obtained in our experiment.

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ADVANCES IN BENTONITE GEOCHEMISTRY USING BIBLIOGRAPHIC DATA.

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The distribution and behaviour of trace elements within clay materials has not yet been defined. The most interesting question when talking about trace elements associated with clay minerals is where they are located. Some studies suggest that trace elements are adsorbed on the edges and basal surfaces of the particles (Coppin et al., 2002), others that they are located in the interlaminar space (Kuzmann et al., 2016), and others that they may occupy octahedral positions (Kuzmann et al., 2016). There are numerous studies of trace elements in clay materials, but they are generally carried out to compare concentrations with the parent rock from which they originate by observing relative enrichments and depletions of specific chemical elements as in Namayandeh et al., (2020). The lack of knowledge on the crystalchemistry of trace elements may be due to various factors, such as the materials being of different origin, being formed in different environments, or being composed of different clay minerals and therefore having different properties, such as different particle sizes (Honty et al., 2008).

This work is part of a global study on the crystalchemistry of trace elements in bentonites by mean of statistical tools applied at the geochemical data. This study was carried out in two steps: 1) on the analysis of a wide group of samples of high purity, which preliminary results were shown in (Lorenzo et al., 2022), and 2) on data obtained from an in deep revision of the literature, which results are shown in this work.

In this work, it was tested whether the results obtained in the statistical analysis with the previously studied samples could be replicated with the samples from the literature to ratify or not the conclusions obtained. For this purpose, 56 high-purity bentonite samples were selected from scientific articles. In the statistical study, a Shapiro-Wilk test was performed to check the distribution of variables and a Spearman correlation matrix was performed to observe relationships between trace elements, major elements, and geochemical families. A Wilcoxon test was also carried out to observe significant differences in the abundances of trace and major elements between dioctahedral and trioctahedral smectites, and a PLS-DA (Partial Least Square Discriminant Analysis) was carried out to test whether it was possible to know whether a smectite was dioctahedral or trioctahedral from the concentrations of the constituent elements, excepting major elements. The results agree with those obtained in the preliminary study and show the group of elements that are related with dioctahedral and trioctahedral smectites, respectively.

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A VERSATILE ELECTROSPUN POLYLACTIC ACID NANOFIBER MEMBRANE INTEGRATED WITH HALLOYSITE NANOTUBES FOR INDOOR AIR PURIFICATION, DISINFECTION, AND PHOTOCATALYTIC DEGRADATION OF POLLUTANTS

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Electrospinning nanofiber membranes (ENMs) have been studied extensively as high-efficient air filters, but still subject to low filtration efficiency for submicron PMs and limited function. Meanwhile, filters based on ENMs originated from petroleum seriously increase the burden on the environment. Polylactic acid (PLA), a bio-based biodegradable polymer with non-biotoxicity, degradability, and environmental sustainability, is a highly promising material from air purification perspectives. However, it is still a challenge to improve the air filtration performance, disinfection, and formaldehyde degradation of PLA ENMs simultaneously. Here, we feasibly present a versatile PLA ENMs integrated with natural electret halloysite nanotubes (HNTs) and silver phosphate (Ag_3PO_4) *via* the electrospinning assisted with spraying technology and continuous winding device. The HNTs improves the free-standing properties of the PLA ENMs and endows it with electret effect, which can enhance the electrostatic interaction with submicron PMs and bacteria as well as extend the service lift. Furthermore, Ag_3PO_4 was distributed onto HNTs and then incorporated into PLA nanofiber which enables HNTs@Ag_3PO_4/PLA ENMs to display a remarkable disinfection and good photodegradation ability towards gaseous formaldehyde. Additionally, the HNTs@Ag_3PO_4/PLA ENMs exhibits excellent photodegradation ability towards methylene blue and tetracycline under the visible light irradiation, effectively solving the problems such as difficult separation and recovery of powdery photocatalysts. Such PLA based composite membrane with enhanced electrostatic interaction and photocatalytic property could show the versatilities, *e.g.* improving the efficiencies and service life on filtering PMs, killing bacteria, degrading VOCs, *etc.*, which provides a new idea and feasible method for purifying indoor air and water based on green polymer and electrospinning technology.

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THE INTERCALATION OF POLY(ETHYLENIMINE) AND POLY(2-METHYL-2-OXAZOLINE) INTO MONTMORILLONITE

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Nanocomposites prepared by the intercalation of polymers into montmorillonite (Mt) have attracted great interests in recent years, both as novel materials with enhanced properties and as ideal systems for the study of polymer adsorption on the inner and/or outer surface of Mt. This study compares the interaction of Na-Mt with two structurally similar but differently-charged polymers: linear cationic poly(ethylenimine) (PEI) and non-ionic poly(2-methyl-2-oxazoline) (PMeOx). The effect of various polymer loadings on the interlayer structure and physico-chemical characteristics was investigated using XRD, TG/DTG and IR spectroscopy. The different charge characteristics of the polymers affected their intercalation into Mt. For PEI-Mt, almost complete exchange of Na^+ with PEI cations was found, implying that the PEI chains interacted with the Mt interlayer surface electrostatically. In PMeOx-Mt, the content of Na^+ remained the same as in Na-Mt, indicating that PMeOx chains are adhered to the Mt surface by hydrogen bonds and/or van der Waals forces. The XRD patterns of PEI-Mt showed gradual increase of the d_{001} value from 1.25 nm (Na-Mt) up to 1.38 nm for sample with PEI concentration corresponding to ~100% CEC of Na-Mt. No change in the basal spacing was observed for the samples prepared with higher cationic polymer loadings. In contrast, a stepwise expansion of the interlayer space of Mt up to 2.06 nm with increasing amount of non-ionic PMeOx revealed unexpected and very high adsorption of PMeOx on Mt interlayers. The carbon, TG/DTG and IR analysis, however, indicated a gradually increasing content not only for PMeOx but also for PEI in the samples prepared with higher polymers loadings. The positions and intensities of the bands in the IR spectra of the samples prepared with the highest polymers concentration significantly resembled those of pure PEI and PMeOx. It is evident, that at high loadings some of the polymer chains were adsorbed on the Mt outer surface. The obtained results widen the knowledge on the interactions between polymer and montmorillonite essential for designing novel composites for environmental and/or industrial applications.
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IMPACT OF CARBONATE ON THE STRONTIUM AND CAESIUM REACTIVITY ON NATURAL CLAY-RICH MATERIALS

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Understanding chemical adsorption phenomena is essential to predict radionuclide mobility in the environment. Studies on the behaviour of radionuclides in soil environments have shown that caesium and strontium are mainly adsorbed on clay minerals surfaces [1, 2]. Nevertheless, trace elements retention on soil is highly dependent on the physicochemical context, especially in presence of carbonates which are frequent in soil environments. The aim of this study is to understand the influence of carbonates occurring both in solution (HCO_3^-) and in crystallised form ($CaCO_3$) on the sorption properties of strontium and caesium on a natural material composed of clay minerals and calcite. This impact is studied by considering the effect of HCO_3^- species on Sr^{2+} sorption on clay minerals, the inhibition or lack of accessibility to sorption sites due to calcite crystals inside the clay fraction and the competition between Ca^{2+} and Sr^{2+} or Cs^+ in solution towards the sorption sites.

Retention experiments are carried out on the clay size fraction extracted from a sedimentary alluvium, in basement of a calcosol. Sorption isotherms of Sr and Cs are performed on both the bulk carbonated clay fraction and the decarbonated clay fraction. Decarbonatation is performed by dissolving calcite in HCl 1M solution. Adsorption isotherms are carried out under fixed pH conditions (pH 7.7 and 7.2 for carbonated and decarbonated material respectively) and Sr or Cs concentrations are ranged between $10^{-2}$and 10^{-8} mol.L^{-1}), in competition with calcium at two constant ionic strengths (10^{-2} and 10^{-3} mol.L^{-1}). Isotherms are interpreted by using a multisite ion exchanger model (MSIE) [3] and by considering an additive approach combining the sorption properties of clay minerals respecting their relative proportion in the material. For this purpose, clay minerals proportions are quantified by modelling the X-ray diffraction pattern in both air-dried and ethylene-glycol-solvated states, acquired on the decarbonated clay size-fraction with the Sybilla© software developed by Chevron™ and constrained by the measured cation exchange capacity (CEC) of the clay fraction. The mineralogical composition of the clay size-fraction, containing kaolinite, illite, smectite and chlorite, is therefore assimilated to 65 % of illite and 5 % of smectite. This approach has already shown successful results in modelling the sorption behaviour of Cs and Sr on a mineralogical assemblage in a calcium medium [1]. In the case of strontium, Sr sorption on clay fraction remains similar with or without calcite, except for Sr concentration higher to 10^{-3} mol.L^{-1}. Above 10^{-5} mol.L^{-1} Sr in solution at pH 7.7, Sr speciation records an increase of $SrHCO_3^+$ complex in solution, which decreases the Sr^{2+} concentration in solution. Moreover, the solution used for carbonate media is equilibrated towards calcite ($CaCO_3$) over the whole concentration range and strontianite ($SrCO_3$) for Sr concentration higher than 10^{-4} mol.L^{-1}. This suggests that $SrHCO_3^+$ may be formed and co-precipitated on the calcite surface, above a Sr concentration about 3 10^{-3} mol.L^{-1}. By increasing the calcium concentration in solution (10^{-2} mol. L^{-1}), the Sr^{2+} adsorption on clay minerals decreases. In this condition, Ca competes more with strontium. This is revealed in particular on the high affinity and low capacity site of illite at low Sr^{2+} concentration in solution.

These results show that carbonate have a negligible impact on the retention of Sr at trace level but also on Cs on clay minerals under our physicochemical conditions.

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APPLICATION OF SARDINIAN KAOLINS TO THE HYDROTHERMAL SYNTHESIS OF ZEOLITES AND CHARACTERIZATION OF THE RESULTING PRODUCTS

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The kaolin deposit from Donigazza area (NW Sardinia, Italy) has been investigated to test its possible use as raw material for zeolite synthesis. The perspective is to draw a better exploitation of this mineral resource, as the deposits of NW Sardinia are mainly exploited to manufacture vitrified tiles and/or sanitary ware. Chemical and mineralogical investigations were performed by X-ray fluorescence (XRF), powder X-ray diffraction (XRD), and scanning electron microscopy (SEM). The Donigazza kaolin is mainly composed of kaolinite±dickite, and minor amount of opal-CT and quartz. The low iron content (likely as hydroxides), the high amount of kaolinite and amorphous silica, as well as the low amount of quartz encouraged investigation on the possible conversion of these rocks into zeolites.

A representative sample was powdered, split, and hydrothermally treated with NaOH at 100 °C in sealed Teflon-lined stainless-steel vessels, under autogenous water vapor pressure. The vessels were placed in a thermostated oven equipped with a rotating device inside. Thirty experiments were performed by varying the concentration of NaOH solution (1, 2, 3, 4, and 5 mol L^{-1}) and the reaction time (12, 24, 48, 72, 96, 168 hours); the liquid/solid ratio was 1:5.

XRD analyses documented that different mineral species formed after kaolin hydrothermal alkali activation: NaP1 zeolite, NaP2 zeolite, gobbinsite, analcite, laumontite, chabasite, sodalite, hydroxy-sodalite, hydroxy-cancrinite, phillipsite. Amounts of residual kaolinite (from 0 to 70%) depend both on the NaOH concentration and on the reaction time (higher the time and NaOH, lower the amount) being undetectable at $t \geq 48$ hours and NaOH ≥ 3 mol L^{-1}. Consequently, relative abundances of zeolites (up to 91%) change significantly depending on the experimental conditions: as expected, NaOH strongly influences the abundance and mineral type but also time plays an important role thus indicating that a given mineral is in metastable condition. Microscopic observations documented the presence of idiomorphic crystals, whose dimensions vary from 100 nm up to 10 µm, as well as subspherical aggregates (up to 10 µm in size) of crystals (200-400 nm) having pseudo-octahedron shapes. Globular nanoparticles (usually < 50 nm), isolated or aggregated to form subspherical micrograins, are also present. It is likely that they are Al-Si gels. As expected, their amount, as well as the ratios among mineral species, depends on the length of the experiment and NaOH concentration. Results obtained in this experimental study document that kaolin deposits from NW Sardinia (Italy) are an excellent raw material for zeolite production.

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APPLICATION OF NATURAL AND SYNTHETIC ZEOLITES FOR PFAS UPTAKE OF CONCERN IN ENGINEERED WATER AND WASTEWATER TREATMENT SYSTEMS

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Per-polyfluoroalkyl substances (PFAS) are environmental emerging contaminats. Thermal stability and lipid/water repelling characteristics ascribed their use as surfactants intermediates, waterproofing treatment for textiles and household products. These global and highly persistent contaminants have recently drawn great attention due to their persistence and toxicity. Among the various removal approaches of PFAS, adsorption from complex waste and surface water through microporous materials proved to be highly effective. The aim of the present study is to explore the sorption capacity of different zeolites differing for topology, Si/Al ratio (SAR), and free window apertures and quantify their removal efficiency towards long- and short chain PFAS for potential use in wastewater and groundwater remediation. Sorption of 18 long- and short chain PFAS from lab solution and four PFAS contaminated real water samples (raw water of drinking water plant, wastewater effluent of wastewater plant, landfill leachate, and landfill groundwater sites) from Uppsala, Sweden contaminated sites was investigated and compared in batch experiments. The selected zeolites were: 1) Beta powders (SAR=25 and 300, respectively); 2) Y zeolites (SAR=30, 60 and 500); 3) Mordenite zeolite powder (SAR=240); 4) synthetic zeolite L (SAR=6.1);) zeolites from fly ash in their as-synthesized and silver exchanged form. 6) natural chabasite (65% wt. chabazite). The sample studied in this work is a natural chabasite zeolite supplied by the Zeolite Italia Company composed by 65%wt. chabazite, 5%wt. philipsite, 4%wt. K-feldspar, 2%wt. biotite, 4%wt. pyroxene, and 20%wt. volcanic glass. The performances of these microporous materials were also compared under the same conditions with those of powder activated carbon (PAC), representing to date the most used material in PFAS adsorption technology. To evaluate the adsorption capacity a series of batch experiments were conducted from 0 to 24 h at room temperature. Concentrations of PFAS in water samples were analysed by solid-phase extraction (SPE) and ultra-performance liquid chromatography coupled to tandem mass spectrometer interfaced with an electrospray ionisation source in a negative-ion mode (UPLC-(-)ESI-MS/MS). Pristine zeolites and PFAS loaded samples were characterized by X-ray diffraction and thermal analyses to: 1) obtain chemical and mineralogical information; 2) verify their modifications and stability after adsorption; 3) evaluate the thermal desorption of the organics upon heating and 4) estimate the best regeneration temperature in order to reused upon saturation. X-ray powder diffraction (XRPD) patterns were collected at room temperature by using Bruker D8 Advance Diffractometer with a Sol-X detector, Cu Kα1, α2 radiation. Le Bail refinements were performed using the GSAS package with EXPGUI graphical interface. Thermal analysis of all samples were performed in constant air flux conditions from room temperature up to 1400 °C using an STA 409 PC LUXX® – Netzsch (10 °C/min heating rate). Uptake of PFAS was greatly influenced by concentration of the solution, PFAS chain length, polarity of the zeolites and their pore system. XRPD data reveal lattice modifications in unit cell parameters after adsorption and thermal regeneration maintaining the crystallinity of the samples. Thermal analysis showed that PFAS are expelled up to ~700°C and some trapped carbonaceous materials can be degraded until 1400°C. The results of this study indicate that calcined Beta zeolite with SAR=25 is the most promising material for the removal of PFAS from water. The PFAS uptake was not subjected to competitive species in the PFAS contaminated real water samples. Thermal analyses demonstrated that zeolites thermal regeneration appears to be a valid method to reuse exhausted zeolites; on the contrary PAC suffer for structure damage during heating. Zeolites can optimize and design innovative PFAS adsorption remediation technologies to remove PFAS pollutants from water.

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TERAHERTZ TIME DOMAIN SPECROSCOPY AND RESPONSE OF RARE EARTH ELEMENT MODIFIED SMECTITES

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Composite materials containing layered silicates can be used for the preparation of functionalized systems with desired properties. The composites based on both suitable polymers and inorganic fillers can be formed by additive manufacturing technologies utilized for the production of functional parts or testing prototypes. Such composites can be successfully transformed into functional ceramic bodies by debinding of organic part and sintering of clay-based filler. The introduction of rare earth elements into clays offers the opportunity to modify the optical response and functionality of the materials prepared. Novel and advanced experimental techniques are required for further investigation and prove of the material properties and successful modification strategies. In comparison to conventional FTIR spectroscopy, the Terahertz-time domain spectroscopy (THz-TDS) with enhanced signal-to-noise ratio covers frequencies 0.1-300 cm^{-1}. The THz-TDS was used for the inspection of selected smectites and effect of the sample treatment temperature on resulting spectroscopic modification using rare earth elements (REE). The advantage of THz-TDS is, that the spectral response at low frequencies (far-IR), also corresponds to radiation energies that are harmless to biological tissues. For suitably modified materials valuable information about environmental changes of the REEs or matrix used can be investigated by designed UV-VIS and THz-TDS experiments. Based on thermogravimetric measurements, appropriate temperatures for heat treatment of Erbium-modified smectites were selected. Depending on selected smectite, enhancement of dielectric constant and distinct absorption bands at about 3.2 and 3.6 THz were found for the materials sintered at 1200°C.
Keywords: Layered silicates, composite materials, additive manufacturing, THz-TDS, Far-Infrared, UV-VIS.
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ADDITION OF ULTRASONICATED KRAFT LIGNIN AND MONTMORILLONITE TO HYDROXYPROPYL METHYLCELLULOSE FILMS FOR POTENTIAL APPLICATION IN BIOPLASTIC ACTIVE FOOD PACKAGING

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Hydroxypropyl methyl cellulose (HPMC) has been proposed as a renewable resource to replace conventional plastics, taking advantage of its biodegradability, lack of toxicity and the possibility of improving its properties through the incorporation of different additives [1]. In order to improve the barrier and active properties of HPMC to fit those required for food packaging applications [2], the current work evaluates its combination with montmorillonite (3 % w/w) and kraft lignin (0-10 % w/w) under ultrasound irradiation. For instance, the water vapor permeability (WVP) of the HPMC-based bionanocomposite containing both montmorillonite and 1 % w/w lignin showed a reduction of 43.8% compared to the pristine HPMC film, in contrast to the reduction of 11.4 % obtained after addition of montmorillonite exclusively. The reason for this synergistic effect observed after simultaneous addition of clay and lignin under sonication may be attributed to the strong interaction between both components, which leads to delamination of montmorillonite facilitating its dispersion within the biopolymer matrix and enhancing the barrier properties of HPMC films. These bionanocomposites also showed an important reduction in oxygen permeability (OP), up to 65.8 %, compared to unmodified HPMC. Moreover, the addition of kraft lignin provided the bionanocomposite films with other interesting properties for food packaging applications, such as UV-shielding (while keeping good transparency in the visible region), antioxidant capacity and antibacterial activity against *Escherichia coli* and *Staphylococcus aureus*. This study confirms the remarkable features of HPMC/lignin/montmorillonite bionanocomposites prepared under ultrasound irradiation for application as active food packaging, and reveal the potential of kraft lignin to produce bio-organoclays that could facilitate clay exfoliation and dispersion in other polymeric matrices in the development of new bionanocomposite materials.

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OPTIMIZATION OF NON-ANTIBIOTIC BIOMIMETIC FILMS CONTAINING CHLORHEXIDINE-CLAY MINERAL NANOHYBRID FOR WOUND HEALING PURPOSES

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Montmorillonite (Mnt) and halloysite (Hal) are getting great interest in wound healing as naturally abundant biocompatible materials, being also able to promote cell proliferation and hemostasis, as well as entrap drug molecules protecting them from unfavorable environments and/or modulating their release [1,2]. Antibiotic resistance due to the misuse of antibiotics in the treatment of chronic wound infections could be addressed with the alternative use of non-antibiotic agents such as chlorhexidine (CHX), which exhibits antimicrobial activity against Gram positive and negative bacteria [3]. Recently, CHX has been loaded into Mnt and Hal by means of the spray drying technique to protect CHX molecules from debris of the necrotic tissue present at wound bed, thus increasing its antimicrobial efficacy [4]. The aim of the present work is to design and develop biopolymeric films based on the interaction between natural materials, such as chitosan and hydrolyzed collagen, loaded with CHX-clay nanohybrids to achieve new advanced therapeutic systems for *in situ* application on infected chronic wounds. Films were prepared through solvent casting technique using chitosan medium molecular weight (Cs; Merck Life Science, S) and hydrolyzed collagen powder (HC; Kelisema S.R.L., I). Polyethyleneglycol-1500 (PEG-1500; Guinama S.L., S) and glycerol (GLY; Guinama S.L., S) were added as plasticizers to improve films mechanical properties in terms of elasticity. A design of experiments (DoE), especially a central composite design, was employed in order to study, on a statistical basis, the contribution of three different factors (concentration of HC and of the plasticizers) on the mechanical properties of the film at three different levels: 1, 1.5 and 2 % w/v for HC, and 0, 10, 20 % w/w for both PEG-1500 and GLY. Maximum tensile strength (MPa) and elongation at break % were selected as the response variables. Mechanical properties have been measured by a TA.XT plus Texture Analyzer (Stable Micro Systems; UK). Then, mechanical behavior of optimized film formulations was compared with that of the nanohybrid-loaded systems. Results showed that the films exhibited a mechanical behavior suitable for their application as biomimetic scaffolds for wound healing purposes.

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NANOMATERIALS BASED ON HALLOYSITE NANOTUBES AND PEPTIDE NUCLEIC ACIDS: NEW STRATEGIES FOR THE LOADING OF ORGANIC MOLECULES

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The development of systems able to deliver genetic material into a target site is a challenge for modern medicine. Single-stranded peptide nucleic acids (PNAs) have attracted attention as promising therapeutic molecules for diagnostic and gene therapy. However, their poor cell membrane permeability represents a drawback for biomedical applications. In the years, to overcome these problems, several systems have been used as PNA carriers. Recently, among them, clay minerals could represent an efficient alternative to conventional nanomaterials due to their intrinsic properties and capability to across cellular membrane, localizing themselves in the cytoplasmatic area [1]. Halloysite nanotubes (HNTs) are a class of aluminosilicate clay mineral, belonging to the kaolin group, that have shown interesting features for application in biotechnology [2]. HNTs possess a different chemical composition and different charges of surfaces (positively charged in the lumen, rich in Al-OH groups and negatively charged on the external surface constated by Si-O-Si groups) that allow their chemical modification, both covalent and supramolecular. Herein we report the synthesis and characterization of nanosystems based on PNA molecules loaded onto HNTs by different synthetic strategy to develop nanomaterials for the delivery of genetic material into cells [3]. Firstly, the supramolecular loading of differently charged PNA tetramers, as models, was investigated. Similarly, the same PNA tetramer was covalently grafted onto HNTs external surface to obtain a carrier system for the potential targeting of future specific nucleic acids in living cells.

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CRYSTAL CHEMISTRY EFFECTS ON DISSOLUTION KINETICS OF SYNTHETIC FE-RICH SMECTITES

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Dioctahedral Fe-rich smectites are ubiquitous in fine soils fraction. These clays having an important cation-exchange capacity and a large specific surface area, figure prominently in bio-geo-chemical reactions that regulate the mobility of metals or the availability of nutrients in soil environments. Some studies highlighted the crystal chemistry effects on the dissolution rates of smectites in acidic conditions (from pH 3 to pH 6)[1,2]. However, the specific contribution of the amount, the nature, and the location of substitutions in the smectite structure remains unclear. The natural smectite samples are heterogeneous and commonly include impurities that challenge their purification. Therefore, the use of synthetic smectites allowed to control their physicochemical properties[3] to study in details the effects of the crystal chemistry and size on their chemical reactivity. The synthesis of three Fe-rich smectites with simple crystal chemistries ($(Si_{7.4}Fe^{3+}_{0.6})(Fe^{3+}_{3.4}Mg_{0.6})O_{20}(OH)_4Na_{1.2}$; $(Si_{6.86}Fe^{3+}_{1.14})(Fe^{3+}_4)O_{20}(OH)_4Na_{1.14}$; $(Si_{7.34}Fe^{3+}_{0.66})(Fe^{3+}_4)O_{20}(OH)_4Na_{0.66}$) was previously performed and products finely characterized. Then dissolution kinetics were measured at room temperature in flow through reactor and for a pH range value from 1.8 to 5.5 (in HNO_3 medium). The Si, Fe and Mg concentrations were measured along the time in the output solutions by ICP-MS, MP-AES or colorimetry depending on elements and concentrations. The residual solid samples were collected at the end of alteration experiments and analyzed with IR spectroscopy and TEM. Dissolution rates of synthetic smectites (calculated from the Si concentration at steady state, in $mol.g^{-1}.s^{-1}$) decrease with increasing pH as it observed in literature regarding the dissolution of silicates. No major effects of crystal chemistry were observed between each synthetic smectite. However, synthetic smectites have systematically faster dissolution rates than reference smectites previously published. The relation between saturation states of the solution and dissolution rates for several reference smectites and the present synthetic Fe-rich smectites allowed to highlight several of the mechanisms involved. As for reference smectites, the dissolution rates of synthetic ones increase as the system moves further from equilibrium. However, clear differences of behaviors are displayed between Fe-rich and Al-rich smectites. High dissolution rates happen closer to equilibrium for Fe-rich smectites than Al-rich ones, with a steeper slope of the $R=f(\Delta G)$ function. These observations highlight the higher instability of smectites with a large amount of Fe. In more acidic conditions (pH 1.8 and 2), the crystal chemistry and the mineralogy of samples change during the dissolution, with an important loss of the tetrahedral Fe compared to the octahedral Fe, and the formation of amorphous silica phases. These results show that the amount as well as the nature of substitutions impact the behavior of smectites. Thus, the use of a universal law to describe the dissolution of smectites seems compromised. The present study highlights the high reactivity of these small synthetic clays (<100 nm) that evolve in few days to adapt to environmental conditions, representing a primordial stake towards the global changes through the evolution of the availability of nutrients.

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SANDWICH-LIKE ENCAPSULATION OF FUNCTIONAL SPECIES IN THE INTERLAYER SPACE OF SYNTHETIC HECTORITE

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When manufacturing devices such as optoelectronic sensors, organic light-emitting diodes, and light-emitting electrochemical cells the ability to produce high-quality thin films is of great importance. For the protection of photo-functional entities, the interlayer space of clay minerals acts as an ideal host as it can provide a protective environment against undesired reactions (mainly with oxygen and water vapor) degrading the overall photo-functional performance. Moreover, by exerting an electrostatic pressure on functional species (cationic complexes and small molecules) improves their thermal stability and increases photoluminescent quantum yields.[1] The functionalization process of osmotically swollen (delaminated) clay mineral with cationic species usually proceeds via coagulation and precipitation steps making further post-processing, due to formed agglomerates with non-uniform sizes and shapes, more complicated or even impossible. To solve this problem, it is desirable to produce monolayered functional species encapsulated between two layers of clay mineral with a high aspect ratio. The preparation of the so-called double-stacks proceeds via crystalline swelling and partial ion exchange of the functional species into a synthetic layered silicate yielding an ordered heterostructure with two types of strictly alternating interlayers containing a monolayer of cationic species and a monolayer of solvated sodium cations.[2] At this stage, osmotic swelling is desired as it triggers the repulsive formation of double-stacks in dispersed form.

The layer charge of clay minerals directly controls the number of functional species per area, allowing to tune the photophysical properties of the final material. As the swelling of clay minerals is hampered by increasing layer charge in the case of vermiculite-type layer charge densities, crystalline swelling is limited to the two-layer hydrate, while osmotic swelling requires additional ion-exchange with bulky and hydrophilic organic molecules.[3] In pure water, the swelling is restricted to a crystalline regime, with the addition of dimethyl sulfoxide, osmotic swelling sets in at some threshold composition. When the dimethyl sulfoxide concentration is increased further, swelling is again at some threshold composition restricted to a crystalline regime.[4] Therefore, repulsive osmotic swelling is observed in a narrow composition range of binary water−dimethyl sulfoxide mixture enabling to produce double-stacks even with vermiculite-type layer charge densities. Due to their uniform thickness and high aspect ratio, double-stacks prepared in a previously mentioned manner allow for easy solution processing of low-cost optoelectronic devices.

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MODIFIED ZEOLITES IN THE TREATMENT OF WATER CONTAMINATED WITH CEPHALEXIN

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The continuous use of antibiotics is alarming, since these compounds are not completely metabolized by the body, being excreted into the environment as active metabolites. Drugs can also cause damage to the ecosystem and contribute to the selection of bacteria resistant to antibiotics, hindering the treatment of infectious diseases significantly. Cephalexin belongs to the class of cephalosporins and is indicated as a medication for the treatment of various infections. However, it has low degradability, being evaluated as a potential mutagenic and carcinogenic agent.

In this context, adsorption is an advanced water treatment technique that exhibits several advantages, such as high efficiency, low cost and operational flexibility. Zeolites represent a promising alternative in water treatment of water due to their well-delineated pore structure, selectivity, thermal stability and cation exchange possibility. Therefore, the objective of this study was to evaluate the use of modified zeolites in the adsorption of cephalexin from the aqueous medium.

The adsorption tests were carried out by adding 0.020 grams of chemically modified natural zeolite with the commercial name Watercel ZF (granulometry of 0.425 to 0.600 mm) into 0.030 liters of cephalexin solution (30 mg L-1). The flasks containing the adsorbent and the adsorbate were placed in an incubator with orbital shaking at 150 rpm and 25°C. In principle, the effects of adsorbent dosage were studied with 0.33; 0.67 and 1.00 gram of adsorbent per liter of solution. Subsequently, the pH of the solutions was adjusted to values of 4, 7 and 10 with 0.1 mol L-1 HCl and NaOH solutions. Kinetic assays were conducted by collecting aliquots at predetermined time intervals. At the end of the experiments, the solutions were filtered through a cellulose acetate microfiltration membrane and the final concentrations were determined by a UV spectrophotometer (HACH DR 5000) at a wavelength of 262 nm.

The highest concentration of adsorbent (1.0 g L-1) resulted in better drug removal (77.9%), due to the greater amount of active sites available for the contaminant molecules. As the pH affects the surface charges of the molecules involved in the process, the tests showed that adsorption was favored in media with a higher degree of acidity. At higher pH values, cephalexin molecules become negatively charged, disturbing electrostatic interactions between adsorbent and adsorbate. In order to investigate the mechanisms that control the cephalexin adsorption process, the models of pseudo-first order and pseudo-second order were applied to the experimental equilibrium data. Both models represent good adjustments to the experimental data. However, the pseudo-second order model provided the highest value of the linear correlation coefficient (R^2), demonstrating that it is possible that the limiting step of the process is chemisorption. The adsorptive process reached equilibrium after 4 hours (38.19 mg of cephalexin adsorbed per gram of zeolite), without major variations in the adsorptive capacity up to 24 hours of adsorption.

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EFFECT OF PH ON ADSORPTION OF SERTRALINE FROM AQUEOUS MEDIUM USING NATURAL ZEOLITES

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Among the contaminants of emerging concern, the presence of residual drugs and metabolites in domestic sewage and in aquatic environments is a matter of extreme importance in the global scenario. Drugs compromise the potability of water, since they are persistent and bioaccumulative compounds in surface and groundwater (Barrocas et al., 2020). Sertraline is a drug widely used in the treatment of depression, but some studies indicate that this compound is capable of invading the cell membrane, presenting carcinogenic potential (Khosrokhavar et al., 2020). Recent studies show that zeolites stand out among the inorganic materials used in adsorptive processes for water treatment, mainly in the removal of emerging pollutants. These materials have high selectivity, adsorptive capacity and good adsorption kinetics, in addition to being easy to recover (Roshanfekr Rad and Anbia, 2021). Thus, the aim of the study was to evaluate the adsorptive capacity of natural zeolites on sertraline solutions with different pHs. Natural zeolite (clinoptilolite) with the commercial name Watercel ZN is mainly composed of 68.5% SiO_4; 11.0% Al_2O_3; 2.8% CaO and 1.8% K_2O (weight percentages). The material has an apparent density of 1.0g cm^{-3} and a cation exchange capacity of 1.35 meq g^{-1}. To evaluate the Zeta potential, the zeolite was submitted to a DelsaTM Nano C charge analyzer (Beckman Coulter). The adsorption tests were carried out with polyethylene bottles containing 0.02 g of the adsorbent (granulometry of 0.425 to 0.600 mm) and 0.03 L of the sertraline solution (20 mg L-1). The solutions had their pH adjusted to 4, 7 and 10 using hydrochloric acid (HCl) and sodium hydroxide (NaOH) with concentrations of 0.1 mol L-1. The flasks were placed in an incubator with orbital shaking at 150 rpm at 25°C for 24 hours. At the end of the experiments, the solutions were filtered through microfiltration membranes and the final concentrations were verified using a UV spectrophotometer (HACH DR 5000). From the Zeta potential analysis, it is observed that zeolite present negative surface charges throughout the evaluated pH range (2,0 – 10,0). According to the adsorption tests, it is noted that the pH has an influence on the drug adsorption process by natural zeolites, and the highest drug removal rates (71.3%) were obtained in neutral medium (pH 7). This fact can be explained from the Zeta potential of zeolite and also from the characteristics of the drug. At pH values lower than the pKa of sertraline (9.47), the contaminant molecules are predominantly positive. Therefore, at natural pH of the sertraline solution (6.09) and at neutral pH, higher values of adsorptive capacity are obtained (21.38 mg g-1) due to the electrostatic attraction existing between the negative surface charges of the adsorbent and the protonated form of the contaminant (Chauhan et al., 2020; Khosrokhavar et al., 2020).

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KAOLINITE-BASED NANOTUBES – CURRENT STATE OF KNOWLEDGE ON SYNTHESIS, PROPERTIES AND APPLICATIONS

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Nanomaterials built from particles with strictly defined morphology have attracted attention in materials science. One popular example are carbon-based materials including single- and multi-walled nanotubes as well as fullerene-like cage structures (e.g. C_{60}). However tubular and fibrous morphology is also characteristic for other groups of chemical compounds including clay minerals (e.g. halloysite, chrysotile and imogolite) as well as niobates, hydroxides, hydroxide salts, sulphides (e.g. WS_2) and some layered double hydroxides (LDH). Many years of research revealed that formation of nanotubes is directly related to structural and chemical properties of parent 2D material [1]. The high reactivity of partially bonded rim metals was shown to be responsible for folding of nanolayers into hollow, closed structures in the case of carbon-based materials. The driving force for bending of layers may also result from lattice strain which is observed for asymmetric 2D structures.

The raw or functionalized nanotubular materials with desired properties are promising for use in a wide variety of potential technological applications. Some examples include: selective adsorption, catalysis, polymer-clay nanocomposites, sensing applications, photodegradation of pollutants, luminescence, drug delivery applications, photovoltaics, energy harvesting and optoelectronics. However despite wide opportunities the use of nanotubes in real applications is strongly limited. This is mainly due to issues associated with their mass production.

Kaolinite is the most common member of kaolin group minerals and the most abundant clay mineral. The knowledge on its modification possibilities involving intercalation and grafting has greatly evolved. Kaolinite is a 1:1 layered aluminum silicate with asymmetric structure. It was shown that intercalation of 1:1 layers with appropriate guest molecules allows to transform its morphology to obtain halloysite-like nanotubes of mesoporous texture [2, 3]. This opens the possibility for using kaolinite as a parent material for mass production of nanotubes. Throughout the last 2 decades many reports were published on nanotubes synthesis procedures, focus was also put on characterization of their properties. Finally the kaolinite nanotubes were tested in many applications including photodegradation of pollutants investigated by our research group. The presentation will provide a summary of knowledge we have on nanotubes derived from kaolinite.

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HIGHLY EFFICIENT STYRENE REMOVAL BY SMECTITES IMPREGNATED WITH NI, CU AND AG TRANSITION METALS

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Styrene is one of the most important and essential industrial chemicals belonging to volatile organic compounds (VOCs). Chemically it is an aromatic hydrocarbon with vinyl group in the structure. This increases its reactivity including the ease of polymerization. In industry large quantities of styrene are used in the production of e.g.: polystyrene, polyester resins, and fiberglass. However the compound itself is considered harmful even at very low concentration. In manufacturing facilities workers are mostly exposed to styrene vapors when working with unsaturated polyester resins. Especially the gelcoat spraying technique leads to high release of styrene. The emission can be substantially reduced by using closed molding techniques but still this is not always possible. Therefore a highly-efficient ventilation system is necessary in the workplaces. Such system usually contains a set of filters filled with granulated activated carbon. Although this material is efficient it cannot be regenerated or reused after saturation.

Our earlier research showed that surfactant-intercalated smectites show a very high uptake of styrene [1]. In most cases the adsorption was higher than for activated carbons. This was connected with simultaneous hydrophobization of clay mineral surfaces and expansion of the interlayer space due to intercalation of cationic surfactants. Most importantly the smectite-based adsorbents saturated with styrene can be introduced into several products. One drawback of this approach is connected with a relatively large content of surfactant that must be used for smectite modification (~20-30% wt.). Earlier reports showed that doping the surface of mineral materials (e.g. zeolites) with transition metals improves adsorption of aromatic hydrocarbons. Therefore we decided to investigate the effect of Ni, Cu and Ag impregnation of smectites on the styrene uptake.

The montmorillonite from Texas (STx) and beidellite from Idaho (BId) were modified by wet impregnation method using Ni(II), Cu(II) and Ag(I) in varying amounts. The styrene uptake experiments were conducted in a closed system to study the adsorption at the highest possible styrene concentration in gaseous form. The research revealed that small content of introduced metals (below 2% wt.) led to a remarkable increase in styrene uptake (from ~1% wt. for the raw smectites up to ~200-350% wt. styrene content in the materials after 48 h). These values were even higher than for the surfactant-intercalated smectites (~40-80% wt.) and desorption of styrene in time was not observed. The presence of metals dispersed on clay surfaces gave rise to new active centers which were responsible for p-complexation properties of smectites. The simple ion-exchange with *d*-block metals induced high selectivity for p-electron-rich styrene molecules.

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CONSTRAINTS ON THE CLAY MINERALOGY OF GALE CRATER'S SEDIMENTARY ROCKS FROM H2O DETECTED DURING EVOLVED GAS ANALYSES BY NASA'S MARS CURIOSITY ROVER

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Curiosity has been exploring Gale crater to understand the rock record of martian geologic and environmental history, and habitability. Several rocks have been analyzed with the Chemistry and Mineralogy (CheMin) X-ray diffraction (XRD) instrument and the Sample Analysis at Mars instrument suite's Evolved Gas Analysis Mass Spectrometry (EGA) mode. CheMin XRD enables quantitative mineralogy. SAM EGA heats samples, and volatiles detected (e.g., H_2O) and their evolution temperature can constrain mineralogy. Clay minerals have been of interest since they can indicate habitable environments and possibly facilitate organic compound preservation. Detailed comparison to lab EGA data enables more constraints, but generally, trioctahedral smectites will dehydroxylate at higher temperatures than dioctahedral, and trioctahedral smectites with octahedral Fe will have a lower dehydroxylation temperature than those with Mg. Here we focus on clay mineralogy constraints enabled by SAM EGA.

Soon after landing, Curiosity analyzed mudstones at Yellowknife Bay. CheMin provided the first in situ XRD-based evidence of smectite clay minerals on Mars, Fe-rich trioctahedral smectite (Fe-saponite) [e.g., 1]. SAM EGA H_2O data was consistent with dehydroxylation of Fe-saponite. Samples from the lowest explored strata of Gale crater's central mound ("Mt. Sharp") at Pahrump Hills also contained clay minerals. Low abundances made XRD identification difficult, EGA was consistent with Mg-rich trioctahedral smectites plus possible Fe-rich dioctahedral phases. Up-section in the sample Marimba, CheMin detected abundant smectites [2] and EGA indicated Mg-rich saponite and Fe-montmorillonite. Further up-section, below Vera Rubin ridge (VRR), a sample contained smectites and EGA indicated nontronite. EGA data from VRR samples was also consistent with Fe-rich dioctahedral phases, either nontronite or ferripyrophyllite. After VRR, Curiosity explored a clay-bearing unit in which CheMin detected nontronite, and minor other phyllosilicates such as mixed layer talc-serpentine or greenalite-minnesotaite [e.g., 3]. EGA supported these detections. Recently, the rover explored the transition to a sulfate-rich area. Here, EGA data has indicated a progression towards lesser, and finally no, phyllosilicates.

This variety of phyllosilicate observations indicates variability in alteration conditions. For example, rocks in which dioctahedral phases dominate may have been exposed to environments with more open system conditions than those where trioctahedral phases dominate. Also, ferripyrophyllite or talc-serpentine may point to relatively warm settings in their depositional or post-depositional environments or source regions if they are detrital. Our presentation will further discuss clay mineral observations and implications for the nature of fluid-rock interactions on Mars.

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PRODUCTION OF UREA/CITRIC ACID POLYMER WITH DIFFERENT CLAY LOADS

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Mechanochemistry, an enabling technology, recently produced a new Urea/Citric Acid polymer. The method of synthesis is a catalyst and solvent-free clean route. The synthesized polymers presented superior thermal stability and crystallinity compared to the solution process. Furthermore, this method made it possible to produce a selective condensation reaction of urea in the solid state. In this work, improvements in the production process were carried out by adding a hygroscopic material. In addition, modifications were made to the polymer structure by adding different clays (Veegun HS and Sepiolite PS9), aiming to change the material's physicochemical properties to improve the processability of the obtained polymer. After synthesis, the obtained polymeric material was filtered off and dried. The polymer was characterized by Infrared spectroscopy (FTIR), Matrix-Assisted Laser Desorption Ionization Process – (MALDITOF), XRPD-Solid-state Characterization, Thermogravimetry analysis – TGA, Differential scanning calorimetry– DSC and Scanning Electron Microscopy. Preliminary results suggest modification of the reaction, altering the molecular mass of the polymer with the addition of magnesium sulfate and structural changes with the addition of clays. This polymer has biodegradable characteristics and possible applications in the cosmetics industry.

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HOW GOOD ARE CLAY MINERALS AS PROXIES FOR CLIMATE?

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Clay minerals formed or concentrated during surface weathering have long been suggested to provide a general proxy for climatic conditions (1). These assemblages accumulate in soils and sediments and may be preserved in rock lithologies that are not strongly overprinted by subsequent alteration after burial in the Earth's crust. The best insight into the relationship between clay minerals and climate is obtained by looking at soil profiles across the northern and southern hemispheres. Here, it is well known that kaolinite, halloysite and smectite chemically precipitate around warm equatorial latitudes whereas detrital illite and chlorite are more prone to alteration. In contrast, cold climates favour the physical enrichment of illite and chlorite over the precipitation of kaolinite or smectite. Similar trends in clay minerals and climatic zones are mirrored in the deep ocean sediments (2)

This contribution uses a recently published global clay mineral inventory (3) to assess just how well clay mineral assemblages reflect climate. The relative abundance of the main clay mineral groups (the 1:1, 2:1 and 2:1:1 hydrous phyllosilicates) is also used to evaluate the Clay Mineral Alteration Index (CMAI), which is compared with current latitudes and the Köppen-Geiger climatic zones. This CMAI relationship is defined as:

CMAI = (2:1LE+2:1:1LE) – (1:1LE+2:1HE)

(physically weathered – newly formed)

where, LE = Low to no expandability, HE = high expandability and CMAI values range between -100 (warm tropical) and +100 (cold polar).

For selected soil types, such as the alfisols, some general correlations do exist between CMAI values and distance from the equator. However, the database indicates that lithological controls on clay mineral assemblages introduce a large degree of heterogeneity to the system, which makes a direct interpretation based on numerical indices difficult to implement. Improved correlations can be made by selecting particular soils on the same types of host rocks (e.g. soils on Silurian shales, 4), where very good correlations can be attained if the climatic parameters of temperatures and rainfall are both considered. A refined correlation between CMAI and current climatic conditions is put to the test on palaeosols and shales from the geological record.

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BENTONITE-CHITOSAN BIOCOMPOSITE: A THERMODYNAMIC, KINETIC, AND ISOTHERM STUDY FOR THE REMOVAL OF GLYPHOSATE IN WATER

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In recent years, the lack of clean water has become a growing concern around the world, affecting millions of people and threatening economic and ecological stability. This issue is caused by a variety of factors, such as increasing demand due to population growth, climate change, and the degradation of water with the massive use of herbicides.

One of these herbicides, glyphosate, which is widely used to destroy plants, can contaminate surface and groundwater sources. When present in water at high levels, it can harm human health.

Glyphosate has been classified by the International Agency for Research on Cancer as a probable human carcinogen and has negative effects on reproductive and developmental systems. The minimization of glyphosate concentrations in water is important for protecting human health.

This study aims to synthesize and create a biodegradable, cost-effective, and environmentally friendly adsorbent with highly desirable properties for the adsorption of glyphosate. To achieve this, a biocomposite based on natural clay materials and modified with chitosan has been synthesized to increase its adsorption capacity.

The biocomposite was characterized using a variety of techniques, including Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), and scanning electron microscopy (SEM) with energy-dispersive X-ray spectroscopy (EDS), to gain a deeper understanding of the adsorption mechanism. The Langmuir isotherm equation provided the most accurate interpretation of the experimental data. The results of the adsorption thermodynamics and kinetics of the glyphosate showed that this biocomposite adsorbent had a good adsorption capacity for glyphosate compared to raw clay, with 58 mg/g and 35 mg/g, respectively.

Additionally, the analysis suggested that the pseudo-second-order rate equation could explain the adsorption kinetics admirably, and the adsorption thermodynamic characteristics demonstrated that the process is spontaneous.

The conclusion of our study demonstrates the remarkable efficacy of the material that we have synthesized. Our results show that biocomposite materials possess the capability to effectively remove glyphosate and reduce its presence in water sources, thus offering a promising solution to one of the pressing environmental challenges of our times.

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MULTI-SCALE MODELING OF THE SWELLING-SHRINKAGE OF CLAYEY GEOMATERIALS

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Swelling of clayey geomaterials finds its origin at the diffrent scales of the clay material. However, deformations are noticeable at the macroscopic scale. Clay minerals swelling, is governed by two different phenomena: crystalline and osmotic swellings. The first type of swelling occurs when the water molecules access the interlayer space between two 2:1 clay layers in a stepwise manner following an order of one water layer (aka 1W) to three water layers (aka 3W).

In this work, we propose a multi-scale numerical model that considers both the crystalline swelling, interlayer osmotic swelling (four water layers accumulated 4W and more), following the formalism of Cariou et al., 2013. To this end, we itemized the different interactions that arise in the interlayer space with respect to the disjoining pressure. Along with that, the model also account and for the first time for interparticular osmotic swelling occuring in the interaprticular porous space. The overall model is based on the upscaling of the constitutive law from the nanoscopic scale to the macroscopic scale by adding all the different interactions that appear while upscaling. In addition, the general constitutive law developed can be considered as a new definition of the effective stress governing the chemo-hydro-mechanical (CHM) behavior of clayey geomaterials. The numerical model is then implemented in Code_Aster Finite Element software for hydro-mechanical coupling models. The validation of our model is conducted by reproducing constant-volume swelling test available in the literature for the Callovo-Oxfordian argilite. The simulation results demonstrated good agreement between the experimental results and the numerical modeling with comparison to classical models (i.e. linear elasticity) that overestimates the final swelling pressure (1.1 MPa) compared to the model developed in this work.

Testing the pertinence of the developed model also relies on its ability to reproduce the experimental results of the swelling tests conducted in this work, using a newly developed experimental setup. It is a testing procedure that involves X-Ray µTomography to investigate the swelling-shrinkage behavior of compacted Illite powder. For the swelling behavior, the saturation is assured by capillarity ascension, for two different ionic forces of the NaCl Solution i.e. 0.001M and 1M. As for shrinkage, it is performed using saline solution method at a fixed relative humidity of 80%. These imaging techniques were then coupled to a digital image correlation algorithm to quantify the diffrent strains locally. This will provide us with further comprehension of the chemo-hydro-mechanical behavior of different clay materials; before testing the relevance of both the numerical model and the experimental protocol for naturally based clay geomaterials namely, COx argillite and Marais Poitevin soil.

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MODELLING OF MICRO-POLLUTANTS ADSORPTION OF ONTO CLAY MINERALS

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The increasing use of emerging micro-pollutants stemming from industrialization, agriculture or daily life activities leads their dissemination in the environment and in particular into soils. Because of the large surface area exchange capacities and adsorption properties, Clay minerals have been identified as a key mineral species for the retention of bio/organic molecules in soil.
Various experimental techniques (adsorption isotherm, spectroscopic) are used to understand the adsorption process of organics onto lamellar materials such as clays, thus providing information on the potential adsorption sites and allowing to draw a possible view adsorption mechanism. The confirmation of these hypotheses is not always possible through experiments and theoretical modelling is of great help, if not ubiquitous, in order to identify the nature of intermolecular interactions and thus clays' structural properties, chemical composition, hydration and ionic force, involved in the adsorption process.
As such we will briefly explain how theoretical modelling has been used in combination to adsorption isotherms and X-ray diffraction experiments to determine the role of phyllosilicates in the retention of paracetamol or carbamazepine [1]. And we will present a detailed study of the intermolecular interactions responsible for the adsorption of diazepam or oxazepam onto montmorillonite [2]. In particular, we will show how the stereoisomers introduce a variant into the adsorption process of oxazepam, thus explaining the experimental differences observed.

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HALLOYSITE CLAY NANOTUBES FOR HIGH-PERFORMANCE HEMOSTATIC AGENT APPLICATIONS

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Halloysite nanotubes (HNTs), as a traditional mineral Chinese medicine, has been used to stop bleeding for thousands of years. However, the coagulation mechanisms of HNT and practical application forms have not been fully identified. Also, the peel-off of hemostats from the cotton fibers often poses a risk of distal thrombosis. In this work, HNTs were found with accelerate hemostasis effect via multiple-dependent approaches. To solve the difficulty of application of powder, a HNTs coated polyester fiber dressing was designed by impregnated method. And HNTs was tightly bound onto commercial cotton fibers, which was capillary mediated by biopolymer alginate with Ca2+ crosslinking. The robust clay nanotube dressing materials maintain high procoagulant activity after harsh water treatment, and only a few residuals of HNTs exist in the wound area. Gold@HNTs-chitin composite hydrogel with high antibacterial and hemostatic activity as well as promoting wound healing function were also developed. Compared with commercial hemostats QuikClot® Combat gauze, HNTs composite dressing exhibits hemostatic properties both in vivo and in vitro with high safety. The hemostatic mechanism of the dressing was attributed to activating platelets, locally concentrating clotting components in the nanoclay, halloysite coagulation factors, and alginate cross-linked with Ca2+. This work inspires robust self-assembly of clay nanotubes on textile fibers and offers a hemostatic material with balanced high hemostatic activity, minimal ingredient loss, and biocompatibility. The robust dressing based on halloysite tightly bounded cotton shows great potential for military, medical and civil bleeding control with low health risks.

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SWELLING CHARACTERISTICS CHANGE OF BENTONITE BARRIER AFTER FIVE YEARS OPERATION

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In-DEBS (In-situ Demonstration of Engineering Barrier System) is a field test to study the behavior of the engineering barrier of the high-level radioactive waste repository. The test involved using compressed Gyeongju bentonite blocks as a buffer material to mimic the actual repository. After five years of operation, the buffer was collected and the samples were analyzed through laboratory experiments. The study first presents the prediction model of Korean bentonite swelling pressure using laboratory samples by analyzing the effects of dry density and water content. The study also compares the results of swelling pressure tests conducted on the samples obtained from the In-DEBS field test, and the laboratory experiment prediction model. The results show that bentonite samples collected in the field swelled less overall than the bentonite samples prepared in the laboratory, but some samples located near the heater swelled more than the predicted model.

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MODELLING OF EUROPIUM ADSORPTION ON A BENTONITE CLAY IN THE PRESENCE OF ORGANICS

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Clays and specially bentonite are envisaged as barrier materials in radioactive waste disposals. One of the main properties of the clays is their high capability for retaining radionuclides (RN), delaying their migration to the geosphere. The presence of natural or anthropogenic organic substances entails a potential risk because it may affect the environmental behavior of RN or heavy metals, often increasing their solubility, due to the formation of stables aqueous complexes, and decreasing their retention in solids.

The role of organic ligands on RN migration depends on the source (type and concentration of organic) and the physicochemical conditions of the environment (pH, ionic strength, type of ion in solution, amongst others). This means that processes must be understood at the mechanistic level to extrapolate the knowledge to different scenarios. Thermodynamic sorption modelling is a powerful tool to describe RN behavior in complex systems and under variable conditions and it can be applied to develop predictive models able to support the long-term safety assessment of different radioactive waste storage concepts.

The specific objectives of this study are: 1) to analyse the adsorption behaviour of ^{152}Eu, as a homologue of trivalent actinides, on a well characterised smectite (FEBEX bentonite) in the presence of different organics (citrate, phthalate and ethylenediaminetetraacetic acid, EDTA); 2) to model the adsorption behaviour in the presence of these organics using the presently available thermodynamic data for Eu and selected organic aqueous and solid species [1].

Adsorption data (K_d) were obtained with increasing organic concentration [ORG], from $1 \cdot 10^{-6}$ to $1 \cdot 10^{-3}$ M, with the RN at a trace level ([Eu]=$4 \cdot 10^{-10}$ M) and at two different pH (5 and 9 approximately) to evaluate possible differences in the behaviour depending on the main Eu retention process (cation exchange or surface complexation). The initial K_d data (without organics) were calculated based in a previous work [2].

Results showed that the strongest effect on Eu retention is produced by EDTA, with a reduction of the K_d of 3-4 orders of magnitude with a concentration of the organic as small as $1 \cdot 10^{-5}$ M at both pHs. The effect of citrate is also relevant, even if the decrease in adsorption is limited to 2 orders of magnitude when the highest organic concentration ($1 \cdot 10^{-3}$ M) is reached. The effect of phthalate is more limited (maximum K_d reduction of 1 order of magnitude at pH 9, and almost no variation at pH=5.

Satisfactory modelling of the Eu sorption in the presence of organics could be obtained. The availability of thermodynamic data on RN-organic ligands will be discussed.

Acknowledgements

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RADIONUCLIDE MIGRATION IN CLAYS: KEY ASPECTS FOR RADIOACTIVE WASTE REPOSITORIES

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The deep geological repository (DGR) is widely acknowledged as the most scientifically substantiated solution for the permanent disposal of high-level radioactive waste. Its primary objective is to isolate the waste and hinder the migration of radionuclides that could potentially be released into the environment. The DGR concept relies on multiple layers of protection to mitigate potential hazards: engineered barriers are specifically designed to prevent the release of radionuclides and maintain long-term structural integrity, while the host rock acts as a natural barrier.

Within this framework, clayey materials play a crucial role. In most DGR concepts, the principal engineered barrier consists of high-density compacted bentonite; furthermore, clay rocks are considered highly suitable geological formations for hosting a DGR. Radionuclide adsorption within the barrier materials is a fundamental process to ensure the safety of the DGR by significantly reducing the migration and release of these radioactive elements into the surrounding environment.

To develop a comprehensive understanding of the various mechanisms involved in radionuclide transport and retention is essential to establish a thorough and comprehensive Safety Case. To achieve mechanistic understanding, and to acquire predictive capability, several studies need to be conducted, based on in-depth knowledge of the physical, chemical, and mineralogical properties of the clays, as well as the characteristics of the radionuclides and their evolution. Of paramount importance are those factors that can increase radionuclide migration, as they have the potential to compromise the security of the system. All these studies encompass a combination of laboratory investigations and large-scale or *in-situ* experiments, geochemical and thermodynamic modelling.

In summary, primary objective of this talk is to provide a comprehensive overview of the fundamental aspects related to radionuclide migration in clay materials and their importance for the safety assessment of radioactive waste repositories.

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SATURATED WATER CONTENT AND ADSORPTION PROPERTY IN ORGANOMONTMORILLONITE INVESTIGATED BY MOLECULAR SIMULATION

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Adsorption property of the aromatic compounds in the organoclay has historically been investigated, where understanding of the interlayer structure has been desired. However, it is even difficult to determine the saturated water content of the organoclay experimentally. By using molecular simulation, we have previously reported the nanostructure of organically-modified montmorillonite containing the aromatic compounds [1,2]. In the present study, we developed the simulation method to estimate the saturated water content and the adsorption property of phenols in montmorillonite modified with the hexadecyltrimethylammonium ions (Mont-C_{16}).

Mont-C_{16} was modeled under the periodic boundary condition by the method similar to that reported previously [1]. The interface forcefield was used for the Mont, while pcff was for the interlayer molecules. Various number of the H_2O molecules was inserted in the interlayer by the Monte Carlo method, followed by the NPT-MD for 20 ns to model the water-containing Mont-C_{16}. Phenol and 3,4,5-trichlorophenol were placed in the interlayer, and NPT-MD was conducted for 10 ns. Dependency of the initial orientation of the phenols was preliminarily removed by the annealing NVT-MD.

Mont-C_{16} swells nonlinearly to the water content. The non-bonding energy of the inserted H_2O molecules gets higher along with the water content, and is consistent with that of the bulk water at 13.2wt%, which is reported by the thermogravimetric analysis [3]. Thus, the saturated water content is found to be estimated by analyzing the water-containing models thermodynamically. By comparing the solvation free energy of phenols in the interlayer with that in the aqueous solution, the adsorption property is also rationalized: the energy of phenol in the interlayer is higher, while the opposite holds for 3,4,5-trichlorophenol. This result is consistent with the experimental result [4]. Therefore, it is concluded that both the saturated water content and the adsorption property in the organoclay are predictable by the molecular simulation.

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NUMERICALLY CALCULATED SMALL-ANGLE SCATTERINGS OF NANOSHEET ASSEMBLIES

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Single-layer nanosheets dispersions of layered crystals are one of the ideal states for maximizing the merit of the ultra-large specific surface area and anisotropic morphology of the layered materials for the applications such as adsorbents, catalysts, polymer fillers, rheology modifiers, etc. Besides, nanosheet superstructure formation is important because they significantly contribute to intriguing rheological, electrical, and optical properties. The formation of card-of-house structures and fractal networks have been believed to be the origin of the gelation of clay sols. Formation of mm-scale oriented domain and sub-μ scale swollen lamellar structure lead to colloidal liquid crystals with optical birefringence and structural colors[1].

For the structural analyses of such super-structured nanosheet systems in the colloidal state, small angle scattering (SAS) is a very important technique since in-situ and high-resolution observations are possible with simple operation and a small amount of samples as distinguished from other techniques. In the SAS analyses of uniform and dilute nanosheet dispersions, experimental data are easily fitted to theoretical scattering curves such as disk form factor and lamellar structural factor.[2] However, experimental systems usually consist of complicated hierarchical structures, partial orientation, and random aggregation so that precise structural analyses by SAXS are sometimes not straightforward.

Here, to avoid those problems, we tried the structural analyses of nanosheet assemblies by comparing the experimental data with numerically calculated SAS curves. The scattering curves in the scattering vector q range of $10^{-3} < q\ (\mathrm{nm}^{-1}) < 10^{2}$ were calculated by simply summing up the scattering from all or part of the atoms in the nanosheets or nanosheet superstructures. First, we confirmed that the numerical SAS curves of uniform isotropic dispersion of nanosheets coincide with analytical and experimental data. Then, the experimental SAS data of various nanosheet superstructures were finely reproduced by the numerical calculations.

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MONODISPERSE NANOSHEET MESOPHASES

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Inorganic nanosheets are usually obtained by exfoliation of layered crystals and are known to form intriguing colloidal liquid crystals (LC) under a certain condition[1,2]. They have been applied for fabrication of anisotropic polymer composite materials[3], structural color materials,[4,5] etc. However, large polydispersity in lateral size limited more precise design of the self-assembled structures and materials properties.
Here, we demonstrate that very unusual mesophases are reversibly formed by self-assembly of monodisperse titanate nanosheets that were synthesized by the bottom-up method[6]. Small angle X-ray scattering (SAXS) and transmission electron microscopy revealed the formation of one-dimensional long columns of stacked nanosheets. With the increase of the nanosheet concentration, the columnar nematic LC phase appeared as confirmed by polarized microscopy and SAXS; this is the very first observation for colloidal nanosheet systems. In some cases, the columns formed micrometer-scale fibrous bundles with well-defined supercrystalline structures. The formation and dissociation of these structures were reversible and controllable by several factors such as temperature. While monodisperse CdSe nanosheets have been reported as the only example to form similar long columnar structures under limited conditions,[7] the present system is distinguished by the widely controllable reversible formation of the various hierarchical superstructures. The formation of these structures is rationalized by weak nanosheet-nanosheet attractions as well as by entropic excluded volume effect.

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SUITABILITY OF WHITE TABARKA CLAYS USE IN PORCELAIN STONEWARE TILES PRODUCTION

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The continuous increase of white-firing clay demand, mainly for porcelain stoneware tiles production, lead the supply feasibility a critical parameter. This aspect is made even more critical by the instability and precariousness of the traditional commercial channels because of the current geo-politics situation. Therefore, the possibility to exploit the ball clays deposits from Mediterranean countries is really attractive. For this purpose, the Tabarka clays in Northern-West of Tunisia have been studied. Already been investigated for various types of ceramic tiles production, their effect on porcelain stoneware production is still not evaluated. The technological behavior of traditional stoneware formulation (40% clay) was assessed by reproducing the industrial tile manufacturing process on a laboratory scale. Two samples of the Tunisian clays were selected and compared with as many currently used ball clays (respectively with high and low plasticity). Tabarka clays exhibits a finer grain size distribution and plasticity approaching the most plastic ball clays currently used. Any changes were observed during grinding, pressing and drying for the bodies containing the new clay, with a technological behaviors fully compatible with the reference system. Only a slightly higher sintering temperature was observed, reaching the commercial properties required. This effect can be due to the kaolinite-rich composition of TC, more refractory than ball clays taken as reference, which contain illite and illite-smectite interstratified terms, along with kaolinite. The achieved results show that the Tabarka studied clays can satisfactorily fulfil the technical requirements for porcelain stoneware tiles

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CRYSTAL CHEMISTRY AND MINERALOGY OF PHILLIPSITE AND ANALCIME FROM SURTSEY (ICELAND)

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Investigations on zeolites from pyroclastic rocks of Surtsey island (SW Iceland) were carried out in this work throughout petrographic studies, X-ray powder diffraction analyses, and SEM-EDS analyses performed at the Department of Earth, Environmental and Resources Sciences (DiSTAR), Federico II University, Naples, Italy. Emplacement of pyroclastic and volcaniclastic deposits during episodes of active volcanism can be followed by syn- and post-depositional minerogenetic processes, resulting in the formation of secondary minerals: zeolites, as well as clay minerals, are notably among the most common authigenic minerals in pyroclastic and volcaniclastic deposits [1] and their formation affected also the very young volcanic island of Surtsey (SW Iceland) since its formation (1963-1967) [2]. Therefore, the island and its peculiar geological environment represents one of the most suitable sites to investigate the formation of these secondary mineralizations, which in this case form as mineral precipitation in vesicles of basaltic pyroclasts, in both subaerial and submarine Surtsey deposits.

This work reports preliminary crystal-chemical and mineralogical results on phillipsite and analcime from drill cores retrieved in 1979 and 2017, in the frame of the Surtsey Underwater Volcanic System for Thermophiles, Alteration processes, and Innovative concretes (SUSTAIN) ICDP drilling project. Zeolites formation and their abundance is investigated as function of temperature, depth (above or below water table), fluid composition and activity of alkaline and alkaline-earth cations in the investigated environment.

Investigations on zeolites of Surtsey tuff deposits are still in progress: the systematic analyses of the 50-year-old tuff from one of the most well-monitored volcanic sites on Earth provide a reference framework to evaluate mineralogical evolution in other young Surtseyan volcanoes.

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GRAFTING DOPAMINE ON KAOLINITE: A THEORETICAL APPROACH

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The kaolinite (Kao) surface properties can be tuned by grafting molecules with specific functional groups, especially on the alumina surface (Al–OH). This modification can enhance the compatibility and affinity with other molecules, e.g., hydrophobic organic compounds. Besides, the grafted molecules present a more stable immobilization on the surface, high thermal stability, and resistance to hydrolysis and leaching [1]. Thus, this work aimed to investigate the adsorption and grafting of the dopamine molecule on the kaolinite Al–OH surface. The Density Functional Theory method in the solid state was used with the PBE functional [2] and the Tkatchenko-Scheffler scheme [3] for dispersion corrections to study the dopamine-Kao models: adsorbed on the Al–OH surface and grafted monodentate and bidentate in different arrangements.

The results have shown that dopamine can interact with the OH surface, regarding to the calculated adsorption energy of –155 kJ·mol^{-1}, i.e.in a semi-planar arrangement. Mainly weak hydrogen bonds, O–H_{kao}···C, C–H···O_{kao}, N–H···O_{kao}, O–H_{kao}···N, generating stronger ones, O–H_{kao}···O and O–H···O_{kao}, with the catechol part of the molecule were observed. Moreover, when dopamine was grafted on the OH surface, the disposition was perpendicular to the Kao surface, where the amine group displayed different arrangements related to the location of the alumina-catechol bonds on the Kao surface.

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IMPORTANCE OF NON-HYDROXYL RADICAL SPECIES UPON AIR-OXIDATION OF NANOSIZED MAGNETITE AND IRON-SULFIDES AT NEUTRAL PH

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Heterogeneous Fenton-like reactions using airborne O_2 as sole oxidant are gaining a fast-growing interest to eliminate organic contaminant in soils and groundwaters, Indeed, Fe(II)-nanominerals, including clay minerals, have been recently proven to generate reactive species upon sole air-oxidation and to degrade organic pollutants. However, the identity and efficiency of the reactive species produced upon such air-oxidation reactions may depend on physicochemical conditions and thus deserve to be further studied.
In this presentation, we will provide new spectroscopic findings on the ability of widely studied nanominerals, i.e. magnetite (Fe_3O_4), mackinawite (FeS) and pyrite (FeS_2), to produce reactive species upon air oxidation. We show, using Electron Paramagnetic Resonance (EPR) spin-trapping analysis that the hydroxyl radical ·OH is not the dominant species produced upon air-oxidation of these substrates at neutral pH in the presence of phosphate and we discuss the potential production of Fe(IV) as a major reactive species under these conditions. These results have important implications for the understanding of the reactivity of iron(II) minerals in O_2 -based Fenton-like chemistry, which is a strongly growing research field. Such minerals are indeed recognized as putative catalytic substrates for organic pollutant degradation under sole air-oxidation. Thus, despite our study still leaves open questions, we hope it could contribute to the collective active research effort to provide long-term efficient technologies for soils and groundwater cleaning.

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EFFECT OF BOVINE BONE ON PHYSICAL PROPERTIES OF POROUS CERAMICS INTENDED FOR WATER FILTRATION

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At the global scale, 25% of the world's population lives in areas where water is physically scarce [1,2], and over one billion people live where water is economically scarce, or places where water is available in rivers and aquifers, but the infrastructure is lacking to make this water available to people [1]. In developing countries like Cameroon, the water treatment system is not secure, and most people do not have access to drinking or tap water. In order to satisfy their water needs, they generally used imported filters based on synthetic oxides such as alumina, mullite or cordierite membranes. Consequently, the high cost of production of such filters combined with the increase of marketing cost, tend to significantly limit their accessibility. In order to contribute to drinking water supply, the present work aims to produce and characterize high-performance and more affordable porous ceramics that can be used as filtration membranes. They are developed from kaolin clays (MY3 and KG) from West Cameroon [3] as main components and from bovine bone (OB) as pore-forming and fluxing agents [4]. Various proportions of agents ranging from 0 to 25wt.% have been investigated. Disc-shaped ceramic samples have been unidirectionally pressed under 12 MPa. The as-obtained samples were oven-dried at 40°C for 48h and 100°C for 24h, and then sintered at 1000°C and 1150°C for 2h. Different physical properties of the as-sintered porous ceramics were characterized: porosity and pore size measurements, mechanical resistance through 3points bending tests, BET specific surface area and identification of phases with XRD analyses. The results obtained showed an improvement of the mechanical properties with increasing OB content which is due to the reduction of pore volume faction. The open porosity varies between 35.40% (25% OB) and 45.82% (0% OB) whereas the flexural strength goes from 10.5±0.5 MPa to 2.1±0.5 MPa respectively. The average pore size ranges between 0.09 µm (0% OB) and 0.04 µm (25% OB), thus these membranes are suitable for micro and ultrafiltration applications. Physical properties (pH value, conductivity, turbidity, etc.) of filtrates obtained are in agreement with international and French standards. This study is part of a sustainable, responsible and multidisciplinary approach (recovering waste and local raw materials, depolluting water).

Keywords: kaolinitic clay, bovine bone, porous ceramics, mechanical properties, filtration

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WASTE ROCK AND BENTONITE MIXTURES FOR GAS MANAGEMENT WITHIN GEOLOGICAL DISPOSAL FACILITIES

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The geological disposal facility (GDF) is the most common planned method for the disposal of radioactive waste. GDFs utilise a multi-barrier concept designed to prevent the release of radionuclides into the surrounding environment, collectively known as the engineered barrier system (EBS). The EBS is a key component for GDF safety as it slows the inflow of water to limit corrosion, protects the structural integrity of the container, and prevents radionuclides from being released into the environment.

The EBS also manages gases that are produced in the GDF during container corrosion and waste degradation, providing pore-space and passively controlling gas release to limit pressures and reduce the risk of gaseous radionuclide release. This project explores use of bentonite clay and waste rocks (WR) from quarries, excavated GDF rocks and re-use of other materials for the EBS. Their use as an EBS material would lower the environmental footprint and prevent these materials from filling landfills. We are assessing whether WR/bentonite mixtures meet criteria for EBS usage, including mechanical strength, fluid/gas permeability, microbial activity for gas consumption and the long term performance of these re-used materials. This is being conducted through a series of laboratory based and modelling techniques.

The use of bentonite in the EBS is internationally supported by several waste management organisations due to its high adsorption capacity, swelling properties and its low hydraulic conductivity. The addition of WR aggregate provides increased mechanical strength, improves gas permeability and increases the potential to host communities of gas-consuming microbes. This poster will showcase the results from compaction tests and free swell and constant volume swelling tests.

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STABILITY OF INNER STRUCTURE IN ANTIMONY PHOSPHATE NANOSHEET LIQUID CRYSTALS

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Two-dimensional shaped nanosheets obtained by layered materials represented by clay minerals can possess liquid crystalline nature. One of the nanosheet systems is antimony phosphate nanosheet system which is considered one of the essential origins that opens up the stage of inorganic nanosheet liquid crystal systems and also develops structural coloration (Gabriel *et al*., 2001 *Nature*). However, the stability of the inner structure and coloration have scarcely been investigated, although the discussion has been made based on the stable structure (Davidson *et al.,* 2018 *PNAS*).

Here, we revisited the antimony phosphate nanosheet system and focused on the structural changes with time to estimate the stability. The structural color and the inner structure changed drastically in a month after the preparation. We investigated the time evolution of the structure in the suspension by UV spectrum and small-angle X-ray scattering. We found that the basal spacing is reduced with time after the sample preparation in the biphasic region while almost no change was confirmed in the LC phase. The degree of temporal change is larger for the lower concentration samples to result in less nanosheet concentration dependence of the basal spacing after the long-term observation. The structural change can be interpreted in terms of the ionic atmosphere.

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SORPTION THERMODYNAMICS AS CONTROLS OF SUBSTRATE USE AND MINERALIZATION

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Sorption strength of organic molecules to minerals is among the boundary conditions that shape the channel for energy and matter use by the microbial community of soil systems. Although the stabilization of organic matter against microbial use and mineralization in soil has been linked to sorption, the thermodynamics of sorption processes has not been quantified

To analyze the boundary conditions shaping the channel for energy and matter use, first hypotheses to be tested are that (1) sorption and desorption energies increase with increasing polarity and degree of oxidation of the sorbate and increasing number of surface hydroxyl groups of the soil (clay) mineral sorbent and that (2) microbial substrate use decreases with decreasing deltaG (Gibbs free engery change), increasing thermodynamic sorption hysteresis and activation energy of desorption with thermodynamic thresholds for the use of sorbed substrates.

We perform sorption and desorption experiments using purified illite, kaolinite and goethite as model minerals of defined particles sizes and six model substances (glucose, citric acid, salicylic acid, phenyl alanine, acetyl-glucosamine and a fatty acid), which are low molecular weight organic model structures that represent dissolved organic substances commonly found in soil. Adsorption isotherms will be determined using mineral suspensions of defined concentrations (totaling around 100 mg, uniform BET surface) in 1.5 mL polypropylene tubes. To each tube ^{14}C-labelled model organic substance will be added with the pH adjusted to 5.5 in both 0.1 M and 0.01 M KCl, as background electrolyte. After centrifugation of the solid phase, quantities of desorbed model compounds will be determined via scintillation counting from the separated aqueous phase.

Activation Energies E_a will be determined from Arrhenius plots obtained from desorption experiments of 30, 40, 50, 60

Isothermal titration calorimetry (ITC) is used for heat of sorption with unlabeled model substances to each mineral. This provides enthalpy of reaction ΔHr and equilibrium constant of the sorption reaction K. We will conduct ITC experiments corresponding to the sorption, desorption and activation energy experiment. The instrument used is a thermal activity monitor (TAM III, Thermometric).

Altogether our results will determine Gibbs free energies DG of sorption reactions, sorption enthalpies (DH) and entropies (DS), activation energies E_a of desorption reactions and losses of molar free energy due to sorption hysteresis (T_{ii}) for the model substrates. This will deliver essential insights for the integration of sorption processes to soil (clay minerals) and aggregation into thermodynamic concepts of soil ecosystem functioning and development.

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EVOLUTION OF CONTINENTAL WEATHERING CONDITIONS DURING THE ALBIAN-SANTONIAN INTERVAL: INFLUENCES OF TECTONICS, EUSTATISM AND CLIMATE ON THE FORMATION AND RECORDING OF CLAY MINERALS

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The Albian-Santonian interval (113-83 Ma) is considered as a “hothouse” period characterized by volcanism episodes, high sea level and low tectonic activity. This 30 Myr-longed interval is characterized by a gradual increase of temperature in oceanic domain, which culminates during the mid-Cretaceous thermal maximum, at the end of the Cenomanian (~ 94 Ma). The evolutions of continental weathering and climatic conditions during this key interval have been documented by 50 years of research on clay mineral assemblages, mainly based on studies in the Northern Hemisphere and in low latitudes of the Southern Hemisphere. The compilation of all the data from more than 75 boreholes and continental sections and the acquisition of new ones at high latitudes of the South Hemisphere provides a better comprehension of the variations observed in the clay mineral assemblages at this period.

During Albian, kaolinites and smectites are abundant (20 and 80% respectively) in the Western Australian margin which indicates strong hydrolysis conditions at high latitudes. At the same time, kaolinites and illites are abundant (up to 30%) on the Western African margin while illites are only associated with chlorites and smectites in the North American margins. Illites are gradually by smectites and kaolinites substituted from the Albian to the Late Cenomanian . In the Western Australian margin, kaolinites are progressively substituted by smectites. Theses minerals become predominant until the end of the Santonian. The decrease in illites proportions in favour of smectites and kaolinites characterize the decrease of tectonic activity on the Western African and North American margins by the reduction of the physical dismantling of the massifs and the development of pedogenetic processes. In Australia, the decrease of illites and kaolinites in favour of smectites indicates the major influence of the differential settling of clay minerals associated to the global sea-level rise.

The Cenomanian and Turonian times are characterized by high proportions of kaolinites (up to 40%) recorded in all latitudes in Northern hemisphere and only in low latitudes of the Southern Hemisphere. These clay minerals form nowadays in tropical climatic belt and thus are thought to reflect strong hydrolysis conditions especially at low latitudes. The high proportions of kaolinites in sectors, like the Benue Trough and the Ivorian Basin, where tectonic activity was active a short time before kaolinite increase, also demonstrates the influence of high reliefs on the formation of kaolinites. The well-drained steep slopes allow the removal of the cations in solution during hydrolysis which leads to the formation of kaolinites. This influence of the relief on the formation of kaolinites is confirmed by the absence of these clays on the Western Australian margin despite of a warm and humid climate. In the Northern Hemisphere, the decrease in palygorskite proportions at low latitudes coupled to the increase in the kaolinite proportions at mid- and high-latitudes reflects a warmer and wetter climate during the Turonian. In contrast, in the Southern Hemisphere, the Turonian is characterized by a decrease in the proportions of kaolinites and the appearance of palygorskites. These differences can illustrate either (i) a driest climate in the southern hemisphere or (ii) continents with flat relief on which poor drainage conditions prevent the formation of kaolinites and peri-oceanic basins, submitted to dry climate and evaporation, are favourable to the formation of palygorskites.

During Coniacian and Santonian, the low proportion of kaolinite with respect to smectites indicate reduced hydrolysis conditions compared to the Turonian and poor drainage conditions, associated with the absent of any tectonic activity and flattened landmasses.

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SHRINKAGE AND RETENTION BEHAVIOUR OF A CLAYEY SOIL TREATED WITH SUPERABSORBENT HYDROGELS

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In the Netherlands, flood protection is assured by a complex network of 18000 km of primary and secondary dykes. In recent years, concerns arose on the climate-sensitivity of the infrastructure subjected to drying-wetting cycles, overall temperature rise and drought periods not commonly experienced in the country before. All these factors can affect the serviceability and safety of infrastructures due to irreversible strains and desiccation cracks. Urban sprawl and densification in flood-prone low-lying areas also contribute to increasing the social and economic costs of the problem. A preliminary study has been initiated at TU Delft to assess the feasibility of superabsorbent hydrogels (SAH) as a mitigation measure and to increase soil resilience to drying. Thanks to their cross-linked three-dimensional network, superabsorbent hydrogels can absorb and retain large amounts of water and have been used in various fields such as drug delivery, food storage and hygiene products. In recent years, SAH are increasingly studied as possible soil amendment for drought in agriculture by virtue of their water retention capacity (Saha et al. 2020). In this study, a series of desiccation tests have been conducted to quantify the shrinkage and retention response of a clayey soil treated with SAH. The experimental results suggest a reduction in the evaporation rate for treated soil compared to the untreated one and at the expense of higher compressibility upon drying. The two effects contribute to altering the desiccation cracking mechanics with delayed cracks formation and lower cracked area. A modelling approach is also presented, which stems from the multiscale coupled models for compacted soils (Della Vecchia et al. 2013) to model the retention response of soil treated with SAH. The model will be used to eventually predict the response of earthworks to climate stresses and better assess the sensitivity of the infrastructure.

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DEFORMATION RESPONSE OF NON-EXPANSIVE CLAYS UPON MECHANICAL AND CHEMICAL LOADINGS

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The chemical composition of the pore fluid exerts a large influence on the mechanical behaviour of clays. In general, this influence increases with the specific surface of the mineral, and it is particularly relevant in the case of expansive clays. A large body of knowledge has focused then on the chemo-mechanical behaviour of bentonites, both from the experimental (e.g. Di Maio, 1996) and from the modelling point of view (e.g. Gajo & Loret, 2003, Musso et al, 2013). Less effort has been placed into studying and modelling the behaviour of non-expansive clays, although they also are largely used in engineering works for environmental protection. Chemical changes have been found to have a significant impact on the mechanical behaviour of natural formations dominated by non-expansive clays, such as quicks clays from Norway and Japan (Torrance, 1974), or marly clays from the Langhe region of Italy.

For expansive clays, salinity changes mostly affect the inter-particle distance in a fabric mostly dominated by a face-to-face arrangement of particles gathered within a cluster. A decrease in salinity causes cluster swelling, while an increase in salinity causes cluster shrinkage. The type of fabric remains substantially the same even though the ionic strength of the fluid changes. A multiscale investigation, from the particle to the laboratory scale, has been performed to unravel the main effects of pore fluid salinity on the behaviour of two illitic clays (Musso et al, 2022). In order to obtain a broader framework, the dataset has been enlarged by exploiting literature data for materials with the same dominant minerals. The original and collected evidence suggests that, for non-expansive clays, salinity changes might lead to different types of fabric. Microstructural evidence shows that illite in saline water is characterized by a card-house type of fabric (edge to face, or edge to edge arrangements of particles or group of particles), while it has a dispersed type of fabric in fresh water. Card-house fabric is related to larger macropores and higher void ratios than the dispersed one. A series of evidences at the laboratory scale follows: 1) the fluid content at the liquid limit of expansive clays decreases with salinity, while the one of non-expansive clays is salinity independent or increases with salinity; 2) as the salinity increases, the Normal Compression Line of expansive clays moves towards lower void ratios and its slope decreases, whereas the Normal Compression Line of non-expansive clays Normal Compression Line moves towards higher void ratios and its slope mildly increases; 3) for non-expansive clays, salinization processes mostly induce reversible deformations, while desalinization causes irreversible volumetric compressive strain when the material is normal-consolidated and reversible swelling strains at high OCRs. The laboratory response of non-expansive clays has been finally reproduced by means of a constitutive model formulated in the framework of elasto-plasticity with generalized hardening, by means of the introduction of osmotic suction as environmental variable and by modelling its effect on the size of the yield surface (i.e. the larger the pore fluid salinity, the larger the yield surface).

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INFLUENCE OF TEXTURE AND COMPOSITION ON THE PROPERTIES OF MG-CLAYS FOR ADSORPTION APPLICATIONS

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Samples of clayey materials consisting of magnesian clay minerals from lithofacies of the Miocene Intermediate Unit of the Madrid Basin have been studied. Taking into account their composition and texture, the aim is to evaluate their possibilities for their application as adsorbent clays. In the compositional characterization, XRD, FTIR, DTA-TGA, NMR and elemental chemical analysis were used. The textural study was carried out by optical microscopy (petrography) and electron microscopy (SEM, TEM). The properties analyzed were BET specific surface area and porous system, cation exchange capacity (CEC) and grain-size distribution. Clays with a predominance of fibrous (sepiolite, palygorskite) or lamellar (bleaching clays, bentonite) clay minerals were differentiated. Thus, they have been grouped into four mineralogical assemblages, according to their clay mineralogy, depending on whether fibrous minerals (sepiolite or palygorskite) or lamellar minerals (saponite or kerolite-magnesian smectite) predominate. Petrographically, varied textures have been observed ranging from granular to massive and laminated microfacies, where evidence of recrystallization is common, with several generations of the same clay mineral being observed, especially in the case of sepiolite.

The results indicate that smectite do not control the highest BET specific surface area values, since the samples with values above 250 m^2/g correspond to the samples richest in sepiolite and to the most kerolitic sample, where the smectite content barely exceeds 20%. On the other hand, with respect to cation exchange capacity, it has been observed that, in addition to the percentage, the type of smectite and its texture play an important role. Thus, the cation exchange capacity is especially relevant in the bentonite sample, which is the richest in smectite of mostly saponite composition; however, the samples rich in stevensite of the bleaching clays do not exceed the cation exchange capacity of samples with a much lower smectite content. It has been observed that in general, as the volume of mesopores increases, the specific surface area increases, but the cation exchange capacity decreases. This is especially true in samples with several recrystallization stages as those of sepiolites. From the point of view of textural properties (specific surface area BET, porous system), all samples are mesoporous (2-50 nm), but with differences in pore sizes within this wide range. The grain size distributions vary from bimodal to polymodal, with the bleaching clays having the highest median values (76-128 μm) with low contents (<20%) of the fraction smaller than 20 μm.

Despite significant textural differences and varied composition, and according to the elevated BET specific surface area values and CEC, all the samples studied have characteristics suitable for application in adsorption processes.

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MOLECULAR DYNAMICS SIMULATIONS OF HYDROGEN GAS ADSORPTION IN CLAYS: IMPLICATIONS FOR SUSTAINABLE RADIOACTIVE WASTE DISPOSAL

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Currently, clay-rich formations are considered as optimal host rocks for geological radioactive waste repositories. The Callovo-Oxfordian (COx) clay formation has been chosen as the host rock for a radioactive waste disposal facility in France. Clays exhibit unique properties, such as, low hydraulic conductivity, high sorption and retention capability forradionuclides and swelling/self sealing properties which make them excellent candidates for radioactive waste disposal repositories. One crucial factor in ensuring the integrity of the waste disposal repository is taking into consideration the possible risks associated with gas generation and migration. Hydrogen gas (H_2), which is a byproduct of anaerobic metal corrosion and water radiolysis processes, is the most significant gas expected after the closure of the facility. The intricate atomic structure of clay minerals makes them highly effective at adsorbing gases such as hydrogen. Despite our vast knowledge of clay minerals, uncertainties still exist regarding the interaction mechanisms of gases with clays. By better understanding the behavior of hydrogen gas in clay minerals, we can develop effective strategies for managing radioactive waste and ensuring the long-term safety of both human and the environment.
In this work, we perform a comparative study on the structure and energetics of hydrogen gas adsorption on the interlayer, basal, and edge surfaces of a montmorillonite clay model through the use of enhanced molecular dynamics simulations. We pay special attention to the effects of local compositional and structural heterogeneity of the clay mineral. Our results show that on the basal surfaces, hydrogen gas occupies the siloxane cavities, but its occupation is limited by the Al/Si isomorphic substitutions on the tetrahedral sheet of the clay structure. Additionally, it is revealed that the local structure of water plays a critical role in the adsorption energetics of hydrogen gas on the edges and within the interlayer sites of clay mineral nanoparticles. Overall, our findings provide molecular level insights into the behavior of hydrogen gas in clay minerals, which is important not only in nuclear waste disposal, but in several other engineering problems, for instance, in geological hydrogen storage.

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INTRODUCTION OF ADVANCED ENHANCED ROCK WEATHERING (A-ERW) TECHNOLOGY ACTIVELY COMBINED WITH SITE CHARACTERISTICS

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Enhanced rock weathering has attracted attention as a feasible negative emission technology that uptakes and sequestrates atmospheric CO2 into natural mafic and ultramafic rocks as carbonates. A great expectation is found in the famous reports published by IPCC AR6 WG-III [1] and ICEF [2]. However, inaccurate carbon accounting is pointed out as a common problem, including the industrial pretreatment of natural rock, transportation, CO2 mineralization rate, complex changes in the natural carbon cycle, and so on. In other words, net GHG reduction is still under validation in the world.

By utilizing the properties of natural rock easily obtained in Japan and the characteristics of the CO2 mineralization site, we are developing an advanced ERW technology that accelerates rock weathering and CO2 mineralization. Through pre-processing of crushing and grinding according to the rock characteristics extracted through site surveys, and bench-scale weathering acceleration tests for three CO2 mineralization sites which are industrial ERW, application to forest slopes and abandoned mines, and application to farmlands, models are developed to predict CO2 absorption rates, fixation rate, and co-benefits for each of the three sites, and a methodology is established to design a scale-up to pilot demonstration test. In addition, agro-industrial interdisciplinary knowledge is necessary to accumulate quantitative evidence that contributes to clarification and international certification/standardization of carbon accounting from the LC-CO2 perspective in ERW through these applications of acceleration technology. A-ERW is an abbreviation for this research and development project that includes a combination of the adjectives “Accelerated”, “Advanced”, “Active” (active rather than passive in nature), “Agro-industrial”, and “Advantageous” and the meaning of “Accurate carbon Accounting”. The A-ERW project is conducted by four parties and ten subcontractors as one of the “Moonshot Goal 4” research and development programs funded by Japan’s New Energy and Industrial Technology Development Organization.

The A-ERW project consists of six research items that include: (1) Site suitability assessment (geological and business environment assessments), (2) Mining and grinding test, and assay evaluation (prediction of pretreatment energy), (3) Acceleration of ERW (industrial methods and application on open sites), (4) Field testing under real environment and development of effective monitoring (gas-solid contactor, application on forest slop and abandoned mine site, and application on farmland), (5) Information database of accurate carbon accounting (Carbon accounting for industrial CO2 mineralization and natural carbon cycle), (6) Conceptual design of pilot-scale demonstration (conceptual designs of industrial ERW and ERW application on open sites). This paper details the aim and expected output of the above project.

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[2] ICEF, "Carbon Mineralization Roadmap " (2021)

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MODELLING THE ANISOTROPIC SURFACE CHARGE OF KAOLINITE PARTICLES USING COARSE-GRAINED MOLECULAR DYNAMICS

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Pore fluid pH significantly influences the mechanical behaviour of saturated kaolinite. Previous research has suggested that this observed dependency of its mechanical behaviour on pH is caused by the dependency of the microstructure upon pH. Scanning electron microscopy (SEM) images of kaolinite samples prepared with different pore fluid pH values by Pedrotti and Tarantino (2018) showed that in a sample prepared with acidic pore water, face-to-edge particle association is dominant and the void ratio is high, while in sample prepared with alkaline pore water, face-to-face particle association is dominant and the void ratio is low. This difference in microstructure is attributed to the fact that the surface charge of kaolinite particles varies with the pore fluid pH. A kaolinite particle consists of alumina and silica sheets arranged in alternating layers (Mitchell and Soga, 2005), so a kaolinite particle has three different surfaces: an alumina face surface, a silica face surface, and an edge surface. Gupta et al. (2011) revealed that the charges of all three surfaces depend on the pore fluid pH. Their research showed that when the pH is low (i.e. when the pore water is acidic), the alumina surface and the edge surface are positively charged while the silica surface is negatively charged, whereas, when the pH is high (i.e. when the pore water is alkaline), all three surfaces are negatively charged. However, while the observation of kaolinite specimens in SEM images has provided some insight, understanding of the link between the particle interactions and the overall mechanical behaviour remains incomplete. Particle-scale simulations such as molecular dynamics and discrete element methods can enable this link to be made for fine kaolinite particles. The overall aim of our research is to examine the influence of pH- dependent particle properties on the formation of kaolinite microstructure and the overall mechanical behaviour via particle-scale simulation. We have developed a new approach that can model the different charges of each surface by modifying the Gay-Berne potential (Gay and Berne, 1981). Using this modelling method, 3-D coarse-grained molecular dynamics (CGMD) simulations were performed using LAMMPS to create two virtual samples of kaolinite. Referring to Gupta et al. (2011), one simulation used the particle-scale parameters of a kaolinite sample prepared with pH=4, and the second used properties for a sample prepared with pH=8. In our simulations, the samples were isotropically compressed from an initial particle cloud, and we observed the evolution of microstructure and the overall compressibility. The virtual sample created using the pH=4 parameters developed a microstructure in which face-to-edge association is dominant, whereas the simulated samples using the pH=8 parameters showed a microstructure in which face-to-edge association is dominant. These observations agree with the SEM images of kaolinite samples by Pedrotti and Tarantino (2018). Furthermore, the virtual sample using the pH=4 parameters exhibited a higher compressibility than the virtual samples using the pH=8 parameters when the samples were isotropically compressed. This difference in compressibility is in agreement with the experimental results observed in isotropic consolidation tests using acidic and alkaline pore water conducted by Pedrotti and Tarantino (2018).

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QUANTITATIVE ANALYSIS OF SOIL MINERAL CONTENTS TO ASSESS ENHANCED WEATHERING IN THE ROOT ZONE OF BASALT-AMENDED FILED

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Amending basalt powder into agricultural fields is promising for both carbon sequestration and nutrient supply through enhanced rock weathering. We applied X-ray powder diffraction (XRPD) as an effective technique for identifying mineral types present in soil. Three quantitative methods for determining primary mineral content were tested for a wide variety of agricultural soils collected from all over Japan; one wet chemical method and two XRPD-based quantitative methods, i.e., the mineral intensity factor (MIF) method and full-pattern summation (FPS) method performed with the powdR package for R. Correlation analysis revealed that the mineral contents obtained by each of these three methods positively and significantly correlated each other for quartz, micas, K-feldspar, and plagioclase, indicating that any of these methods can provide similar relative values. We grew buckwheat for 2.5 months in the plots with or without amending basalt powder in Fukushima, Japan. The quantitative XRD using FPS method detected a significant increase in Ca-rich feldspar content for the soils immediately after the addition of basalt powder. After harvest, the XRD detected a decrease in the Ca-rich feldspar content in the basalt-amended soils. The decrease was about 6 times greater in the root zone than that in the non-root zone. These spatial variations in mineral weathering should be carefully considered for the accurate estimation of the amount of CO2 sequestration in the field. The buckwheat grain yield did not significantly decrease compared to the control and conventional plot without increasing the concentration of heavy metal (e.g., Ni) in the grain. Judging from these results, we concluded that applying basalt powder can enhance CO2 sequestration without decreasing crop yield.

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SPECTROSCOPIC PROPERTIES OF ANIONIC ORGANIC DYES IN AQUEOUS CLAY COLLOIDS

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Aqueous colloids of smectite-type clay minerals have been utilized as heterogeneous media of photofunctional dyes because negatively charged clay particles immobilize cationic dye molecules. However, we demonstrate the impacts of negatively charged hectorite clay particles on the spectroscopic behavior of anionic dyes [1]. Eosin B dye dissolved in aqueous clay colloids of synthetic saponite (Sumecton) and hectorite (Laponite) exhibits spectroscopic behavior reflecting the clay particles. The absorption and fluorescence maxima are red-shifted with increasing the clay concentration. Removal of the clay particles recovers the spectra of an aqueous solution. Saponite gives stronger impacts than hectorite. A similar influence of clay colloids is observed for the spectroscopic observation of an anionic porphyrin (5,10,15,20-Tetrakis(4-sulfophenyl)porphyrin). However, the spectral properties of Rose Bengal are little affected although its molecular structure is similar to eosin B.

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EFFECTS OF REDOX OSCILLATIONS ON SOIL CLAY MINERALOGY OF A GLEYIC FLUVISOL TOPSOIL FROM THE MULDE RIVER FLOODPLAIN, CENTRAL GERMANY

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In wetland and upland systems, redox conditions may change rapidly on a daily, weekly or seasonal basis due to changing moisture contents and water-table levels and associated biological oxygen production and demand; frequently resulting in distinct redox disequilibria. Our research seeks to better understand mineralogical responses to fluctuating redox conditions in soils, focusing phyllosilicate mineralogy as a function of frequency and duration of reduction-oxidation events. Therefore, we carried out long-term redox experiments using a gleyic Fluvisol topsoil from the Mulde River floodplain, Central Germany. XRD analyses showed the phyllosilicate mineralogy of the starting material to be dominated by kaolinite, illite, vermiculite and chlorite. Hydroxy-interlayered minerals were hardly recognizable. Additionally, rice straw was added to soil in different amounts as an organic carbon (OC) source for soil microorganisms. Reduction was initiated by flooding soil reactors with artificial river water at a soil:water ratio (w/v) of 1:2, whereas soil re-oxidation was achieved by centrifugation, decantation and air-drying of the soil. To simulate leaching conditions, fresh river water was added for each new reduction-oxidation cycle. Soil solutions were continuously sampled and analysed (Fig. 1), whilst soil samples were taken at the end of each oxic period, shock-frozen, and freeze-dried for solid-phase analyses.

With our experimental set-up, we wanted to show, if multiple redox oscillations lead to a rapid (<1 year) transformation of soil phyllosilicates. Therefore, soil samples were dispersed seperate (a) the total clay fraction and (b) coarse and fine clay fractions (0.2-2 and <0.2 μm). These fraction samples were examined by the following XRD-Methods: 1) air-dry; 2) ethylene glycol solvated and 3.) K^+-saturated: vacuum-dried followed by heat treatment in a heating chamber.

Results indicate that rapid mineralogical changes in the fine clay fractions whereas coarse clay fraction XRD pattern show only slight differences.

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MODIFIED NATURAL ZEOLITE CLINOPTILOLITE WITH ANTIBACTERIAL, ANTIFUNGAL AND ANTIVIRAL PROPERTIES

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Antimicrobial materials have quickly become a key tool in the global strategy to combat pathogens. Nowadays, the issue of continuing growth of microbial resistance and the elevation of microbial related diseases necessitates the needs of development of antimicrobial agents [1]. Many of the antimicrobial materials cannot support disinfection properties in long term *per se*. They provide a rapid peak release of the antimicrobial agent at the early age, consequently to the loss of antimicrobial activity over time [2]. On other hand, using modified natural zeolites ensure slow release of antimicrobial cations by ion exchange process, which is considerably slower over time.

In the present research natural zeolite from Beli Plast deposit, Bulgaria, with about 80-85% clinoptilolite content, were used to prepare Ag, Cu and Fe forms of the zeolite using simple ion exchange procedure. The modified zeolites were obtained with varied parameters: solution to zeolite ratio, molar concentration and type of ions. The effect of the pretreatment with 5% NaOH or HCl to ion exchange and antimicrobial effectiveness was evaluated.

The antibacterial activity was evaluated using agar diffusion method against Gram (+) and Gram (-) bacteria. The antagonistic activity of modified zeolite probes against *E. coli, K. pneumoniae, S. mutans, S. auereus, B. subtilis* was assessed. A difference between the samples activity have to be pointed, with higher effect observed for Ag modified zeolites against all of the strains, followed by Cu-zeolites with more pronounced effect against *S. aureus* and no effect on *K. pneumonia*. The natural zeolite and its base and acid forms did not inhibit tested strains.

The antifungal activity was investigated with Agar diffusion method against four fungal strains: *Aspergillus niger, Aspergillus fumigatus, Mucor hiemalis* and *Penicillium griseofulvum*. Clear inhibitory effect (up to 7 days after the beginning of strains cultivation) against all the strains were demonstrated by zeolite modified with copper. Asp. fumigatus was influenced by the Fe modified zeolite up to 7 days.

The virucidal effect and cytotoxicity were tested against Herpes Simplex virus (HSV-1) grown in MDBK cells and Poliovirus-1 grown in HEp2 cells up to 72 hours post infection. Acid activated raw zeolite showed a clear, albeit weak effect, against both viruses while keeping a low cytotoxicity. Other, relatively notable effects were displayed by Cu and Ag modified zeolites.

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GREEN APPROACHES FOR THE SYNTHESIS OF LAYERED DOUBLE HYDROXIDES AND EVALUATION OF THEIR BIOLOGICAL PROPERTIES

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Layered double hydroxides (LDH) consist of brucite-like layers containing di- and trivalent metal ions with interchangeable counter anions and solvation molecules that are present between the layers [1]. LDH find several applications in the pharmaceutical field due to their chemical stability, biocompatibility and high mechanical strength, and they are well known to support cellular processes, such as cell differentiation and viability [2]. LDH have very high potentialities for industrial applications, but their synthesis often requires a high number of steps, which could also lead to the production of great amounts of waste [3].
Given these premises, the goal of the work is the design of sustainable strategies for the synthesis of LDH in view of a continuous manufacturing process. LDH were produced through two well-known methods using new green synthesis conditions and their properties were compared to investigate the differences given by the LDH compositions. In particular, their biological properties were considered for a future application in the biomedical field, especially in tissue engineering.
Nitrate salts of Mg^{2+}, Zn^{2+}, Cu^{2+}, Al^{3+}, and Fe^{3+}, chosen as bio-enabling cations, were used. First, a co-precipitation method through a fast addition of salts and reduced aging time was developed, using ammonia as an alkaline agent. Few studies are reported using this chemical for the synthesis of LDH. Being a volatile molecule, the excess of ammonia could be easily removed and trapped, together with some of the byproducts that might be formed during the process. Second, the urea hydrolysis through microwave and hydrothermal treatment was considered. The synthesis parameters were adjusted to minimize the waste production. In all cases, the LDH were characterized both as prepared and upon centrifugation/washing, in view of a single step synthesis without water and components waste.
The XRD patterns showed that LDH phases represent the major part in the unwashed samples. Both the presence of ammonia and the washing step could affect the interlayer anions (NO_3^-, CO_3^{2-}, $[NH_4(NH_3)_n]^+$) in the structure. Several techniques (TEM, DLS, BET, TGA, ICP/CHN) were used to screen the different LDH and to get a correlation between their composition and their physico-chemical and biological properties. Considering a future application in the biomedical fields, the antioxidant properties alongside cell viability on different cell lines (fibroblasts, Caco-2 and tenocytes) were investigated.
In conclusion, sustainable green approaches were used to produce promising LDH for the development of composite materials to be used in biomedical field through continuous manufacturing processes.

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LAYERED DOUBLE HYDROXIDES FOR THE DEVELOPMENT OF 3D SCAFFOLDS IN SKIN TISSUE ENGINEERING

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Skin wound healing is a multiphase process that involves a series of biological responses following an injury. However, if its progression is altered or if an underlying disease (e.g. metabolic disorders, infections) is present, the wound could become chronic, posing significant health problems [1]. Three-dimensional structures, such as microfibers and microparticles, could act as scaffold which stimulate skin reparation [2]. Clay minerals are well known additives in the development of such scaffolds [3]. Among these, anionic clays like layered double hydroxides (LDH) have already been reported as drug delivery systems or as polymer additives in materials science for biomedical purposes. The combination of their peculiar structure and chemical composition should contribute to support cellular processes [4].

Therefore, the aim of this work was the development of spray-dried microparticles based on ZnAl LDH doped sodium alginate, to enhance the skin tissue regeneration. LDH based on Zn^{2+} were selected since Zn^{2+} proved to enhance wound healing and to be effective as antimicrobial.

LDH containing Zn and Al were synthesized via co-precipitation using ammonia as an alkaline agent. The LDH were then isolated upon centrifugation and dispersed, without further washing, in water under stirring. Sodium alginate was added to the dispersion, which was then spray dried. The microparticles were then crosslinked with $CaCl_2$ [5].

The spray drying process leads to the formation of smooth microparticles with a spheroidal shape. The presence of LDH slightly alters their morphology, which is evident by the hexagonal lamellar platelets visible on their surface. The crosslinking step with $CaCl_2$ allows to obtain water insoluble microparticles without changes in morphology, dimensions as well as LDH loading. In all cases, the mean diameters of the microparticles range from 6 to 8 μm and the LDH doping slightly increases the diameters.

To conclude, it was possible to manufacture sodium alginate microparticles doped with synthetic LDH, based on Zn and Al, and to obtain water insoluble matrixes using crosslinking with $CaCl_2$. These were intended for skin tissue engineering. Mechanical properties, ions release, and preclinical characterizations will be performed to investigate the systems safety and efficacy. Further characterizations will be performed to clarify the LDH role in polymeric matrix performance and tissue regeneration.

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NANOMATERIALS BASED ON HALLOYSITE NANOTUBES AND PEPTIDE NUCLEIC ACIDS: NEW STRATEGIES FOR THE LOADING OF ORGANIC MOLECULES

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Resistance to chemotherapy is a major public health problem. Multidrug resistance and subsequent treatment ineffectiveness are known to be responsible for 90% of cancer-related deaths. Moreover, when a cancer cell acquires the resistant phenotype, it also becomes resistant to anticancer chemotherapy drugs that are structurally and functionally different from the drug that generated the resistance. Therefore, it is an urgent need to find solutions to fight multidrug resistance to improve the effectiveness of cancer therapy. The most common drugs used for this purpose show some limits for their clinical use, and these are often associated to their scarce solubility in physiological media. To overcome these issues, carrier systems need to be developed. Clay minerals are a well-known class of compounds which have been used for pharmacological applications since ancient times [1]. The medicinal use of clay minerals became more and more prominent when, during the Renaissance, the Pharmacopoeia classified clay minerals as drug. Up to now, clay minerals are widely employed in the pharmaceutical industry as common additives. They are for example used as oral treatment of diarrhea or as gastrointestinal protectors, or for topical dermatological applications [2]. Among the different clay minerals, the most commonly used ones for pharmaceutical applications are, as example, kaolinite (Kaol), halloysite (Hal), montmorillonite (MMT), hectorite (Ht), and so on, because of their high biocompatibility, availability in large amount at low cost and ability to penetrate in the cell membrane. This communication will be focused on the latest research on clay minerals for biological applications. In particular, it will be shown the use of halloysite and hectorite as drug carrier and delivery system both for genetic material and chemotherapeutic drugs. The possibility to develop fluorescent nanoprobes based on clays, that represents a challenge to detect any cellular process under a microscope, will be also discussed [3-6].

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NOVEL METAKAOLIN CONTAINING SORBENTS TO DEPOLLUTE ABANDONED MINE DRAINAGE WASTEWATERS

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Acid mine drainage (AMD) wastewaters are highly acidic solutions derived from complex chemical and physical interactions that take place in active or abandoned mines. These effluents contain several toxic heavy metals and typically show pH values below <4, reaching extremely low values (~1) in some scenarios. The very high content of toxic and hazardous chemical species can cause a distressing impact on aquatic ecosystems. AMD remediation can involve active (chemical neutralisation) or passive routes (wetlands and limestone drains). The former not only generates a huge amount of sludge but also has prohibitive costs, while the latter is rather ineffective at low pH/high AMD flows. Geopolymers might be a sustainable and low-cost alternative to treat AMD wastewaters. In the present investigation the use of metakaolin/red mud geopolymer structures that can simultaneously buffer the pH and extract the heavy metals from real AMD wastewaters was studied for the first time. Results show the feasibility of the proposed route to treat AMD waters from an abandoned Portuguese mine.
Keywords: geopolymer, calcined clay, upcycling, wastewater treatment, heavy metals.

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PARTICLE FILM TECHNOLOGY UTILIZING PHILIPPINE NATURAL ZEOLITES FOR DISEASE CONTROL AND INSECT AVOIDANCE FROM MIRID BUG IN CACAO TREES

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Chemically active pesticides are residually present on food, water supplies, in the soil. These chemicals may interfere with animal and human growth and development. New paradigms are needed to control plant pests in a sustainable and environmentally safe way. One popular pest management technology is the Particle Film Technology. Particle film technology was based on a non-chemical kaolin clay made hydrophobic was originally developed for disease control in tree fruits with insect repellent property. Particle films action against insects may be lethal or nonlethal (i.e., repellency or avoidance of treated plants). Mortality results from ingestion of mineral particles, or desiccation through abrasion of the cuticle or adsorption by the cuticular waxes. Thus far, knowledge on the efficacy of kaolin against pests of cacao is very little. Amalin et al. (2015) reported positive repellency of cacao mirid bug on kaolin treated pods tested in the laboratory. Evaluation of the local clay particles as efficient coating agent from the Phase 1 of the Cacao Pest Management Program showed zeolite as comparable to the surround, the commercially available US kaolin for agricultural use as coating agent. Zeolite as a particle film will act as a physical barrier to repel insect pests as well as disease inoculum. This technology is an alternative to the laborous and expensive sleeving of cacao pods with plastic bag, which is being practiced by cacao growers not only in the Philippines but also in other countries growing cacao. However, moisture produced by sleeving becomes suitable to the growth of *Phytopthora*, the causal organism of black pod rot. Zeolite is found to be the most efficient carrier of entomopathogen (BCA) and microbial control agents (MCAs) against cacao mirid bug and black pod rot from our laboratory tests. The entomopathogen, *Metarhizium anisopliae*, and the microbial agent, *Trichoderma* sp., remained viable within a week on the pods sprayed with formulated zeolite with both *M. anisopliae and Trichoderma, which also suggests the coexistence of entomopathogen and MCA*. Formulated zeolite with MCA and entomopathogen will address the issue of surface coverage dilution as a result of the natural growth of the pods, which will create open area without the zeolite but stretching of the pod from its growth will also spread the reproductive part of the *M. anisopliae* and *Trichoderma* to the open uncovered area of the pod, which can infect CMB or CPB if they feed or oviposit. Trichoderma can also inhibit growth of Phytopthora inoculum in the open surface. Philippine natural zeolite (PNZ) mined by LITHOS Manufacturing has been used as a carrier material for the a particle film technology for managing the cocoa quality in the post-harvest process. The PNZ contains SiO2 (59 .52%), Al2O3 (12.62 %), Fe2O3 (4.57%), CaO (2.53%), Na2O (1.29%), K2O (1.17%), MgO (1.09%) and H2O (9.55%). The superfine particle of the PNZ mineral were modified using a surfactant coconut-based (50% coconut oil:50%glycerin) laundry liquid soap, Perla® that enriches the coating stability of the mineral to the cacao pods. The cacao pods are sprayed with mixture of PNZ-surfactant, water and Perla®. The bio-coat was spayed to the cacao pods using a pressure sprayer monthly until harvesting. The coating serves as insect repellant to avoid infestation from the cacao mirid bug (CMB). Initial result of the pilot field testing showed a complete surface coating of pods and also revealed significantly low lesions or feeding from CMB suggesting the potential of BioCoat-Z as coating agent for pest control.

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EFFECTS OF ALKALI AND ACID TREATMENT ON THE PHOTON SHIELDING PROPERTIES OF PHILIPPINE NATURAL ZEOLITE: A CHARACTERIZATION STUDY USING EPIXS SOFTWARE

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The effects of chemical treatment on the radiation shielding properties of Philippine natural zeolite from Lithos Manufacturing are theoretically investigated using the EPICS2017 library interpolated by EpiXS software. Firstly, the changes in the crystallinity and chemical composition of the zeolites are studied through XRD and EDX. Results show that chemical modification using NaOH and HCl solutions causes deterioration of crystallinity due to desilication and dealumination, respectively. Alkali treatment reduces the O content of the zeolite while acid treatment eliminates Fe and Ca. This causes a negative impact on the cross-section of the HCl-modified zeolite. X-ray and gamma-ray interactions occur most likely according to the order of NaOH > Raw > HCl. The mass attenuation coefficient (*MAC*) of the zeolite samples at energies 100 to 10^4 keV has almost similar values. The *MAC* of the raw, NaOH-, and HCl-modified zeolites at 1332 keV are 0.0545, 0.0544, and 0.0548 cm^2/g, respectively. At 100 to 10^4 keV, the linear attenuation coefficient (*LAC*) depends on the density and is ranked in the order of HCl > NaOH > Raw. In the energy range of 100 to 16000 keV, the mean free path (*MFP*) and half-value layer (*HVL*) values are in the order of HCl < NaOH < Raw. Above 16000 keV, the order is NaOH < HCl < Raw. Raw and NaOH-modified zeolite have comparable effective atomic number (Z_{eff}) while the HCl-treated zeolite has significantly lower values. The exposure buildup factor values are lowest in the X-ray region and highest in the intermediate gamma energies.

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BENTONITE ROCK INTERACTION IN KBS-3 DISPOSAL CONCEPT

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Clay is applied as a buffer material between the waste canister and bedrock in the KBS-3 disposal concept planned to be applied in Finland. Our focus was on hydraulic and mechanical interaction of the engineered clay barriers and crystalline host rock: to produce experimentally quantitative data on the hydraulic and mechanical behaviour of the clay components when they interact with the surrounding host rock.

Transport phenomena at the bentonite-rock interface were studied using X-ray tomography (CT). Compacted cylindrical bentonite (Bara-Kade) samples (d = 42 mm and h = 21 mm) were kept in a constant volume in specific sample chambers and wetted from the upper end. Three wetting geometries (wetting through filter disc, 3 mm hole and cracked rock), two dry densities (1.40 and 1.65 g/cm^3) and three water pressure levels (0, 2 and 4 MPa) were used in the experiments. Each sample was imaged 10–16 times during the experiment (1–4 months) using an in-house built Jtomo microtomography device. The obtained CT images were analysed using the previously developed and here improved method. The method yielded 4D (3D + time) dry density distributions, water content distributions and displacement fields in bentonite samples.

An experimental process for fully controlled mechanical testing of bentonite elastoplastic properties in altering conditions was created. The bentonite powder was wetted to a chosen water content either by water vapor equilibrium technique or mechanical mixing of liquid water to the powder. Solid pre-samples were compacted from the wetted bentonite powder with isotropic pressure using a triaxial cell (GDS Instruments 32 MPa cell with silicone oil in a 250 kN hydraulically actuated load frame). The material volumetric compressibility was studied throughout the compaction with a simultaneous volume measurement and the compaction was performed cyclically to enable the separation of elastic and plastic deformations. Finally cyclic shearing tests at constant pressure in the triaxial cell were performed on the samples with the load frame axial piston. Load-deformation data was collected, and shear strength can be demonstrated.

The CT was performed with a GE phoenix v|tome|x s instrument. For VTT sample quality control the settings were always the same, with a 100 kV accelerating voltage and a 0.5 mm copper filter, about 70 minutes per sample. For the natural clay fractures the accelerating voltages were 100 – 150 kV with a 0.5 mm copper filter, scan times varying between 25 and 183 minutes. The clay fracture samples were also investigated using two types of hyperspectral instruments, X-ray diffraction (XRD), scanning micro X-ray fluorescence (µXRF), scanning electron microscopy with energy dispersive spectroscopy (SEM-EDS) and optical microscopy with a digital camera. Hyperspectral measurements were also conducted for several clay fracture samples with a handheld Terraspec HALO spectroradiometer) and a hyperspectral imaging setup located at Spectral Imaging Ltd. (SPECIM) in Oulu, Finland, working in the shortwave infrared range.

Monitoring transport phenomena at the bentonite-rock interface using 4D X-ray tomography and image analysis revealed that water transport in high density bentonite samples resembles diffusion, while in low density samples advection seems to be important. Bentonite transport measurements showed that only small amount of bentonite was eroded from the samples into rather small fractures used in this study. An experimental process for bentonite mechanical testing covering the full cycle of bentonite sample preparation from bentonite powder to shearing the final samples was developed. The data from the cyclic, isotropic compression were used for creating constitutive large deformation elastoplastic mechanical models. Fracture mineral investigations showed that the short wave infra-red methods can aid in clay characterization at the fracture rock interface and aid specifically in swelling clay identification.

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IMPACT OF HIGH TEMPERATURE ON MECHANICAL BEHAVIOUR OF CLAY MATERIALS IN RADIOACTIVE WASTE REPOSITORY

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Most of Safety Cases for spent nuclear disposal facility limit maximum disposal container surface temperatures to 100°C to protect undesirable evolution. Higher temperature limits could have significant advantages such as allow disposal of higher enrichment/burn-up spent fuels and shorter interim storage/cooling requirements. EURAD HITEC Project aims to improve Thermo-Hydro-Mechanical (THM) description of clay based materials at elevated temperatures. The host rock clays will be studied under saturated conditions under 120°C, while buffer bentonites will be studied both in saturated and unsaturated conditions under 150°C.
The buffer bentonite task deploys knowledge on hydro-mechanical behaviour at high temperatures. The investigation of buffer behaviour at high temperatures is important for the design optimization of the underground nuclear waste disposal facility and for the long-term safety. The increase of temperature may result in strong evaporation near the heater and vapor movement towards the external part of the buffer. HITEC seeks to understand if such conditions are tolerable or if they would impair buffer safety functions. The research is divided into 3 domains. First investigates properties of thermally treated bentonite. Second investigates bentonite properties at elevated temperatures. Third uses laboratory models to investigate bigger picture. At the same time a numerical models based on new results are developed. The results show no influence on swelling pressure. A slight influence has been observed only for dry treated material.
The THM behaviour of the host clay rocks is significant for the design and long-term safety. When temperature increases, the pore water is compressed due to the difference between thermal expansion coefficient of water and the solid skeleton of the rock, leading to an over pressure. In far field, this could induce rock damage and reactivate fractures/faults. In the near field characterised, this could induce fracture opening or propagation in this fractured zone, altering the permeability. Short-term triaxial compression tests at different temperatures and confining pressures were performed on the COx (Callovo-Oxfordian) claystone. It resulted that the peak strength decreases overall with the increase of temperature up to 100°C for both orientations (parallel and perpendicular to the bedding plane). Self-sealing tests were also performed at different temperatures on the COx claystone. Sealing of the initial fracture occurs more quickly on a parallel sample than on the perpendicular sample. In addition, the self-sealing process is fast at the beginning of the test and stabilizes after one month. These first results are very promising and give confidence to the positive impact of the self-sealing process on the fractured rock. The temperature impact on the self-sealing process has still to be analysed
The experiments and modelling at higher temperatures has required much development work, which has been carried out successfully. Key results are new experimental observations and models for both materials studied in HITEC: clay host rock and buffer bentonite.
EURAD programme has received funding from the European union’s Horizon 2020 research and innovation programme under grant agreement n°847593.

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EVALUATION OF TERBINAFINE/LAPONITE HYBRID FORMATION AS A CONTROLLED RELEASE SYSTEM

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Terbinafine hydrochloride (TBF) is the most commonly used antifungal drug to treat nail disorders, such as onychomycosis, due to its lipophilic nature, but it is a lengthy treatment requiring multiple daily uses. Thus, the aim of this study was to evaluate the formation of a hybrid system made from the clay mineral laponite® (LAP) for the controlled release of terbinafine hydrochloride. To obtain the nanostructured hybrid systems (NHS) TBF/LAP, the influence of pH was evaluated by adding a fixed mass of 0.08 g of LAP to TBF solutions (in methanol) of 1 mg ml^{-1} at pH 2.0 to 7.0 for 720 min. Adsorption isotherms were performed with TBF solutions at pH 5.0 and concentrations ranging from 0.1 to 2.5 mg mL^{-1} for 720 min. Adsorption kinetics were performed with TBF solutions of 1.6 mg mL^{-1} (pH 5.0) and 0.08 g of LAP for times ranging from 1 to 720 min. All evaluated parameters were performed in triplicate, on a shaker operating at 200 rpm at 25°C. Mathematical models of isotherm and kinetics were applied. The NHS obtained at different pHs were characterized by XRD and FTIR. The equilibrium solubility of TBF was evaluated in HCl buffer solutions at pH 1.2. The dissolution performance was carried out with isolated TBF and the NHS obtained at pH 5.0, at a concentration of 1.6 mg mL^{-1}, under a time of 720 min (LAP/TBF-5). The test (in triplicate) was performed using 500 mL of HCl buffer solution at pH 1.2, at 37°C ± 0.5°C, under agitation of 150 rpm, with 1 mL aliquots taken at times ranging from 5 to 4320 min. The samples were collected and quantified by ultraviolet spectroscopy at 243 nm. The results were applied to mathematical models of dissolution kinetics. The highest adsorption of TBF was at pH 5, due to the ionization of this drug in the medium, being dependent on the concentration, with a maximum value of 144.97 mg g^{-1}, and fitted to Langmuir, with high adsorption capacity, even at low concentrations of TBF. The reaction occurs in two steps, with the faster one taking ≤ 60 min (k_2 = 7.49 x 10^{-3} g mg^{-1} min^{-1}) and the slower one reaching equilibrium in 720 min (k_2 = 0.34 x 10^{-3} g mg^{-1} min^{-1}), fitting to the pseudo second-order model. The basal distance of LAP (d_{001}) in the SHN was higher at pH 5.0, at 1.68 nm, which was greater than the d_{001} of raw LAP at 1.2 nm, suggesting intercalation of TBF into LAP. The band at 1415.71 cm^{-1} characteristic of the (C-N) vibration of TBF changes in intensity with increasing pH, suggesting interaction with LAP. The concentration of maximum solubility of TBF occurs at pH 1.2 (1188 µg mL^{-1}), being pH-dependent, due to the pKa 7.1. The dissolution profile of isolated TBF exhibited an immediate release, with 92.67% released in 180 min, whereas LAP/TBF-5 exhibited a controlled release profile, with continuous increase in release, with 4% released in 5 min, 10% in 180 min, and 94.62% in 4320 min (3 days). The adjusted kinetic model was Peppas-Sahlin, with $k_1 > k_2$, where the particle flow from the interior of the matrix to the medium constitutes the controlling process of dissolution due to erosion/relaxation, followed by Fickian diffusion. Thus, these NHSs may be promising alternatives to compose formulations for controlled release of the terbinafine hydrochloride drug.

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NATURAL ZEOLITE AS AN ECO-FRIENDLY CATALYST SUPPORT FOR DYE REMOVAL

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Access to potable and unpolluted water is a top priority goal in light of modern society's development and the exponential rise of industry. One of the major issues is the contamination of water resources caused by contaminants such as organic dyes released by the textile, food, printing paper, pharmaceutical, and cosmetic industries. Among organic dyes, methylene blue (MB) and basic fuchsin (BF) are widely used in the wood, silk and cotton industry. These substances are bio-accumulative, persistent in the environment and, in many cases, toxic to the ecosystem and humans. Many methods are available for water purification, including adsorption, membrane filtration, photocatalyst, coagulation and Fenton oxidation. Actually, the adsorption process is highly efficient, simple, and cost-effective method [1]. Moreover, among the low-cost available adsorbents, such as activated carbons, natural materials (clays, zeolites, silica), biomass, agricultural and industrial wastes [2], zeolites are particularly suitable for use in adsorption processes due to their porous crystalline structure, high specific surface area, and ion exchange properties. Recent studies have shown that various non-toxic biopolymers, such as Polydopamine (PDA), can be used to properly functionalize the surface of natural zeolites in order to enhance their performance in the adsorption [3] of metal ions and organic pollutants. In this research activity, composite systems based on natural zeolites (Phillipsite and Clinoptilolite-rich tuff), metal silver and PDA were synthesized. Polydopamine was exploited as both reducing and chelating agent for silver ions in order to produce environmentally friendly metal-based catalysts for both adsorption and degradation of organic dyes. MB and BF were used as reference dyes and the regeneration and reusability of the developed catalysts were also investigated for long-term use. More in detail, both zeolites were functionalized through two different innovative procedures: *Procedure a)* exploiting the ion exchange properties of the zeolites, both substrates are first charged with silver ions and then the PDA layer is deposited to reduce Ag^{+}. *Procedure b)* both substrates are first surface-functionalized with PDA, whose reducing properties are then exploited to reduce the silver ions. The structural characterization of all composites and raw materials was performed by various physicochemical technologies such as X-ray diffraction, FT-IR, BET, SEM and Thermal Analyses. Adsorption tests were carried out at different concentration of selected dyes and the obtained catalysts are proved to be remarkably effective in the removal of hazardous organic dyes. Furthermore, in order to find out the possible reusability of the produced materials, reduction steps were conducted in an aqueous solution of $NaBH_4$, to catalyse the dyes' reduction to their low-toxic colourless leuco-form. The synthesised samples show better behaviour than bare zeolites up to more than 15 reuse cycles without any loss of efficiency. Overall, this novel approach for the synthesis of eco-friendly metal based catalysts demonstrates the promising potential of such materials as efficient, regenerable and reusable catalysts for removal of toxic pollutants from both industrial and urban wastewater.

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CHLORHEXIDINE ADSORPTION BY HIGHLY CHARGED SWELLING MICA: A POSSIBLE ANTIBACTERIAL MATERIAL

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Microbial resistance has become a global concern due to the possible complications that these microorganisms can cause to human and animal health [1]. Chlorhexidine is a divalent cationic biguanide molecule with high activity against gram-positive and gram-negative bacteria and fung. Due to its cationic nature, chlorhexidine is attracted by the anionic residues present on the bacterial surface and is adsorbed on the cytoplasmic membrane by electrostatic interactions, thus increasing its permeability, resulting in extravasation of low-molecular-weight microbial components, and leading to cell lysis and death [2,3]. However, the uncontrolled and rapid release of chlorhexidine formulations becomes the main disadvantage of using this molecule as an antibacterial agent [4]. Clay minerals are versatile materials with properties that make them excellent for the interaction and adsorption of organic molecules such as chlorhexidine. Among clay minerals that have all these characteristics, high-charge synthetic mica (Na-mica-4) stands out. Therefore, the objective of this work is to study the formation of new hybrids based on chlorhexidine and highly charged mica (Na-mica-4). The synthesis of Na-mica-4 was carried out using the NaCl melt method. Its cation exchange capacity (CEC) is 468 meq 100 g^{-1} and its structural formula is $Na_4[Si_4Al_4]\ Mg_6O_{20}F_4 \cdot nH_2O$. For the formation of the chlorhexidine/mica hybrid, a previous study was followed [3] with some modifications. 50 mg of Na-mica-4 was added to 20 mL of chlorhexidine digluconate aqueous solution at different concentrations (0.1, 0.5 and 1%) and pH 6.5. The resulting solutions were stirred for 24 h at 25 °C. The final pH values were obtained in the range of 6.4 without any adjustment. The chlorhexidine-loaded samples were centrifuged, washed with deionized water, and dried at 60 °C for 24 h. The amount of chlorhexidine incorporated was quantified by UV-Vis spectrophotometer at 254 nm. The chlorhexidine/mica hybrids obtained were characterized by X-ray diffraction (XRD), Fourier transform infrared (FTIR) and zero charge potencial. The XRD patterns for chlorhexidine Na-mica-4 and for hybrids did not show difference in reflection peaks, which correspond to the (001) plane, with values at $2\theta = 7.30º$ (1.2 nm), indicating that chlorhexidine interacts with the outer surface of the clay mineral. The zero charge potential values (ΔpH) indicated a negative charge for Na-mica-4 (-0.7) and a positive charge for hybrids with chlorhexidine (+0.5). Therefore, the electrostatic attraction between protonated amino groups and the negative charge of clay minerals may favor the interaction between these species. The FTIR spectra showed new bands for the hybrids with chlorhexidine, indicating the presence of this molecule. The maximum amount of incorporated/adsorbed chlorhexidine was 552 mg g^{-1}, indicating good interaction between species. Thus, the promising results obtained in this study may indicate a possible new antibacterial material.

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ADSORPTION/DESORPTION OF CURCUMIN IN CLAY MINERALS. SOLUBILITY AND CHARACTERISATION STUDIES

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Curcumin (Cur) is a polyphenolic pigment that belongs to the curcuminoid family of the tropical plant Turmeric. It has great therapeutic interest due to its antioxidant, anticancer, anti-inflammatory, and antimicrobial properties, in addition to its low toxicity and good organoleptic properties [1]. However, limited bioactivity is demonstrated due to chemical instability, poor solubility in water, rapid metabolism and excretion, and low bioavailability [2]. Therefore, interest in developing a new pharmaceutical dosage form suitable for therapeutic use is high. Clay minerals have interesting technological characteristics and are used in various formulations to increase the stability of active ingredients, due to their high specific surface, rheological characteristics, and excellent adsorption capacity [3].

The objective of this work was to incorporate Cur in different types of clays to study the mechanisms of adsorption / desorption, water solubility, and characterization properties of the complexes, in order to determine a possible formulation proposal for therapeutic use of the Cur.

Three laminar silicates of 2:1 type were used. One of them of natural origin, montmorillonite (MTT), an expandable synthetic mica of high charge (Na-mica-4), and Na-mica-4 organofunctionalized with primary amines of 18 carbon atoms (C18-mica-4). Adsorption assays were designed with saturated hydroalcoholic solutions of curcumin. The adsorption was monitored by pH and HPLC, and the complexes obtained were characterized by XRD, infrared with Fourier transform, Z potential, BET surface, scanning microscopy (SEM), and thermogravimetry (ATD-TG). For desorption tests, acetone, ethanol and acetonitrile were used as solvents.

The solution medium showed different pH values as a function of clay, ranging from 7.9 (in C18-mica-4) to 8.9 (in Na-mica-4). Na-mica-4 showed better efficiency in curcumin adsorption than the rest of clay minerals tested, being 60 % of adsorbed-curcumin approximately; acetonitrile was the solvent with better results in curcumin desorption from clay.

The results of structural and morphological characterisation indicate that the interaction between clay and curcumin under the test conditions may occur on the surface through electrostatic interactions, but other mechanisms may be affecting to the complexing procedure, such as hydrogen bonds, interlamellar deposition, etc., based on the basis of change in zeta potential (without significant statistically differences in the adsorption process (-34.9 ± 2.5 mV Na-mica-4 vs. -36.5 ± 1.9 mV complex) and with significant statistically differences in the desorption process (-13.9 ± 0.3 mV Na-mica-4 vs -31.5 ± 0.9 mV complex). The results obtained and previous studies showing the safety of Na-mica-4 [4], allow us to think that this mineral clay could be very interesting as a potential support for curcumin in therapeutic formulations, stability studies, and future applications.

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THE IMPACT OF VARIOUS TYPES OF SMECTITES ON SOLVENT BITUMEN RECOVERY

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The Alberta oil sands deposit has one of the largest reserves of oil on the planet. The Alberta oil sands are mixture of sands, clays, bitumen and water. The mined Alberta oil sands consist of four petrologically different types of oil sands. Different types of oil sands have different properties which affect the bitumen recovery. Generally, clays have detrimental effect on bitumen extraction from the oil sands. Kaolinite and illite are the main clay minerals constituent of the Alberta oil sands, but chlorite, smectite and interstratified clay minerals are also often present in smaller amount. The main goal is to better understand the impact of various types of smectites on solvent bitumen extraction. The Source Clays SapCa-1, SHCa-1, SWy-3, SCa-3, SBId-1, NAu-1 and SWa-1 and Slovak bentonites J and L were used in the present study. The samples included variety of dioctahedral and trioctahedral smectites, high-charge and low-charge smectites and different size fractions of smectites (0.2 – 2 μm and <0.2 μm) in order to evaluate the effect of these parameters on bitumen recovery. In the experiments, smectites (pretreated at 0% and 90% RH conditions) were mixed with bitumen and smectite-bitumen mixtures were stirred for few days. Then the mixtures were washed with cyclohexane to extract the bitumen. More residual organics after experiments indicated more detrimental effect of given smectite on bitumen extraction. Samples were examined by XRD, FTIR, ICP, CHNS analysis, CEC, BET, SEM-EDX and particle size distribution measurements. The preliminary results showed no significant correlations between the amount of residual carbon and crystal chemistry, CEC and layer charge of the studied smectites. Data rather indicate that the amount of residual organics is controlled by surface characteristics of smectites. We believe that the dimensions and arrangement of smectite particles within the sample may substantially affect the amount of residual organics. Upon exposure of smectite to 90% RH conditions, smectites showed different ability to swell and different degree of particles delamination. Smectites (e.g. SWy-3) with higher swelling ability and more pronounced decrease in particle thickness due to swelling retained more residual organics. Samples containing larger number of thin particles displayed lower bitumen recovery.

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RETENTION OF SELENITE ON THE HOST ROCK OF A POTENTIAL HIGH-LEVEL RADIOACTIVE WASTE REPOSITORY

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In several European countries, argillaceous rock is considered for the deep geological disposal of high-level radioactive waste (HLW). Boda Claystone Formation (BCF) is considered as the potential host rock in Hungary. The main aim of the present work was to evaluate the radionuclide retention capacity of argillaceous rocks of BCF, through studying sorption and diffusion properties of albitic claystone and pyritic sections of the BAF-2 drilling core.

In order to study the sorption properties of selenite on BCF, the crushed rock was conditioned prior to the experiments using the dialysis technique. The experiments were conducted under atmospheric conditions. Sorption isotherms were collected in the 10^{-3} – 10^{-10} M region using inductively coupled plasma optical emission spectrometry (ICP-OES) in the high concentration region (above 10^{-6} M) and liquid scintillation counting (LSC) using Se-75 radiotracer in the whole concentration range. The reversibility of sorption was studied by isotopic exchange experiments, adding Se-75 radiotracer after reaching equilibrium with inactive selenite and measuring the uptake using LSC. Sorption was also studied on petrographic thin sections prepared from claystone, the distribution of selenium and rock-forming elements was recorded using microscopic X-ray fluorescence (micro-XRF) with a spatial resolution of around 30 μm. The oxidation state of selenium was investigated using X-ray absorption near edge structure (XANES) using synchrotron radiation both on thin sections and on crushed rock samples in the form of pressed pellets. Through diffusion experiments were launched with selenite ions at 10^{-3} – 10^{-5} M concentrations. After experiencing break-through state, each diffusion cell was opened, the disc was cut and then investigated with micro-XRF and XANES.

Microscopic measurements on thin sections showed good correlation between Se–Fe and Se–K suggesting that selenite is mostly sorbed on clay minerals. Results of ICP-OES and LSC methods of the liquid phase agree and altogether show a typical sorption isotherm for selenite, comparable to those reported for illite and illite-smectite minerals and for other European argillaceous rocks [1,2], especially in the low concentration region (below 10^{-5} M). Isotopic exchange experiments using ^{75}Se radiotracer indicate reversibility of sorption in the 10^{-8} – 10^{-4} M selenite concentration range.

With the initial SeO_3^{2-} concentration of 10^{-3} M, the effective diffusion coefficient was obtained as $D_e = 1.1 \times 10^{-12}$ m^2/s similar to that reported for Callovo-Oxfordian clay [2]. Based on the diffusion profile of selenium inside the rock obtained using synchrotron-radiation micro-XRF, XANES measurements were performed at selected representative positions. Overall, in each form of the studied rock undergone sorption or diffusion experiments (crushed rock, thin sections, compacted diffusion sample) no change in the oxidation state of selenium was experienced. However, at certain positions with enriched pyrite content reduction to Se(0) could not be excluded.

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THE GENERATION OF THE CARBON DIOXIDE FROM THE BOOM CLAY UPON HEATING AT 80-200°C

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Considerable amounts of gas can be generated in a geological repository for radioactive waste, due to e.g. anaerobic corrosion of steel or thermal degradation of the organics in the engineered barrier or the surrounding host rock. The Boom Clay is considered as potential host formation for the disposal of radioactive waste in the Netherlands and Belgium. Because of its relatively high organic matter content (up to 3.5 wt%) of low thermal maturity, the generation of gases as a result of the thermal organic matter decomposition needs to be evaluated. With this aim, a set of hydrothermal tests have been performed under water saturated conditions without a free gas phase at 200 bars accompanied by continuous analysis of fluids and therein dissolved gases. CO_2 is by far the most abundant gas product released upon heating of the Boom Clay in the T range of 80-200°C, followed by the hydrocarbons CH_4, C_2H_6 and C_3H_8. The amount of the produced gases increases with temperature. The quantification of dissolved carboxylic acids (mainly formic, acetic, oxalic and propionic acid) has shown a significant formation during heating, and then a transformation most likely to CO_2 at elevated temperatures and longer experimental times. The stability of the organic acids to thermal decomposition differs strongly [1]. Hence some organic acids are considered to be important precursors of CO_2. The stable carbon isotopic composition of dissolved CO_2, more precisely the exsolved CO_2 (g) of the fluid sample, showed relatively large variations over the course of the experiment at 80°C, these variations tend to decrease with increasing temperature. Based on published carbon isotopic fractionation factors in the system CO_2(g)-CO_2 (aq)-HCO_3^- -calcite [2, 3, 4], theoretical delta^{13}C values of the various phases in equilibrium with the measured CO_2 (g) were calculated for different temperatures. Overall, the near equilibrium concentrations of dissolved CO_2 at longer experimental times and the isotopic analysis indicates that dissolved CO_2 produced during heating will be ultimately buffered by carbonate minerals present or newly precipitated in the system.

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TEMPERATURE-DEPENDENT IMPULSE EXCITATION AS A THERMAL ANALYSIS TECHNIQUE FOR KAOLINS AND AS AN ELASTICITY TESTING TOOL FOR KAOLIN-BASED CERAMICS – A CASE STUDY WITH KAOLIN SEDLEC IA

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The impulse excitation technique (IET) is a non-destructive mechanical testing method that allows the determination of elastic constants, e.g. Young's modulus, from the resonant frequency of flexural vibrations of bars. When IET equipment is integrated into a high-temperature furnace, it can be used to measure these resonant frequencies up to high temperature (e.g. 1600 °C), and since these measurements can be performed in situ and in real time, the temperature dependence of elastic constants can be obtained during heating and cooling. In this contribution we show – exemplified by a case study with the Czech standard kaolin Sedlec Ia – that the IET can be used both as a thermal analysis technique for kaolins and as an elestic property testing tool for kaolin-based based ceramics. Thus the IET is useful both for monitoring the temperature-dependent response of the kaolin to thermal loads or heat treatment (e.g. in ceramic sintering processes) and for determining the high-temperature elastic properties of kaolin-based ceramics (i.e. the products of ceramic sintering processes). In this work, which is part of the project "Impulse excitation as an unconventional method for monitoring phase changes and microstructure evolution during thermal loading of materials" (grant no. GA22-225562S), funded by the Czech Science Foundation, commercial high-temperature IET equipment, namely a resonant frequency and damping analyzer / RDFA 23 integrated into a high-temperature furnace / HT 1600 (both produced by IMCE, Belgium) is used to determine the temperature dependence of Young's modulus from room temperature to temperatures ranging from 1000 °C (for kaolin-based ceramics sintered at different temperatures in the range 1100–1500 °C with a heating rate of 2 °C/min and 2 h dwell time at the maximum temperature) to 1400 °C (for uniaxially pressed and initially unsintered kaolin compacts), with preset heating and cooling rates of 5 °C/min and a very short dwell time at the maximum temperature (5 min). It is shown that during heating of initially unsintered kaolin compacts – apart from the generally increasing trend of Young's modulus with temperature – all the major events, such as drying (70–130 °C), dehydroxylation to "metakaolin" (500–600 °C), formation of the defective Al-Si spinel-type phase with silica release (around 930 °C) and mullitization with silica release (around 1200 °C), are clearly discernible and in summary lead to a stepwise increase of Young's modulus from the initial room temperature value of 2.5 GPa for the unsintered powder compact to 44 GPa for the sintering ceramic at 1400 °C. Moreover, during cooling from 1400 °C there is a discontinuous jump in Young's modulus at around 1270 °C (due to stiffening of the glass phase and / or precipitation of cristobalite) to values of approximately 92 GPa, followed by a further slight increase in Young's modulus with decreasing temperature, until maximum values of 105 GPa are attained at around 800 °C, which remain constant down to around 200 °C, below which they decrease as a consequence of the displacive high-to-low-temperature cristobalite phase transition to around 100 GPa at room temperature. On the other hand, the IET study of kaolin-based ceramics (previously sintered with a dwell time of 2 h) shows that bodies sintered at temperatures 1200, 1300 and 1400 °C contain significant amounts of cristobalite (beside mullite), which reveal themselves (both during heating and cooling) by elastic anomalies at temperatures around 200 °C (phase transition of cristobalite), whereas bodies sintered at 1100 °C contain only quartz (but no cristobalite), which reveals itself (during heating) by a clear elastic anomaly below 600 °C (phase transition of quartz), and bodies sintered at 1500 °C, which contain only mullite (and glass phase) exhibit gradual softening during heat without any elastic anomalies.

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SYNCHRONOUS SYNTHESIS OF NITROGEN-DOPED GRAPHENE AND CARBON NANOTUBES IN A NANOLAYERED SILICATE

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Synthesis of Nitrogen(N)-doped graphene in the confined space of a nanolayered silicate can be vital for real-world electronic applications, as it supresses formation of quaternary N, which typically forms when doping graphene with N by other methods, and thus allows for band gap opening. Here we report formation of N-doped graphene islands simultaneously with metal-free carbon nanotubes in the interlayer of synthetic fluorohectorite clay at 750 degrees C, by intercalation and subsequent pyrolysis of two different cationic dyes – safranin and malachite. Detailed characterization by X-ray diffraction, X-ray photoelectron spectroscopy, Atomic force microscopy, Raman spectroscopy, as well as magnetic property measurements allow us to describe this system, and postulate a plausible mechanisms for formation of single layer graphene islands, alongside with carbon nanotubes. Synthesis at this unusually low temperature allows significant reduction of energy cost in carbon industry applications.

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LARGE BAND GAP OF INSULATOR CLAY NANOSHEETS

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Two dimensional materials possess many unique properties. From the electronic structural point of view, one can find conductive, semiconducting and insulating single nanosheets. Here we report a wide band gap insulator (band gap energy up to 7.1-8.2 eV) nanosheets obtained by delamination of synthetic fluorohectorite clay testifying these nanosheets to be one of the largest band gap insulators in the world. The band gap has been determined by electron energy loss spectroscopy in a high resolution transmission electron microscope. Fluorohectorite clay 1 nm thick single nanosheets can be synthetized with high-aspect ratio and lateral dimensions up to dozens of microns. This property renders the synthetic fluorohectorite nanosheets promising candidates for practical applications in electronic devices, serving as insulating nanosheets for deposition of graphene and various (semi)conductive 2D materials by self-assembly.

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INFRARED STUDY OF ORGANOMODIFIED SMECTITES FUNCTIONALIZED WITH A LASER DYE

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Hybrid materials based on organoclays and laser dyes are usually studied for their luminescent properties. However, other methods are also important for characterizing these materials to evaluate the relationship between individual components. Identification of dye molecules in materials can be problematic because of low concentrations of the dye molecules in such systems. Smectites and organic species dominate, and dye molecules represent only a minor component. One of the methods that could help evaluate the presence of the photoactive component is infrared spectroscopy. The pigments exhibiting luminescent properties were synthesized using smectite, tetraoctylammonium, and -phosphonium cations and a cationic type of dye, rhodamine 6G [1]. The amount of organic surfactants varied from 0-100 % with respect to the cation exchange capacity of smectite, and dye concentration was in the range of 0.001 to 0.08 mmol/g.

Besides absorption bands of particular smectite, the IR spectra in the middle (MIR) and near-infrared (NIR) regions displayed the absorption bands assigned to the C-H vibrations of both organic cations, with the shape of the bands depending on the type of cation. The intensity of the bands within the series increased with the content of an organic phase.

The presence of R6G at the concentration of 0.08 mmol/g was detectable in the MIR spectra of organoclays based on the bands assigned to the C=O and C-H vibrations of aromatic rings or methyl groups 1717, 1650, 1610, 1533, 1502 cm^{-1} [2]. Those bands were detectable even for the samples with the highest loading of organic quaternary cations, i.e., for samples with pronounced overlapping bands of both organic molecules. Visibility of the bands decreased significantly with the dye amount of 0.005 mmol/g and were not detectable anymore for the samples of the lowest concentration (0.001 mmol/g). It was difficult to detect R6G in the higher wavenumber region, above 2700 $cm^{-1,}$ and in the NIR region, even in the samples with the highest dye concentrations. The interesting feature is the appearance of small but sharp bands at 3440 cm^{-1} and 6744 cm^{-1}, not visible in a pure dye spectrum. The intensity of those bands depended on the amount of water present in the systems. The bands' intensity diminished with the increasing loading of the organic surfactants. The phenomenon could be attributed to the interactions of dye cations through the N-H bonds with water molecules via hydrogen bonding. The chemometric and statistical analyses of the spectra will help to better evaluate components contributing to the spectral profiles and to discriminate absorption bands of dye.

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INVESTIGATION OF THE STRUCTURAL EVOLUTION OF THERMAL TREATED IMOGOLITE NANOTUBES

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Thermal treatment is one of the most commonly applied process to modify the structure, porosity, and surface reactivity properties of clay minerals. Among them, imogolite nanotubes, $(OH)_3Al_2O_3SiOH$, have a unique structure consisting of a curved octahedral $[O_3Al(OH)_3]$ outer layer and isolated $[SiO_3(OH)]$ tetrahedron units in inner surface connected through three mutual oxygen atoms [1]. The family of imogolite(-like) nanotubes also includes methylated imogolite nanotubes, where inner hydroxyl groups are replaced by methyl units, or to germanium-based imogolite nanotubes, where silicon is replaced by germanium. A recent study by Monet et al. [2] has shown that three different intermediate stages occur during the thermal annealing of hydrophilic aluminogermanate imogolite nanotubes, until re-crystallization into a Ge-mullite compound beyond 950°C. Interestingly, after dehydroxylation, a metaimogolite structure is formed with both six-fold and five-fold coordinated Al atoms, which further reorganizes into Al(VI) and Al(IV) at temperature higher than 600°C.
A comprehensive investigation of thermal induced reorganization of the whole imogolite family is still lacking. In particular, it was shown that the rolling mode of methylated and hydroxylated nanotubes are different [3], so that the effects of temperature can be different. Here, we investigated the thermal transformation of methyl-modified ($(OH)_3(Al_2O_3(Si,Ge)CH_3$) and of hydrophilic aluminosilicate ($(OH)_3Al_2O_3SiOH$) imogolite nanotubes by performing in-situ X-ray Absorption Near Edge Spectroscopy and X-ray diffraction from room temperature to ~1000 °C, coupled with ex-situ characterization. Typical dehydration and dehydroxylation (demethylation) have been observed up to 500 °C, followed by complex structural transformations and atomic re-organization at higher temperature. Typically, the Al coordination shows a strong evolution from an Al(VI) octahedral environment to a combination of Al(IV), Al(VI) and probably Al(V) sites. To go further, the Multivariate Curve Resolution with Alternating Least Squares (MCR-ALS) chemometrics quantitative analysis is applied to recover the XANES spectra and concentration evolution of different species during thermal annealing. The results have shown a different behavior among imogolite nanotubes, with respect to transformation temperature and to the components of metaphases. They should represent a benchmark for further studies concerning the properties of these transformed INT-based compounds.

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A PRELIMINARY STUDY ON PHYSICAL, MINERALOGICAL, CHEMICAL, AND RHEOLOGICAL CHARACTERISTICS OF MG-FE-SMECTITE AND PALYGORSKITE-RICH CLAYS OF THE VENZTIA BASIN, GREVENA, GREECE.

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In the present study, some physical properties of palygorskite and Mg-Fe-smectite of the Ventzia basin Grevena, Greece were determined, such as the apparent bulk density, water and oil absorption, pH and absorption of methylene blue. In addition, the rheological behavior and the filtration capacity of clays with the addition of polymers were studied. The mineralogical composition was examined by X-ray diffraction (XRD), while their chemical composition by X-ray fluorescence spectroscopy (XRF). Low apparent bulk density, low absorption in methylene blue solution, high absorption in oil and high performance in salt solution and high filtration loss, characterize the palygorskite-rich samples. In contrast low apparent bulk density, high absorption in water, and methylene blue solution, low filtration loss are characteristic for the Mg-Fe-smectite-rich samples. The performance of the Mg-Fe-smectite deionized water suspensions was improved using carboxymethyl cellulose and causticized lignite producing fluids according to API 13A 2010. In contrast, palygorskite suspensions were improved by using guar gum, (a natural polysaccharide) in different aqueous environments (deionized and salt water). Strong correlations between physical, mineralogical, chemical and rheological characteristics were identified by statistical analysis.

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ROLE OF CONTENT AND CRYSTAL CHEMISTRY OF ANALCIME ON CATION EXCHANGE CAPACITIES OF ANALCIME RICH ROCKS

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The Abinky sedimentary formation is composed of analcimolites (i.e., rocks with more of 70 wt% of analcime) that underlies the Tchirézine 2 (Tchi2) formation, known for hosting the Imouraren uranium (U) deposit (Niger). Tchi2 is mainly composed of sandstones which can contain analcime cement (> 25 wt%) as well as some analcimolitic levels. A potential project is under consideration by Orano to recover U from the Imouraren deposit by using an acidic leaching (In Situ Recovery [1]) of the sandstone aquifer. Consequently, assessing the ion-exchange properties of analcime-rich rocks (both sandstone and analcimolite) is the first step to understand and predict the mobility of water and solutes in these different geological formations.
Analcime ($NaAlSi_2O_6.H_2O$) belongs to the zeolite group and is a hydrated tectosilicate presenting isomorphic substitutions of Si^{4+} by Al^{3+} leading to a permanent negative charge of the crystalline edifice. Such charge unbalance is compensated by incorporating hydrated Na^+ atoms in the structure thus enabling cationic exchange properties. The reactivity of some natural and synthetic zeolites (e.g., clinoptilolite, chabazite…) has been studied for a wide range of applications (water treatment, catalysis…). However, studies dedicated to the reactivity of natural analcime bearing rocks for environmental conditions are scarce. Thus, the objective of this study is to understand the link between the Cation Exchange Capacities (CEC) of analcime-rich rocks as a function of (i) the analcime content and (ii) the crystal chemistry of the analcime present inside. Mineral quantification was obtained by Rietveld refinement (BGMN; [2]) on disoriented powders ground at micron scale. Internal standards (30 wt% ZnO) were added to each sample to quantify potential amorphous material. The percentages of crystalline and amorphous phases deduced from this method are verified by modal calculations based on chemical analyses of total rocks. In addition, analcime crystal-chemistry deduced from Rietveld refinement was compared to local analyses of crystalline phases via Scanning Electron Microscopy coupled with Energy Dispersive Spectrometry in order to validate the results of the Rietveld refinement.
At room temperature, maxima CEC values were obtained at neutral pH by performing NH_4^+-for-Na^+ exchange (CEC_{Na_NH4+}), with aqueous sodium measured by atomic absorption spectrophotometry. The results show that there is a positive correlation between CEC_{Na_NH4+} and analcime content, and that around 6 % of the total amounts of Na^+ presented in the analcime can be exchanged by NH_4^+ and H^+. Experimental Na^+/H^+ exchange isotherms were also obtained for some samples characterized by high analcime content. For these data, experiments were performed in chloride and sulfate media to assess effect of aqueous speciation, and in conditions where dissolution can be neglected based on aqueous dissolution measurements. Na^+/H^+ selectivity coefficients interpreting these data were assessed by using PhreeqC [3].

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THE IMPACT OF THE MINERALOGY OF CLAY RAW MATERIALS ON THE SINTERING OF THE WHITE TYPE STONEWARE CERAMIC MATERIALS WITH CONSTANT CHEMICAL COMPOSITION

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The white stoneware materials are characterized by low porosity, high mechanical strength and chemical resistance. Thanks to these properties and a relatively low firing temperature, it is widely used in the Polish tile industry (floor tiles) and ceramic table ware. The aim of the presented work was to determine the influence of the mineralogical composition of clayay raw materials on the sintering process during thermal treatment while maintaining a constant chemical composition of the system. In addition, the final qualitative and quantitative phase composition of the obtained ceramic materials and the resulting differences in their sintering degree were examined. For this purpose, five clay raw materials were selected (two kaolins, KOC and KDH and three kaolinite clays JNN, LAK, CW). Other raw materials; feldspars, quartz sand, chalk were unchanged in compositions. The clayay raw materials were tested in terms of mineralogical composition (XRD) and characteristic temperatures (HSM). The experimental masses were prepared by grinding the raw materials in a planetary-ball mill for 35 minutes and after drying, formed by pressing. The measurements of shrinkage, apparent density and open porosity were carried out on them after firing. In turn, thermal analysis (DSC-QMS) was used to study thermal transformations occurring in the masses. The XRD X-ray diffraction method was used to determine the phase composition taking into account the amount of amorphous phase. Observation of the microstructure and characterization of chemical composition of the crystalline and amorphous phases was carried out under a SEM microscope with EDS function. All studies confirmed the assumed thesis, that clay raw materials and, above all, their mineralogical composition, have a significant impact on the properties of white stoneware ceramic materials.

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PROPERTIES OF CORN STARCH THERMOPLASTIC FILAMENTS REINFORCED WITH DIFFERENT ADDITIVES FOR FDM 3D PRINTING.

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Three-dimensional (3D) printing technology has grown exponentially in pharmaceutical field allowing the development of customized formulations designed *ad hoc* for the patient. This technology is constantly evolving allowing the exploitation of natural and new sustainable materials suitable for 3D printing[1]. Fused deposition modeling (FDM) is the most widely used 3D printing technique. The objective is to develop flexible, homogeneous and printable corn starch filaments suitable for FDM. With this idea, they were prepared starch-based thermoplastic (TPS) filaments consisting of: 70% w/w corn starch and 30 % w/w glycerol (Gly) as plasticizer. Clays, citric acid (CA), magnesium stearate (MgSt) were added as reinforcing agents to improve the extrusion process, thermal and mechanical properties of the filament formulation. In addition, swelling capacity of the different TPS filaments was studied. The use of the cationic clays halloysite (HAL) and montmorillonite (MMT), at 2 parts per hundred parts (phr)[2] showed that HAL did not improve TPS control filament brittleness while MMT promotes a slight decrease of brittleness higher homogeneity. However, difficulties in the extrusion process were observed. A further modification consisted in the introduction of CA, added to 3 phr of TPS, and MgSt to 2 phr of TPS. CA produces a change in the polymeric interaction, decreasing the fragility. This is mainly attributed to the acidity of CA that promotes the fragmentation and dissolution of the starch granules. Additionally, CA and Gly are responsible for the rupture of inter and intramolecular hydrogen bonds, plasticizing the starch under shear and temperature conditions[3,4]. The result is a homogeneous and less fragile filament. MgSt was added to improve the filament flowability during the extrusion process[5] . The filaments were produced by hot melt extrusion (HME) at 134, 140 and 145 °C. Different filament formulations showed modified physical and chemical properties. The following TPS filaments: 3/2 phr CA/MgSt; 3/2/2 phr CA/MgSt/MMT prepared showed potential for printability. Methyl sulfonyl methane (MSM) at 2.5 phr was loaded into the latter formulation. Loaded TPS filament showed good structural homogeneity, higher flexibility and low brittleness than the previous ones. They showed a good hydration capacity. Mechanical and printability studies are ongoing.

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METAL-ORGANIC FRAMEWORK@CLAY HETEROSTRUCTURES FOR SUSTAINABLE WATER APPLICATIONS

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Fibrous clays, like sepiolite, are an ideal platform to immobilize functional nanoparticles [1] to produce novel materials with promising performances at lab scale that present a lack of conformation and integration in different processes towards industrial application. In these materials, the fibrous clay plays a key role to assemble the nanoparticles and, in certain cases, to reach specific processing of the resulting systems.
Metal-organic framework (MOF) is a new class of porous materials with high performance surface properties. MOFs are an exceptional class of materials that have attracted much attention since their discovery 30 years ago. [2] These materials are formed by the self-assembly of metal or cluster of metals interconnected with organic molecules typically by coordination bonds, known as linkers. Their synthetic versatility leads to an enormous amount of possible combinations of metal nodes and organic linkers and results in many different crystalline structures, chemical compositions, particle size and morphologies, which make them suitable for a number of different industrially relevant applications, such as gas separation, storage, catalysis, drug delivery, and sensors among others. [2] Especially relevant are those applications based on surface phenomena where MOF has performed outstanding values breaking several word records in terms of specific surface area like gas retention storage.
In this communication we introduce the development of novel functional nanoarchitectures based on the production of MOF nanoparticles supported on sepiolite clay in view to their potential exploitation in water applications, which include rotary industrial desiccators and heat exchangers like AHT (adsorption heat transformation) systems. This study will show how the heterostructures can be synthesized, processed and integrated under sustainable conditions to reach active materials that can be directly applied in the selected industrial processes.
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TECHNOLOGICAL CHOICES OF POTTERY PRODUCTION FROM THE EARLIEST FOUNDRY OF PRE-ROMAN PADUA, NE ITALY: BLACK WARES OF THE EARLY IRON AGE IN THE SOUTHERN VENETO

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One of the earliest known settlements of Pre-Roman Padua, Veneto region (north-eastern Italy) was located in the very centre of the present-day city, strategically positioned near the river that then crossed the proto-urban area of Padua. The archaeological excavations accomplished between 2000-2001 revealed structures related to craft activities (copper and pottery workshops) and residential areas datable from the late 9th to the 1st century BCE [1].

The potsherds from the Early Iron Age found at the site included coarse and fine wares, chiefly corresponding to cooking, table, storage and transport functional class, that shown textural and compositional similitudes with other pottery productions located nearby Padua [2]. Many of the pots found were composed by very dark-colored ceramic bodies that corresponded to a specific ceramic class typical of the Veneto repertoire [3]. Such pottery has been study with a multi-analytical approach, consisting in macroscopic and petrographic descriptions as well as mineralogical and geochemical analysis, in order to define the provenance issues and the technological choices.

Whereas the coarse wares shown heterogenous textured bodies and brown hue smoothed surfaces, the fine wares have very uniform textured bodies and black hue polished surfaces. Many of these very dark-colored pots correspond to a local pottery production that used common geo-resources, consisting in illitic-chloritic clays rich in quartz and alkaline feldspars. Firing regime conditions with a wide range of maximum firing temperatures (always < 950 °C) and consistent with pit firing methods were adopted. For the manufacturing of the fine wares, the purification of the raw clays and/or the tempering of the clay pastes with diverse grain-size silica-rich inclusions were accomplished. Besides, very specific procedures were adopted for the production of other black fine wares, such as the tempering of clay pastes both with silicate and carbonate inclusions and with sparry calcite crystals and the adoption of low firing temperatures (< 700 °C).

The very specific procedures adopted for the production of the black fine wares, may point out different local/regional productions and/or the adoption of specific technological choices within the same production. The location of specific potsherds in the site may also point out the regional trade of fine wares during the Early Iron Age in the southern Veneto territory.

This research has been funded by the Project of Excellence CARIPARO (Call 2021) “The earliest foundry of Pre-Roman Padua” (VIDA_ECCE22_01).

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CALCINED CLAYS FROM SECONDARY RAW MATERIALS FOR CEMENT PRODUCTION

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There are major challenges which the cement industry and the entire cement and concrete value chain are facing in their quest for climate neutrality. This is due to the fact that large quantities of CO_2 are released in the production of cement and its preliminary product, cement clinker. The large-scale industrial transformation processes impact not only the future technology of cement production, but also the availability of primary raw materials. Resources like fly ashes and granulated slag, which were used in great quantities during the last decades, are not going to be available in the near future anymore and have to be replaced.
It is assumed, that Germany will need 4,3 Mio t of calcined clays in 2050 as a reactive main component of cement [1]. Aside from production of calcined clay from primary clay deposits, calcination of secondary deposits from gravel and sand production or waste rock piles are spotlighted for a sustainable cement production. Generally, clays with low ceramotechnical properties are appropriate for cement production. In view of the future increase in demand for calcined clays in the context of the decarbonization process, it will be necessary to build or retrofit significantly more rotary kilns and flash calciners for clay calcination.

In a research project, samples from various primary and secondary clay deposits were chemically and mineralogically characterized and calcined at different temperatures. Reactivity determinations using different methods like ASTM C 1897-20 (heat of hydration and chemical bound water at 7 days of hydration) and reactive SiO_2 (acc. EN 197-1) led to the selection of ten samples that were used for performance tests of laboratory composite cements with 25 and 40 mass % of calcined clay respectively. Four of these cements with 25 mass % clay and two with 40 mass % clay were also used for durability tests of concrete.
The results show, that most of clay-containing raw and waste materials, that have clay contents of more than 50 mass %, were suitable for the production of calcined clays for the cement industry. These clays included filter cakes, plastic clays, mudstones, and waste rock. Even with the usage of these broad range of calcined clays, the production of composite cements according to the requirements of the European cement standards was possible.

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MUSSEL SHELLS AS ALKALI-ACTIVATED BINDER FOR GEOMECHANICAL STABILISATION

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The use of alkali-activated binders (AABs) to improve engineering properties of clayey soils is a novel solution, an alternative to the widespread improvement based on the use of conventional binders such as lime and cement. The development of these binders reduces carbon dioxide emissions, costs and permits the reuse of waste products of different origins (i.e., natural and artificial pozzolana, metallurgical waste or CaCO3-rich waste limestone). Alkali activated binders are generally synthesised by reacting silico-aluminate precursors such as calcined clay, natural pozzolans, fly ash or blast furnace slag with an alkaline solution made of sodium hydroxide (NaOH) and sodium silicate (Na2SiO3). Despite the growing interest in AABs, limited research has focused on the alkaline activation of CaCO3-rich natural materials and waste limestone as precursors in the synthesis. The presence of limestone in these binders modifies the molecular structure of the reaction products and increases their underwater stability. Alkaline activation of limestone results in the formation of crystalline carbonate phases such as pirssonite, gaylussite, portlandite or thermonatrite, which are finely intermixed with amorphous calcium silicate hydrates (CSH), silica gel, calcium-silicate gels incorporating sodium (NCSH) and/or sodium silicate gels (NSH).

In the present work, an experimental investigation of the chemo-mineralogical evolution and mechanical behaviour of an AAB based on the activation of mussel shell powder (MSP) has been developed. Mussel shells are a widespread waste from the aquaculture industry. Their global production for human consumption is about 14% of the total marine production. Rich in calcium carbonate (95%), shells are a non-biodegradable type of residue, which is difficult to compost and requires long and expensive disposal. This research is moving towards a virtuous reuse of such residues, following the encouraging results obtained by the authors when MSP was used as a partial replacement for cement in the mechanical stabilisation of marine sediments. Two different alkaline solutions were considered for the treatment of MSP (i.e., NaOH_12M solution and Na2SiO3+NaOH_12M solution). For both mixtures, the reactivity of MSP was monitored over time using X-ray Diffraction (XRD) and Scanning Electron Microscopy (SEM). The mechanical behaviour of the binders was monitored over curing time by Uniaxial Compressive Strength tests (UCS). The mineralogical analyses revealed a high reactivity of the alkali-activated MSPs as a calcium source, promoting the precipitation of new crystalline carbonate hydrated phases. SEM observations showed a progressive transformation of MSP, evidenced by a coating of gel-like phases on the particle surface and crystallisation of carbonate phases. The UCS of the alkali activated MSP was found to increase with curing time, i.e., in line with the chemo-mineralogical evolution of the binders. For a given curing time, the addition of a sodium silicate solution resulted in a higher increase in the compressive strength of MSP compared to the use of sodium hydroxide solution alone.

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GEOTECHNICAL BEHAVIOUR OF TREATED SEDIMENTS WITH MUSSEL SHELL POWDER AND CEMENT: GEO-CHEMO-MECHANICAL INTERACTION PROCESSES.

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The report presents the results of an experimental research on the geo-chemo-hydromechanical stabilisation of fine sediments dredged from a recharge basin in the port of Taranto (Ionian Sea, Italy). This research was carried out in intensive collaboration with ETH Zurich and Italcementi HeidelbergGroup and supported by a MIUR- PON RI DRSATE PhD grant.

Like many port areas worldwide, Taranto faces the problem of disposing of two materials that are currently considered waste: dredged sediments and mussel shells. In Europe, about 150 million m^3 of sediments are dredged every year. Mussel shells is a bio-waste that is currently disposed of in large quantities (about 230 kt/year in Europe) through complex and expensive processes in landfills.

The stabilisation of marine sediments by hydraulic binders is associate with environmental issues. The presented study proposes the treatment of fine sediments by innovative and eco-sustainable solutions. Specifically, CemShell binders, originally produced by partially replacing commercial cements with mussel shell powder are proposed for stabilisation of the dredged fine sediments. Results of this research will be presented which were obtained through a multi-scale and multiphysics experimental programme using three different types of commercial cements: Type III Termocem Green Blast furnace, Type I traditional Portland 52.5R and Sulfoaluminate cement as well as using CemShell and biochar as a further additive with adsorption capacity (CemShellBio). The mechanical and chemical-mechanical effectiveness of the different stabilisation solutions was investigated for both unpolluted and artificially polluted sediments.

Complete information on the sediment behaviour at both micro- and macro-scale in the natural and treated state were obtained. The investigation focused on: i) Chemical, geochemical and thermal, ii) microstructural and iii) geotechnical characteristics of the natural and treated geomaterials.

The integration of the microstructural, geotechnical, and geochemical/chemical data produced a global picture on the effects of the chemo-mechanical interaction processes on the geotechnical behaviour of both untreated and treated sediments. This study provides useful insights towards original, effective, and sustainable stabilisation solutions in the field of soil waste management.

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MINERALOGY AND PALEOENVIRONMENT OF ASSOCIATED LITOFACIES TO LAKE PELLEGRINI NA-BENTONITE DEPOSIT (NEUQUÉN BASIN, ARGENTINA)

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The Na-bentonites from the Lake Pellegrini deposit occur in the Upper Cretaceous Allen Formation in the Neuquén Basin (Argentina). The bentonites are associated with claystones, mudstones, siltstones and hetherolitic facies that have been previously interpreted as perimarine to continental. In this paper we study the textural features and composition of the facies associated with the bentonites. The aim is to better understand the sedimentological context and consequently the conditions involved in the formation of the authigenic Na-smectite. The mineralogical study has been carried out by XRD and the description of the lithofacies by petrography from resin embedded thin sections.

The siltstones are dominated by phyllosilicates (40-56%) with subordinate quartz and plagioclase (>10%) and traces of potassium feldspar and gypsum. The presence of clinoptilolite-heulandite stands out, reaching 7%. Petrographically have been identified: muscovite, biotite, opaques, rutile, monazite, garnet, zircon and volcanic rock fragments. The clay minerals can be microlaminated, acting as a cement enclosing the skeletal components.

The mudstones/claystones are dominated by phyllosilicates (60-82%) with quartz (14-30%) and to a lesser extent (<5%) potassium feldspar, clinoptilolite-heulandite and gypsum. Petrographically, muscovite, biotite and volcanic rock fragments were identified. The clay minerals may be laminated or with a groundmass aspect, the latter sometimes containing fragments of the laminate. Bioturbation (burrows) may be filled with detrital grains.

The heterolithic facies are dominated by phyllosilicates (33-67%), quartz (9-33%) and plagioclase (6-20%), with lower contents of potassium feldspar (<5%) and clinoptilolite-heulandite (2-6%). Petrographically, muscovite, biotite, zircon and volcanic rock fragments were identified. Occasionally, broken mudstone laminae are observed enclosed by a coarser detrital component (very fine-grained sand to silt).

The three facies described, overlying or including the bentonite beds, are characterized by fine-grained siliciclastic facies, thinly laminated, with parallel and cross-beddings. Flaser, lenticular and wavy lamination are commonly observed, indicating alternation of tractive and settling processes, and the presence of clay-chips indicates reworking of previous mudstones during higher energy periods. All these features are characteristic of mixed sand-mud tidal flats where bentonite beds were formed under low energy conditions probably in ponded areas (lagoon) toward the continent.

In all lithofacies analysed, dioctahedral smectite with interlaminar Na is practically the only clay mineral identified. This implies an authigenic formation of the mineral from volcanic rock fragments or even from other inherited clay minerals, the only phyllosilicates that remain unaltered being the micas. The presence of marine waters justifies the sodium character of smectite. Under diagenetic conditions, zeolites and gypsum would also form.

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FACTORS INFLUENCING THE SUITABILITY OF CARBONATES-RICH CLAYS AS PRECURSORS FOR AABS

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The study on the suitability of natural polymineral clays, rather than pure kaolinite, as aluminosilicate raw materials for the synthesis of AABs is of relevant interest in the perspective of the sustainable use of widely available raw materials. Although very abundant in the Earth'sn crust, polymineral clays are characterized by very high chemical and mineralogical variability, which largely influences their potential reactivity for AAB purpose. Due to the mineralogical complexity of the most common 1:1 and 2:1 clay minerals, the understanding both of pre-activation treatments (thermal, mechanical, chemical), and of the factors influencing clay reactivity, phase assemblages and properties of final products, needs nowadays to be further improved. This study deals with the evaluation of the suitability of carbonate-bearing multimineral clays as raw material to produce AABs. As the key issue in the reactivity of carbonate-bearing multimineral clays is not only the quantitative content of minerals but also the identification of the optimal clay processing methodology to increase their reactivity, the results of different clays activation methods (i.e. thermal, mechanical activation and a combination of them), are discussed in this study [1]. Analogously, the influence of the type and concentration of activating solutions, as well as of curing parameters on properties and reaction products of samples obtained from different clay processing methods are also assessed [2]. Furthermore, the partial substitution of carbonate-rich clays with industrial by-products such as F fly ashes, ground granulated blast furnace slags and water potabilization sludges, is explored as a solution for reducing the use of natural non-renewable resources and, at the same time, to compensate the energy consumption related to the pre-treatment of the clay [3]. The best results are obtained for thermally treated samples which show as the main reaction product a mixture of C-A-S-H/(N, C)-A-S-H type gel depending to the availability of Ca, and reach compressive strengths over 30 MPa after 28 days. Higher (6 or 8 M) activator concentrations gave a more compact matrix than those prepared with 4 M NaOH [2]. In the case of mechanical activated clays, the best results were only obtained using sodium silicate as activating solution, reaching up to 20 Mpa. The paste composed by 1:1 weight proportion of pre-treated clay and blast furnace slags showed the most compact matrix, achieving the remarkable mechanical strength value of 45 MPa after 28 days [3]. Based on the obtained results, carbonate-bearing polymineral clays are a promising mineral source for AABs, but due to their mineral complexity further studies are needed to optimize compositional and technological parameters in the perspective of their adoption for AABs preparation.

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THE MECHANISM OF ADSORPTION-INDUCED EMISSION OF PSEUDOISOCYANINE CATION IN SMECTITE COLLOIDS

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Adsorption of cationic dyes on the surfaces of clay mineral particles can lead to significant changes in their photophysical properties, which can be observed as shifts in spectral bands' maxima, enhancement, or emission quenching.[1] Optical parameters are most often influenced by solvation, intermolecular interactions, or the structure of the molecules.[2] Therefore, the most common causes of changes in spectral properties in hybrid systems are primarily dye molecular aggregation, energy transfer, or changes in the geometry of molecules. Recently, the phenomena of aggregation-induced emission as well as adsorption-induced emission, are increasingly coming to the fore.

In this work, we investigated the photophysical properties of pseudoisocyanine (PIC) dye in colloidal dispersions of five smectites at variable PIC/smectite ratios. Under specific conditions, the hybrid samples exhibited strong fluorescence, which was attributed to the monomeric dye species. For the PIC, the fluorescence of J-aggregates at ≈570 nm is typical and well-studied, whereas a strong emission from monomers at ≈535 nm has been observed for the first time. Theoretical and computational chemistry methods were used to analyze the vibronic structure of the spectra and explain the strong luminescence of the PIC monomer[3]. In an aqueous solution, the bending of the molecule supports the nonradiative deactivation of the excited state. Adsorption of PIC molecules on the smectite particles caused the change of the dihedral angle between pyridine subunits of the PIC molecule, which hinders the nonradiative deactivation channel and promotes emission.

Ongoing research indicates that a similar phenomenon can be expected for other types of dyes. An important role is played by the selection of smectite and hybrid system composition.

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ASSESSING MINERAL SURFACES FOR BIOMARKERS PRESERVATION POTENTIAL: A MOLECULAR MODELLING STUDY ON NONTRONITE AND AMINO ACIDS

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The quest to discover signs of ancient life on Mars faces a multitude of challenges, one of which is the harsh and inhospitable environment on the planet. Mars is bombarded by ionising radiation, and the oxidising molecules in the regolith and atmosphere can rapidly break down any exposed biomolecules. Despite this, research has shown that certain mineral surfaces can adsorb and effectively protect these biomarkers from degrading conditions. Therefore, mineral matrices have become a prime target location in the search for biomarkers on Mars. [1] We conducted a comprehensive molecular modelling study to categorise the capacity of two nontronite surfaces to selectively concentrate 21 different proteinogenic amino acid species. Amino acids are prevalent on Earth and in extra-terrestrial objects, which renders them an intriguing topic for a showcase study on biomarker preservation. Our findings indicate that the adsorption behaviour of amino acids is dependent on the structural composition of the clay, as well as the counterions. This work demonstrates the potential of theoretical screening studies in evaluating the preservation potential of mineral surfaces. We believe that this approach can be advantageous in evaluating the preservation potential of a sampling site based on its geological properties.

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FABRICATION OF GRAPHITIC CARBON NITRIDE@COBALT ALUMINIUM-LAYERED DOUBLE HYDROXIDE COMPOSITE/PVA HYDROGEL FOR PHOTOCATALYTIC HYDROGEN PRODUCTION FROM WATER SPLITTING REACTION

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The design of an efficient photocatalyst for hydrogen production from water splitting reaction is one promising strategy to provide renewable energy and reduce environmental problems. To enhance the activity of photocatalyst, here, the composite of graphitic carbon nitride (g-C_3N_4) and CoAl-layered double hydroxide (CoAl-LDH), g-C_3N_4@CoAl-LDH, was fabricated by facile weight-impregnation method and then combined with a polymeric matrix poly(vinyl alcohol) (PVA) to form a g-C_3N_4@CoAl-LDH/hydrogel to increase dispersibility of the catalyst and made it more convenient to be recycled. After compositing with g-C_3N_4, the diffraction intensities of *(003)* and *(006)* planes increased together with the presence of the *(002)* reflection plane due to g-C_3N_4, indicating the increment of crystallinity of CoAl-LDH, which could enhance the photocatalytic activity by facilitating charge transfer from the bulk to the surface [1]. Besides, the specific surface area of g-C_3N_4@CoAl-LDH (84 m^2/g) was increased compared to that of g-C_3N_4 (24 m^2/g) and CoAl-LDH (51 m^2/g). The increase of the surface area could provide more active sites and increased electron carriers efficiency [2]. The photocatalytic hydrogen production of the synthesized products was evaluated under UV-visible light irradiation using the mixture of 30 %v/v methanol-water as a sacrificial agent. The g-C_3N_4@CoAl-LDH showed the H_2 production of 13.38 μmol, which was enhanced by 3 times compared to the bare CoAl-LDH (4.71 μmol). In addition, the good light transmittance and charge separation of the g-C_3N_4@CoAl-LDH/hydrogel exhibited the highest H_2 production of 50.93 μmol. The increase of the photocatalytic activity of the hydrogel was mainly due to the synergistic effect of both g-C_3N_4 and CoAl-LDH, in which dispersion of g-C_3N_4@CoAl-LDH over hydrogel surface reduced electron-hole recombination [3].

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ZNGA LAYERED DOUBLE HYDROXIDE PREPARED BY EPOXIDE ROUTE FOR EFFICIENT PHOTODEGRADATION OF BISPHENOL A

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With the rapid development of industry in recent decades, different types of pollutants are annually discharged in large quantities into industrial wastewater, leading to a serious threat to environmental sustainability. Moreover, some organic pollutants known as emerging pollutants, like bisphenol A (BPA) are resistant to conventional treatment methods. Consequently, non-conventional methods such as photocatalysis must be implemented. Layered double hydroxides (LDH) with the general formula $[M(II)_{1-x}M(III)_x(OH)_2]^{x+}[A^{n-}]_{x/n}\cdot yH_2O$, $0.20 \leq x \leq 0.33$),[1] have been described as promising photocatalyst for degradation of pollutants because of their tunable properties such as distribution of metal cations into the layer, surface hydroxyl groups, anions within interlayer spaces.[2,3] A control of the composition and the morphology or their association with others semiconductors allowed them to improve their photocatalytic activity strongly. This study investigated the efficiency of Zn_2Ga LDH and its derived mixed oxides for BPA photodegradation and the influence of many parameters discussed. The Zn_2Ga-LDH catalyst synthesized using an epoxide route and the derived metal mixed oxides generated at different temperatures were deeply characterized by XRD, XAFS, FTIR, SEM, TEM, TGA, and BET before and after photodegradation highlighting partial reconstruction of the LDH during the process. Many physicochemical parameters such as the catalyst concentration, the pH of the solution, the addition of oxidant (PS: persulfate) at different concentrations, and the nature of the interlamellar anion were investigated to define the optimized conditions. Finally, the Zn_2Ga-CO_3 LDH matrix calcined at 300°C and tested in the optimal conditions for the system UVA/Catalyst/PS process showed the best photodegradation efficiency, leading to a total photodegradation of BPA after only 110 min of irradiation and a synergy factor of 4.6 times compared to the individual processes. To go further in the description of the degradation process the use of chemical trapping agents allowed the identification of the reactive species generated in the catalyst/PS system, showing that 50% of the degradation efficiency can be attributed to the presence of superoxide radicals $O_2^{\cdot-}$

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CO2 ELECTROREDUCTION EFFICIENCY OF VARIOUS CU BASED LAYERED DOUBLE HYDROXIDES

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The emission of CO_2 by industrial action seriously impacts our environment, requiring us to consider strategies to reduce the emitted CO_2 into the atmosphere. The electrochemical reduction of CO_2 (CO_2ER) into molecules such as CO, HCOOH, CH_3COOH, and CH_4 is one of the many ways to valorize CO_2 as fuels or chemicals[1]. Not only could this help reduce pollution, but it would also convert CO_2 into valuable products to use as feedstock. Amongst the different heterogeneous catalysts investigated, Cu-based electro-catalysts for CO_2ER have attracted much attention due to their unique advantages including hydrocarbon production and product selectivity.[2]

Recently, Cu-based LDH ($[M(II)_{1-x}Al(III)_x(OH)_2]^{x+}[A^{n-}]_{x/n}\cdot yH_2O$, $0.20 \leq x \leq 0.33$), with M(II) = Cu and M(III) = Al have particularly been investigated for CO_2ER. These matrices appear as promising electrocatalyst promoting the electrochemical conversion, in galvanostatic conditions, of CO_2 to CO and HCOOH[3]. A morphology control allowed to improve the catalytic activity by tailoring the structure of active sites and increasing the surface area/number of active sites.[4]

Herein, the electrochemical efficiencies towards CO_2ER of a series of CuAl-LDH matrices were compared. The LDH materials were synthesized by both the coprecipitation and the polyol method and characterized using powder X-ray diffraction (PXRD), Infrared spectroscopy (FT-IR) and scanning electron microscopy (SEM). Electrochemical characterization of the Cu-LDH modified electrodes was carried out following a specific protocol by linear sweep voltammetry and cyclic voltammetry showing that an electrochemical activation of the Cu-LDH occurred at E^{app} >-1.4 V, leading to an enhancement of the electrochemical signal of the copper redox couples, addressing to more accessible catalytic sites and to an increase in current under CO_2 and hence CO_2 activation. The influence of the LDH composition that is the Cu amount into the layer, the presence of Mg or Zn in a ternary layer composition, and the nature of the interlayer anions were investigated showing that the composition $Cu_{1.5}$ $Mg_{0.5}Al$-CO_3 provides the highest faradaic yield of HCOOH formation, reaching 57%.

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THE PHASE COMPOSITION STUDY OF HYDRAULIC BINDER PREPARED FROM CALCINED CLAY, ANHYDRITE AND LIME

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Nowadays, when the emphasis is on ecology and reduction of CO_2 emissions, the preparation of a new hydraulic binder that could at least partially replace the high-emission Portland cement is becoming a topical issue. This work deals with phase composition study of the new hydraulic binder created from metakaolin calcined clay, anhydrite II and lime [1] . It may become an alternative to Portland cement in selected applications thanks to its lower carbon footprint, which is caused by lower firing temperatures of its raw materials [2]. In addition, the possibility of preparing hydraulic binder using by-energy products (CCPs) is offered for the future usage [3].

To be able to use the binder in the construction industry, it is necessary to characterize its phase composition and properties over time. The aim of this work was to prepare a number of pastes with varying composition of calcined clay, anhydrite II and lime, using the same water to binder ratio. Firstly, the input raw materials were characterized; the initial composition (XRF, XRD), particle size distribution and density were determined. After that, cubic-shape specimens were prepared, properly cured and the phase composition was measured using X-ray diffraction with HihgScore Plus software with evaluation after 28 and 180 days. The mineralogical phases and the amount of the amorphous phase, calculated using an internal standard, were monitored. Special attention was paid to the content of ettringite as the main binder crystalline phase.

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DEFORMATION DEPENDENT WATER RETENTION CURVES FOR THE REPRESENTATION OF MEMORY EFFECTS IN BENTONITES

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Strong hydromechanical (HM) coupling effects govern dilatancy-controlled gas flow in highly compacted, saturated clay-rich materials. Since clay-rich materials often play a role in the utilisation concept of a repository for radioactive waste (host rock, geotechnical barrier), the prediction of the HM behaviour of the material, in particular with regard to the flow regime, is of great importance for its safety analysis. An important process parameter in this context is the gas entry pressure that characterises the onset of infiltration of a gas phase into a saturated porous medium. Gas entry pressure corresponds to the capillary pressure at the maximum pore throat and influences the shape of the water retention curve.

The gas entry pressure can be determined by laboratory and in situ measurements. Laboratory studies show that the value is likely to depend on the void ratio of the material, but is often assumed constant. In addition, experimental observations show long-lasting deformation-dependent changes in gas entry pressure after gas flow tests have been performed. This suggests that dilatancy-controlled gas flow can cause microstructural damage that increases permeability but also decreases gas entry pressures, affecting the water retention curve and thus relative permeability.

We have developed a constitutive relationship between material strain and gas entry pressure for confined bentonite. The constitutive equation represents the expansion of pore space as a result of dilatancy controlled gas flow with volumetric and plastic strain. By using volumetric and plastic strains, short and long term effects are investigated which allow the simulation of memory effects of path dilatation. The developed approach is tested using measurements from gas flow tests through bentonite, with an emphasis on simulating repetitions of gas flow tests on the same material. Characteristics of dilatancy-controlled gas flow, such as material memory effects, can be better represented by using this model for bentonite. With additional heterogeneous distributions of material properties, including the initial gas entry pressure, preferential pathways typical of dilatancy-controlled gas flow in bentonite can be simulated.

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SPECIFIC YET REVERSIBLE PHOSPHATE ADSORPTION TO AMORPHOUS NANO IRON-OXIDE DECORATED CLAYS

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Phosphate fertilizer is in growing demand, however, the declining natural resources and the secondary environmental pollution from overuse and effluent disposal necessitate the development of sustainable phosphate (P) removal methods that allow for proper nutrient recovery with minimal energy and chemical strains.

This study highlights the ability of montmorillonite (MMT) clay decorated with amorphous iron oxide nanoparticles (FeOx-MMT) to specifically adsorb P from water and also allows for easy regeneration of the surface and potential use as fertilizer when spent. The nano-sized iron-oxides deposited on the MMT show high adsorption affinity towards P due to the increase in reactivity and surface area. Batch experiments showed rapid adsorption with equilibrium reached after ~1.5 hrs. at neutral pH. Isotherms were fitted to the Langmuir model and capacity was determined to be 5.63 mg-P/gr composite or 92.3 mg-P/gr-Fe. The reaction was most efficient at acidic pH (4) and high ionic strength. Desorption experiments revealed very small hysteresis and high reversibility of the reaction even at neutral pH. Continuous column experiments were performed and compared to a commercially available product, granulated iron hydroxide. The results highlighted that our composite was able to remove higher P concentrations per g Fe and was far more regenerable than the commercial alternative over five cycles. Although further optimization and up-scaling is needed, Fe-MMT has true potential as a specific, low-cost, and regenerable P-sorbent.

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SELF-ASSEMBLING OF ANISOTROPIC NANOCLAY GELS FOR DRUG DELIVERY

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Emulating the three-dimensional (3D) organization of biochemical cues present in the native cellular microenvironment is likely to be key to generate biomaterials with distinct levels of functionality. However, despite advances in tissue engineering (TE), building structures incorporating stable 3D-micropatterning of biochemical cues and that preserve their resolution with an increase in size has proven challenging[1].
Nanoclay-gels have established potential in TE due to their capacity to adsorb, retain and localize proteins bioactivity[2]. In this study we report a unique property of clay nanoparticles to self-organise in protein solutions via reaction-diffusion process that supports localised delivery of 3D protein gradients with enhanced bioactivity for bone regeneration.
Suspensions of a synthetic smectite clay (Laponite®), were exposed to a solution containing biomolecules and ions present in blood plasma to support the self-assembly of 3D micro-patterned gels through a reaction-diffusion process. To characterize the phenomenon, the assembled structures were tested for their ability to pattern fluorescently labelled model proteins under different conditions known to affect diffusion process, including pH, ionic strength, incubation time, protein concentration and protein physicochemical properties. The structures were analysed using a range of imaging techniques, including brightfield, fluorescent, polarized light and electron microscopy. The bioactivity and safety of a structure containing a BMP 2 gradient was assessed in a 60-day murine subcutaneous implantation assay.
Nanoclay/protein gel develops an internal degree of order that allows templating punctuated or gradual 3D gradients of all proteins. By changing parameters known to affect diffusion rate at the assembly step, such as concentration, ionic strength, incubation time and temperature, it was possible to demonstrate control over the spatial localization of the proteins. With this method is possible the assembly of structures at scale with a range of dimensions (0.02 – 1cm) and shapes (droplets, cylinders, strings) while preserving the resolution of protein patterning. The assembled structures displayed a radial birefringence under polarized light, indicating the presence of periodical arrangements of nanoparticles. Finally, the *in vivo* study revealed that punctuated localisation of BMP-2 within the scaffold provided the potential to control the spatio-temporal formation of mature bone.
We demonstrated for the first time the potential to harness interactions between clay-nanoparticles and biomolecules present in physiological fluids to design scaffolds with complex biochemical gradients, dimensions, and shapes for bone with clinical relevance.
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ULTRAMAFIC ROCKS FROM CABEÇO DE VIDE (PORTUGAL): A UNIQUE ANALOG FOR UNDERSTANDING SERPENTINIZATION ON MARS

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Based on the European Astrobiology Roadmap, the sites associated with serpentinization processes, both on Earth and throughout the Solar System, are becoming increasingly compelling for the study of the origin of life. As the crust of Mars and Earth is largely composed of mafic and ultramafic rocks, these observations led to an increased interest in the origin of life, both terrestrial and extraterrestrial.

Serpentinization is a geochemical process in which olivine is hydrated to form serpentine, magnetite and brucite. The oxidation of Fe2+ in olivine leads to the production of H2 and can be metabolically exploited by microbial life. Additionally, H2 can drive the synthesis of organic molecules in Fischer-Tropsch-type reactions, such as methane. This is of vital interest for the global research community focused on the origin of life given the episodic CH4 plumes and detection of organic molecules in Gale Crater on Mars. The recent Mars rover missions allow to study, for the first time, the habitability conditions and possibility of life on another planet with in situ data. Environments prone to serpentinization are of particular interest, because they imply the presence of several of the “key elements” for life as we know it. Also, for this reason, Jezero Crater has been selected as the landing site for a recent rover in NASA’s Mars Exploration Program, the Perseverance (landed on Mars, February 18, 2021). Therefore, the knowledge of the detailed mineralogy of suitable terrestrial serpentines is crucial for interpretation of the data acquired on Mars and contribute to the research of existence of past-extant life on Mars.

Because of its accessibility and active serpentinization, hydrothermally altered mafic–ultramafic complex from Cabeço de Vide (CdV), Portugal, provides a unique opportunity for the investigation of continental serpentinized rocks on Earth, emphasizing the fact, that CdV ultramafics are not ophiolites, but associated with the intrusion of mafic/ultramafic pluton.

In this context, CdV is proposed as excellent mineralogical environment to study as Mars analog, as serpentine detections have been reported at the Mars 2020/Perseverance rover landing site, Jezero Crater. Moreover, besides serpentines, presence of pyroxene, olivine, smectite and carbonates in CdV and Jezero Crater, points out on mineralogical similarities of both sites.

The main aim of this work is detailed petrography of the CdV ultramafic rocks from 22 drill cores (between 30 and 124 meters deep) obtained from AC1 and AC2 CdV boreholes, in what concerns both textural, mineralogical and crystallochemical features, allowing to put forward a genetic model for the serpentinization process. Moreover, a metagenomic approach was applied targeting 16S rRNA gene in selected drill cores to identify taxonomical groups belonging to Bacteria and Archaea preserved in CdV serpentines. The findings of this work will provide greater context on the serpentine bodies on Earth as an important approach to understand the geochemical processes on Mars.

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MODELING ION-EXCHANGE REACTIONS OF MAJOR CATIONS OF NATURAL WATERS (NA, K, CA, MG AND H) AND TRACE ELEMENTS (RA AND PB) ON SWELLING CLAY: THE CASE OF BEIDELLITE.

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Reactive transport codes are widely used to predict the fate of both major and trace elements in the environment, as to explain the mobility's of nutrients in soils and those of contaminants after anthropic impact. In these contexts, sorption of cations in rock and/or soil constituents need to be modeled. Swelling clay minerals, as smectites, are ubiquitous in numerous environments, and due to their high cation exchange capacities have a key role in the control of cations mobility in many surface or subsurface media. However, if numerous studies have been published about sorption properties of various smectites or bentonites materials, (i) a complete set of experimental data associated to (ii) a coherent thermodynamic database allowing to describe the ion-exchange properties of a swelling clay mineral for both trace and major cations of natural waters remain scarce. Moreover, most of the published studies deal with reference montmorillonite materials, and very few used swelling clay mineral having tetrahedral charge such as beidellite. Thus, in this study, our aim is to propose a complete set of experimental and thermodynamic data for a beidellite.

In the contexts related to acidic conditions, as acidic soils and industrial/mining impacted areas, this study reports the modeling of sorption on beidellite of major cations of natural waters, including H^+, and trace cations. This model has been built based on experimental data obtained for a smectite with tetrahedral charge, SBId-1 <0.3 µm Na-beidellite, allowing to discuss possible effects of the crystal chemistry from comparison with literature data obtained on montmorillonite. Ion-exchange isotherms were obtained for 5 majors cations of natural waters (H^+, Na^+, Mg^{2+}, Ca^{2+} and K^+) [1] as well as for trace elements such as radium (Ra^{2+}) and lead (Pb^{2+} et $PbCl^+$)[2], and were interpreted to get a database of ion-exchange coefficients based on a Gaines-Thomas convention using a multi-site approach (3 sites with the sum equal to the measured ion exchange capacity of the material). The results demonstrated the capability of our approach to interpret both major and trace elements sorption for a wide range of physico-chemical conditions (including pH and ionic strength variations) by considering a single and homogeneous ion-exchange model. Our approach does not require to use sites of low concentrations and high affinity to interpret sorption of trace elements by comparison to that interpreting major ones[2].

Both experimental and modeling approaches presented here can be used to build models that can later be integrated into reactive transport codes. This will allow a better prediction of sorption and competition between major and trace cations including H^+. Moreover, sensitivity tests have shown that the choice of the database used to model ion-exchange reactions is crucial and should be adapted based on the natural media studied.

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ASSESSMENT OF SOME PORTUGUESE BEACH CLAYEY MATERIALS USED FOR TRADITIONAL MUD BATHS

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Along Portuguese coast there is a very old and continuous tradition of mud baths empiric practices, for skin and/or bone care purposes. In general, application protocol is very simple, mixing clayey/marly materials picked on the cliffs with sea water. Some cases survive till present time. A research program has been implemented on 3 beaches (Consolação, Parede, Meco), aiming a better understanding of the properties controlling these seaside clay/mud applications. Textural, mineralogical (XRD) and chemical (XRF; SEM/EDS) compositions and a set of technological properties (pH, conductivity, specific surface area, cation exchange capacity, plasticity, abrasivity, specific heat and cooling kinetics) were assessed. A residual clay commonly used on Cucos Thermal Spa treatments was also studied for comparison purposes. All analyses and tests were carried out both in whole sample and in fine-grained size fraction (< 0.063mm) of the prepared saline mud. Studied geomaterials exhibit relative high values for clay fraction content (>50 %), specific surface area, cation exchange capacity and specific heat and adequate values for cooling rate. Smectite and irregular mixed layers illite/smectite are ubiquitous, along other clay minerals (illite, kaolinite and chlorite). Meco samples are richer in phyllosilicates (mainly smectite and kaolinite), whereas Parede are richer in dolomite and illite. All samples show significant amounts of calcium and magnesium; strontium, sulphur, phosphorus and organic matter are common in all of them. Mineralogical and technological data was submitted to Cluster and Principal Components Analysis showing that almost all relevant properties, such as cation exchange capacity, specific surface and plasticity are controlled by silicate minerals (phyllosilicates, feldspars and quartz), with the exception of abrasivity (considered not beneficial) and specific heat, both related to dolomite content. Obtained results allows to conclude that studied beach muds show suitable properties to be used on Mudtherapy/Thalassotherapy

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NANOCOMPOSITES BASED ON GLAUCONITE: INNOVATIVE CONTROLLED-RELEASE COMPLEX FERTILISERS

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Controlled-release fertilisers (CRF) are essential for the future of environment-friendly agronomic activities. Several investigations were conducted to assess the fertiliser potential using different materials, including nanocomposites, such as polymers, clay minerals, or composites of synthetic and natural substances. Compared to most synthetic products, clay minerals are cheap and readily available. Glauconite is a useful “inhibitor”, consisting of nano/micro-sized particles with high specific surface areas. It possesses surface charge and contains exchangeable structural sites (interlayer), facilitating nutrient exchange. This study uses the planetary or rim milling technique to formulate controlled-release fertilisers by the mechanochemical activation of a mixture of powdered glauconite and urea. The nanocomposites show increasing intercalation between ammonium and glauconite. X-Ray Diffraction parameters, SEM images, FTIR peaks and thermogravimetric analysis record the systematic crystallographic changes of the composites.

Three different interrelationships between mineral and urea are as follows: (i) ammonium from urea is intercalated into the interlayer space of mineral, (11) urea substances are absorbed into the micropore space between clay micro-flakes, and (iii) adsorbed urea in the form of films incorporating micro-aggregates. The amount of intercalation between ammonium and mineral achieves by planetary and ring milling. However, the external coating of micro-aggregates thickens with the time of milling operation.

Soil leaching tests, spanning over 60 days, reveal the release of nitrogen and potassium initially at a faster rate, which slows down later. Nitrogen is released from the composites in three stages. In the first stage, the external coating of the composite releases nitrogen in the first few days, and the absorbed nitrogen leaches in the second stage after twenty-one days. Finally, the intercalated portion releases nutrients. Nanocomposites based on glauconite release the potassium in the leached solution, initially at a faster rate, slowing down after seven days. As a result, the composites leached nutrients at a slower rate than the urea sample.

However, plant height growth using urea or the nanocomposite remains broadly similar. Introducing the nanocomposites within weakly acidic soil boosts the seeding and growth of oat and wheat. The glauconite-based nanocomposite is found to be an effective fertiliser for promoting plant growth. The composites and traditional urea are equally effective fertilisers for crop production (dry weight and plant height). Further, it is an environment-friendly option because of the slow release of nutrients. Besides, glauconite-urea nanocomposites are complex multifunctional fertiliser that releases multiple nutrients simultaneously.

Therefore, the composites are classified as a controlled-release fertiliser, saving 10-50% of the urea. Further, the simultaneous release of potassium makes the composite a complex release fertiliser.

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CLAY MINERALS FORMATION WITHIN MARINE OOIDAL IRONSTONE DEPOSIT IN THE WESTERN SIBERIA

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The metal source and processes of iron mobilisation in Phanerozoic ooidal ironstone deposits remain controversial. Clay minerals are an essential component of ooidal ironstones, forming various mineral phases and associations. However, little is known about the spatial compositional variation associated with marine ironstones. This work aims to understand the processes of metal formation in the Cretaceous-Paleogene West Siberian basin based on the origin of clay mineral matrix in ooidal ironstones.

The Bakchar deposit is the main deposit of the West Siberian iron ore basin. The Bakchar succession consists of Upper Cretaceous (Kuznetsovo, Ipatovo, Slavgorod, Gan'kino) and Paleogene (Lyulinvor) Formations. The ore horizons comprise ooidal and peloidal ironstones, glauconitolites, glauconitic sandstones and siltstones, while the intervening siliciclastic intervals are composed of claystones, siltstones, sandstones and gritstones. The main phyllosilicates in ironstone and associated rocks are represented by illite, illite-smectite, kaolinite, montmorillonite, nontronite, saponite, beidellite, berthierine, and chamosite. Mineral and chemical composition of the clay fraction changes from the proximal to the distal zones of the ore deposit. The proportion of illite-smectite and montmorillonite in the clay fraction increases in the distal zone. The kaolinitisation in the ironstone matrix demarcates the proximal fluid flow zones, while smectitisation and montmorillonitisation characterise intermediate and distal zones, respectively. The ratio of 1M type of phyllosilicates (kaolinite) to the primary swelling 2M type of phyllosilicates (illite, illite-smectite, montmorillonite, nontronite, saponite, beidellite) varies in distal, intermediate and proximal zones. This mineral index (K/M) varies from 1.1 to 8.0 in the proximal zones. This ratio ranges from 0.6 to 1.4 and 0.2 to 0.7 in the intermediate and distal zones.

The chemical composition of the smectite group changes under the influence of metal-saturated fluid flow. The proximal zone shows the predominance of nontronite. An increase in the proportion of iron in the octahedral positions is the main characteristic of smectites in the proximal zones. The cross-plot of Fe versus the sum of Mg and Al in octahedral positions shows an inverse correlation between the content of Fe and other metals in octahedral sites, suggesting the progressive replacement of Al and Mg by Fe due to the effect of the iron-saturated fluid flow on the clayey matrix. The inflow of iron-rich fluids possibly transformed montmorillonite and illite matrix into nontronite and nontronite-saponite, which was accompanied by the changes in the isotope composition of siderite cement. The nontronite-kaolinite-chlorite and montmorillonite-saponite-nontronite associations characterise the clay matrix. Dominantly kaolinite with chlorite and nontronite is confined to iron ore layers with the siderite I, with an isotopically light carbon composition. Most likely, the original marine montmorillonite and illite deposits were transformed into nontronite and saponite because of the diffusion of fluid solutions through marine sediments through seeps. Therefore, the proximal zone of the ore deposit is distinguished by the nontronite-kaolinite-chlorite association. The intermediate zone shows montmorillonite-illite-saponite-nontronite association along with siderite II. The distal zone is marked by the unaltered illite-montmorillonite (illite-smectite) associations with rare inclusions of the second variety of siderite.

Thus, compositional variation clay minerals across the ironstone-bearing strata in boreholes reflects the effects of upward flux methanic and metal-bearing fluids in ooidal ironstones of Western Siberia. Likewise, mineral assemblages of cement or matrix, the assemblages of phyllosilicates and their chemical composition in the clay fraction of Phanerozoic ironstones reflect the effects of fluid flux.

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COPPER-CLAY NANOCOMPOSITES LOADED-MICROPARTICLES IN CHRONIC WOUNDS

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Wound healing is a dynamic and regulated process involving a complex series of overlapping events, which are hemostasis, inflammatory, proliferative and remodeling stages [1]. In chronic wounds, as venous leg ulcers, arterial ulcers, diabetic ulcers, and pressure ulcers, the healing process does not lead to anatomical and functional recovery. The employment of antimicrobial agents, particularly antibiotics, in the treatment of infected wounds is particularly controversial due to the possible rising of resistance. However, antimicrobial nanotherapeutics seems a valid option to eliminate bacterial infections, avoiding antimicrobial resistance [2]. Given these premises, the aim of this study was the design and the development of chitosan-based microparticles loaded with clay mineral-copper nanocomposites as a powder for cutaneous application to enhance wound healing in infected skin lesions. To compare natural and synthetic clay-based nanocomposites, two clays were used. The natural clay was a montmorillonite (MMT), while the synthetic one was a layered double hydroxide (LDH). The natural clay nanocomposite was prepared by means of an intercalation solution procedure, while the synthetic clay nanocomposite was obtained through the coprecipitation method. Solid-state characterizations (X-ray diffraction, copper loading, thermogravimetric analysis, and transmission electron microscopy) have been performed. Subsequently, chitosan-based microparticles loaded with Cu-MMT or Cu-LDH have been manufactured. At this purpose, chitosan hydrochloride salt solution was poured into a saturated NH_4HCO_3 for 5 days [3]. The chitosan carbamate ammonium salt prepared was dispersed in water and Cu-MMT or Cu-LDH were added to the blends. The microparticles were prepared by means of a mini spray drier (Buchi 190) and characterized by physico-chemical properties (morphology, size distribution, solid state, and thermal profiles). Moreover, preclinical properties (cytocompatibility, fibroblast adhesion and proliferation, and antibacterial properties) were assessed. All the microparticles were characterized by spherical and smooth morphology and preserved their structures upon hydration independently of their composition. The preclinical *in vitro* results suggested that the microparticles were biocompatible towards fibroblasts. Other experiments are ongoing to evaluate the *in vivo* safety and efficacy in a murine model.

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EXPERIMENTAL WEATHERING OF BASALTIC SEDIMENTS WITH DIFFERING MINERALOGY AND GRAIN SIZE: QUANTIFYING POTENTIAL FOR CO2 REDUCTION BY ENHANCED ROCK WEATHERING

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Weathering of silicate-bearing rocks, especially basaltic ones, is a sink for atmospheric CO_2 over geological time, where rate is typically limited by the low reactive surface area of the rock or sediment. If rate could be increased by decreasing grain size (e.g. pulverization), CO_2 could be fixed more rapidly. In response to increasing atmospheric CO_2 concentrations, a new strategy has emerged that takes advantage of the relatively high weathering rates of mafic (basaltic) rocks, especially when crushed and spread onto the land surface. This approach is known as enhanced rock weathering (ERW), and recent articles have begun to explore ERW potential to mitigate climate change (e.g. Beerling et al., 2020; Lewis et al, 2021; Paulo et al., 2021). Carbon sequestration must be backed by data that quantifies rate of CO_2 fixation from air to (in this case) soil, so this project seeks to employ synthetic weathering experiments to measure weathering rates of basaltic rock powders in a system designed to simulate the humid tropics. Heat and moisture in the tropics foster the highest weathering rates globally, so application of basaltic powders to tropical farms and fields should achieve the highest per-hectare CO_2 fixation rates.

Basalt dissolution rates were determined at 35 ^{o}C in dilute solutions of oxalic and carbonic acid in reactors with a 1 mm thick layer of basalt designed to simulate a tropical soil. The synthetic soil solution is added at a rate comparable to 4000 mm of annual precipitation, and weathering rates of silicate minerals in the basaltic powders are quantified by measuring concentrations of Ca and Mg released to solution over time. Reaction duration is 14 days. Mafic rocks used in the experiments include island-arc andesitic basalts, Hawaiian island basalt, continental rift basalt, and chlorite-rich meta-basalt. XRD, XRF, ICPMS and SEM-EDS were used to characterize compositions of the unweathered basalts as well as weathered basalts. Weathering rates are initially high then decrease in a way that is similar to actual soils, and scaled CO_2 sequestration rates vary by nearly an order of magnitude, from 2.4 tons/ha/year for a sand-sized island-arc basalt powder to 18.1 tons/ha/year for silt-sized Hawaiian basalt, a difference attributed to weathering of glass and augite in the Hawaiian basalt as well as its fine grain size. Weathering locally results in formation of clays and thus is not completely congruent, meaning that measurements of leached Ca and Mg underestimate CO_2 fixation. Results show that Mg-rich clinopyroxene (and chlorite or glass if present) are the most susceptible phases responsible for CO_2 transfer to soil. Grain size is an important consideration – weathering rates increase two-fold from mean powder size of 250 microns (fine-medium sand) to 10 microns (silt). These results indicate that CO_2 reduction potential by ERW is very dependent on the mineralogy, chemical composition and grain size of the basaltic material applied to the land surface.

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THE EFFECT OF THERMAL LOADING ON CZECH BCV BENTONITE – MICROSTRUCTURAL AND CHEMICAL ASPECTS

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BCV bentonite, a SÚRAO reference material, is currently being subjected to study under conditions that simulate the deep geological repository for high-level radioactive waste environment. BCV (Mg/Ca bentonite) of Czech origin is being loaded to a temperature of 150°C under both dry and wet conditions. The experiments were designed as part of the European EURAD HITEC project.

Samples were extracted after 0.5, 1 and 2 years of loading and the chemical, mineralogical and microstructural parameters of the bentonite were analysed in terms of the cation exchange capacity, via the Cu(II)triene method (CEC_{vis}), the determination of the specific surface area using the sorption of ethylene glycol (SSA), powder X-ray diffraction (PXRD) and Fourier transform infrared spectroscopy (FTIR). The sum of the exchangeable cations (CEC_{sum}) was determined via atomic absorption spectroscopy (AAS). The swelling ability of the bentonite was quantified applying the swell index (SI).

Different results were obtained for the bentonite loaded in the dry state (BCV_dry) and the bentonite loaded in suspension (BCV_wet). The BCV_dry samples exhibited a discrete loss of water with basal distances corresponding to 2W, 1W and 0W (d_{001} ~ 14.63 to 9.73Å). The shift was first visible after 0.5 years of thermal loading and remained the same for all the BCV_dry samples. The BCV wet samples became fully rehydrated after 0.5, 1 and 2 years of loading (d_{001} ~ 14.63 to 15.16Å).

The BCV_dry bentonite indicated a continuous decrease in the CEC_{vis} and SSA after 0.5, 1 and 2 years of loading; the same was valid for the SI. In contrast, the BCV_wet bentonite indicated a slight increase in the CEC_{vis}, CEC_{sum} and SSA compared to the unloaded bentonite (BCV_IN). Thermal loading resulted in an increase in the Ca^{2+} content at the expense of Mg^{2+}. The proportion of Na^{+} and K^{+} remained the same for all the samples.

The differing properties of BCV_dry and BCV_wet can be partly explained by the effect of the dehydration and rehydration of smectite. Thermal loading under dry conditions led to the collapse of smectite interlayers as manifested by its aggregation. In contrast, loading in the form of a suspension indicated the possible expansion of smectite aggregates, which rendered them more accessible to water and ethylene glycol.

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ETHYLENE ADSORPTION BY NATURAL AND MODIFIED ZEOLITES DURING KIWIFRUIT SHELF-LIFE

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Fruits can be classified in two main categories based on the respiration pattern and their capacity to produce and respond to ethylene during ripening: climacteric fruit, for which ripening-related events (e.g. loss firmness) are associated to a rise of ethylene production, and non-climacteric, in which ripening is not so strictly linked with ethylene production, despite this hormone can still affect several quality-related processes [1]. As a consequence, climacteric fruit shelf life can be prolonged by reducing ethylene production and/or concentration in the environment (storage rooms or packaging). Different technologies and products can be used to adsorb ethylene, such as potassium permanganate [2] and zeolites [3].
Zeolites are low-cost, environmentally friendly natural minerals with excellent adsorption capacity. Thanks to their cation-exchange ability and to their molecular sieve properties, natural zeolites are already largely used as adsorbents in separation and purification processes, especially for the removal of cations such as ammonium and heavy metals. Modification of natural zeolites can be done through several methods such as thermal treatment, acid activation, organic or metal modification, to improve selectivity towards certain species [4].
In this work, we investigated the capability of natural (ZeoNat), acid-activated (ZeoH), iron-modified (ZeoFe), and copper-modified (ZeoCu) zeolites of adsorbing ethylene and CO_2 during postharvest ripening of kiwi fruit. The modified zeolites were prepared starting from the natural zeolite ZeoNat, which is obtained from Slovakia and is composed of 85% clinoplilotite, 8% cristobalite, 4% illite and 3–4% plagioclast, with a Si/Al ratio of 4.8–5.5. Natural and modified zeolites were previously tested to understand their capacity to adsorb CO_2 and ethylene, and the copper-modified zeolite was found to be the most effective in adsorbing both species.
After 2 weeks of shelf-life at room temperature in PLA (polylactic acid) box of 1.5 L, ZeoCu appeared to significantly adsorb ethylene and CO_2, followed by ZeoNat and ZeoFe in terms of adsorption performances. In agreement with these results, at the end of the shelf-life period the highest values of firmness, as well as the lowest content of total soluble sugars, has been recorded for kiwifruit stored with ZeoCu, indicating that the ripening process has been effectively delayed.
Kiwifruit stored with ZeoFe showed high weight losses in time, while ZeoCu and ZeoH maintained weight loss levels comparable to control fruit even after a period of three weeks of kiwi incubation with zeolites.

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DIFFICULTIES IN THE INTERPRETATION OF VNIR-SWIR SPECTRA OF POLIMINERALIC SAMPLES: APPLICATIONS FOR THE IDENTIFICATION AND QUANTIFICATION OF CLAY MINERALS

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The identification and quantification of clay minerals constitute a key problem for the characterization of natural samples. Among the various most widely used analysis techniques, is the study by visible, short-wave and near-infrared spectroscopy (VNIR-SWIR). This procedure is based on the assignment in the resulting spectrum of the absorption bands characteristic of each mineral. This methodology has been widely applied in remote-sensing studies, including remote mapping and mineralogical characterization of both terrestrial and extraterrestrial terrains. However, in most cases, natural samples and soils present complex mixtures of minerals. As a result, the obtained spectra are commonly difficult to interpret, due to interference between the coexisting individual mineral spectra. In addition, it has been pointed that the reflectance of the minerals is not the same and with similar contents the spectral response can be very different (REFs) which complicates the identification in some cases.

In this study, binary and ternary mixtures have been prepared with different proportions of kaolinite, dioctahedral and trioctahedral smectites, quartz, feldspar, calcite, dolomite and gypsum, with the objective of determine the limit of detection of each mineral in such mixtures. The resulting spectra have been studied after two normalization processes were applied: the continuum removal and the second derivative. Several parameters including the depth, width, area and position of the absorption features and second derivative peaks have been measured in order to ease the comparison between the mixture samples.

The quartz and feldspar content increment entail a decrease in the overall reflectance and blurring of the clays absorption features. Calcite, dolomite and gypsum display absorption features in this wavelengths range leading to very notable impact in the spectra morphology and preventing the correct identification of both the clay minerals and the non-clay minerals. This shows the detection limits for each mineral from a systematic study and highlights the difficulty in identifying significant quantities of some minerals depending on the mineral association.

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CHARACTERIZATION OF PHYSICAL AND THERMAL PROPERTIES OF GEOPOLYMERS USING METAKAOLIN FROM SÃO VICENTE DA PEREIRA AND MINING WASTE FROM MONCORVO

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In recent years, global increases in energy consumption and consequent CO_2 emissions have caused an increasing number of extreme weather events. One of the sectors with larger responsibility on this is the construction sector, especially due to the production of Ordinary Portland Cement (OPC), which, for every ton produced, releases approximately 1 ton of CO_2. This illustrates the need to have a greater understanding of energy conservation when designing new buildings, which can only be reached through new energy efficiency strategies.

Recent research has been conducted on new building materials, especially on groups of amorphous aluminosilicate binders called alkali-activated materials or geopolymers, with the purpose of replacing OPC. These new materials intend to reduce environmental pollution by better managing energy, through a more sustainable and low-cost production methods, without neglecting mechanical and thermal properties.

This work focuses on the mechanical and thermal properties of metakaolin-based geopolymers with the addition of mining waste. The focus was given to the effects of introducing Hematite ore (Hem) from Moncorvo (Portugal) in different percentages to produce more sustainable geopolymers, i.e., decreasing the use of metakaolin (MK). Kaolin from São Vicente da Pereira (Portugal) was used, calcined at 700°C for 4 hours to obtain an amorphous and more reactive clay. Various geopolymers were produced with MK (100%, 90%, 80%, 70%, 60% and 50%) and the rest of Hem. The properties of raw materials and geopolymers were analysed using: compressive strength, apparent density, X-Ray Diffraction (XRD), X-Ray Fluorescence (XRF) and Scanning Electron Microscopy (SEM) along with Energy Dispersive Spectroscopy (EDS). To characterize the thermal properties, a thermal conductivity test was conducted using a thermal needle to geopolymer specimens with 100%, 80% and 50% MK.

Results revealed that the geopolymer with the highest compressive strength is the formulation with 70%MK 30%Hem, with a maximum compression of 44.5MPa at 28 days, having an increase of 4MPa when compared to the 100%MK geopolymer. These values are higher than the OPC (33MPa-43MPa at 28 days). Comparing the densities of the geopolymers, there was a gradual increase with the addition of Hem, with the geopolymer with 100%MK having a density of about 1.50g/cm3 and the geopolymer with 70%MK 30%Hem 1.75g/cm3. As for thermal properties, it was observed that the geopolymers with 100%MK have a thermal conductivity between 0.391-0.455W/m.K. However, the geopolymers with 100%MK 20%Hem have 0.475-0.555W/m.K and the geopolymers with 50%MK 50%Hem have 0.663-0.699W/m.K.

Hence, the formulation with 70%MK 30%Hem has the best results for compressive strength. However, an increasing percentage of Hem causes an increase in thermal conductivity, i.e., the geopolymer does not store heat as well as the 100%MK formulation. Despite, it is a promising material for replacing OCP.

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THE CHARACTERIZATION AND USE OF CLAY BASED NANOMATERIALS

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Clay based materials are used in many geotechnical and environmental technology applications [1]. In the context of deep-geological nuclear waste disposal the integrity of the bentonite in the multi-barrier system and its long-term erosion behavior is still a matter of uncertainty [2]. The use of nanoparticles and the complexity of contaminations demand to so-called composite materials using the properties of different materials to optimize clean-up strategies [3]. Furthermore, continuous industrial developments and the high pressure to reduce the CO_2 footprint of industrial applications lead to the use of e.g. clay-based materials as clinker substituent in the cement industry. The role of calcined clays in combination with limestone (LC^3 technology) reduces the energy demand significantly, but rheology predictions and control are a challenge [4]. These three examples mentioned above alone demands for analytical improvements on the nanoscale, which will be addressed in this talk.

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ADSORPTION OF DICLOFENAC ON HALLOYSITE SPIRAL – A COMPUTATIONAL STUDY

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Keywords: diclofenac, halloysite, molecular calculations, force field

Diclofenac (D)is a non-steroidal anti-inflammatory drug used to treat pain and inflammatory diseases such as gout, which is commercially sold, e.i., under the brand name Voltaren. As a commonly prescribed medication, it can be easily found in an urban, hospital or industrial waste-water. One way for efficient water treatment is using effective adsorbents, such as carbon-based adsorbents (graphene, graphene oxide or graphene mesosponge) or clay minerals (smectites or kaoline group minerals). Clay minerals, as ubiquitous natural materials, are favoured due to their availability and price.

Halloysite (Hal), a kaolinite group mineral with a nanotubular structure, has been widely studied in recent decades due to its excellent adsorption properties. Both experimental and theoretical studies predetermine it for waste-water treatment applications [1] as well as for pharmaceutical applications, i.e., as a drug carrier [2] due to its non-toxic character and its high cytocompatibility that attracts much attention [3].

In this work, the adsorption ability of Hal for D drug was examined by a theoretical approach using the force field computational method implemented in Materials Studio [4]. The structural models with preferred adsorption of D onto the inner surface of Hal known from experimental studies were proposed, and the models with D adsorption on the outer surface of Hal were prepared to verify this obtaining. Two forms of D were used for comparison: anionic (D-) and neutral (D0).

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TROPICAL NORWAY: GEOPHYSICAL, MINERALOGICAL AND GEOCHRONOLOGICAL EVIDENCE FOR MESOZOIC DEEP WEATHERING ON AN 800 M HIGH COASTAL PLATEAU IN WESTERN NORWAY

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(1) Geological Survey of Norway

Despite wide-spread glacial erosion, it has long been speculated that remnants of Mesozoic tropical weathering are preserved in Norway. The NFR-funded BASE-project (grant # 319849) studies basement fracturing and weathering on-/offshore Norway. In order to find proof for the deep weathering hypothesis, the 790 m.a.s.l. top of Gamlemsveten NE of Ålesund/western Norway was selected as a site to study the stratigraphy beneath a periglacial blockfield.

A small-scale ground geophysical survey (Georadar, 50 MHz antennas) was conducted to detect areas of weathered granitic basement. The survey resulted in a 15 x 15 m grid along the SSE-NNW direction, covering a total of 75,000 m^2. Areas of possibly weathered zones were mapped by assuming that sand and gravel naturally offer superior electromagnetic wave reflectivity compared to unweathered rock.

Subsequently, two trenches were excavated down to a depth of ~4 m in what appeared to be the most highly weathered areas. Samples were taken along a vertical profile and studied for geochemistry (X-ray fluorescence) and mineralogy (X-ray diffraction). The bulk samples are mainly composed of granitic gneiss components, such as quartz (35-45 wt%), both K-feldspar and plagioclase (together 30-45 wt%), and minor amounts of amphibole (<5 wt%). Weathering products such as chlorite and epidote (each ~2-5 wt%) along with illite (~7 wt%) and hydrobiotite/illite-vermiculite mixed-layer (<5 wt%) are subordinate compared to the predominance of gibbsite [$Al(OH)_3$] (up to 14 wt%).

K-Ar geochronology yields Carboniferous ages (344-328 Ma) for the coarsest grain size fractions (6-10, 2-6 µm) and Permian to early Triassic ages (285-236 Ma) for the finest grains, indicating a Triassic timing of formation of K-hosting minerals in these finest fractions (0.4-2, 0.1-0.4 µm). The mineralogical composition of the finest fractions consists almost entirely of well-crystallised gibbsite. This mineral is interpreted to be the end-product of a weathering sequence and typically forms through hydrolysis from plagioclase (albite), K-feldspar and white mica. Pollen and microfossils studies of the clay material yield Triassic ages, suggesting that the presently exposed surface was near the surface during that time period. The occurrence of gibbsite most likely records the time when the basement was exposed to weathering under tropical humid climate conditions prior to glaciation.

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FABRICATION OF HYBRID BRAGG STACKS

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One-dimensional (1D) crystalline, monodomain nanocomposites (hybrid Bragg stacks) composed of clay and polymer are a rare class of materials. These ordered single-phase materials show highly anisotropic properties like mechanics or thermal conductivity.[1,2] Typically in nanocomposites entropic loss caused by the confinement of the polymer in the interlayer space triggers rather segregation. Hybrid Bragg stacks will only be observed when sufficiently attractive enthalpic interactions of the polymer chains with the clay surface or the interlayer cations favor it. The fabrication of such Bragg stacks further requires delamination of the clay into monolayers in a solvent that dissolves the polymer. Thus, synthetic hectorite that delaminates spontaneously in water can be mixed with PVP, PEG, or PVOH yielding 1D hybrid Bragg stack films.[1-4] Eventhough such Bragg stack films show superior gas barriers compared to disordered composites, the hygroscopic interlayer cations allow for swelling at a certain humidity threshold causing the barrier to detoriate.[5] Therefore, more hydrophobic interlayer constituents (cation and polymer) are desirable. Moreover, a polycationic nature of the polymer matrix is expected to hamper swelling due to stronger binding of the polymer and the clay surface. However, 1D hybrid Bragg stack films can not be fabricated directly from solution as the combination of the anionic clay and the polycationic polymer would cause heterocoagulation yielding disordered composites. By replacing Na^+ with vinylbenzyltrimethylammonium chloride, we were able to obtain a liquid crystalline suspension of hectorite via 1D dissolution in *N*-methylformamide. Mixing this nematic suspension with bisphenol A glycerolate diacrylate allowed for the preparation of wet coats via doctor blading that subsequently could be photopolymerized. Successfull co-polymerization of the organocation and the diacrylate in the interlayer space was confirmed by infrared spectroscopy. X-ray spectroscopy and cross-sectional transmission electron microscopy indicated the 1D order of this single phase material. Investigation of the gas barrier properties showed excellent oxygen and water vapor transmission rates for the hybrid Bragg stack film. At 50 % r.h. and 23 °C an oxygen transmission rate of 0.21 $cm^3\ m^{-2}\ day^{-1}\ atm^{-1}$ and a water vapor transmission rate of 0.05 $g\ m^{-2}\ day^{-1}$ for a thin hybrid coating of 3.7 µm were observed, underlining the potential of this Bragg stack film for challenging packaging applications.

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DEVELOPMENT OF CERAMIC PROTOTYPES WITH BIO-CALCIUM CARBONATE

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The unsustainable use of natural resources, coupled with increasing population and economic growth, has resulted in a significant increase in waste generation. To mitigate these challenges, a waste valorisation approach has emerged as a viable solution. By converting waste into valuable resources, this approach offers multiple environmental and economic benefits such as reducing landfill waste, conserving natural resources, and creating new revenue streams. The valorization of waste is a crucial step towards building a more sustainable and circular economy, where waste is considered a valuable resource rather than a burden. The ceramic industry consumes vast amounts of raw materials, including calcite, which is a mineral used in the production of wall tiles and earthenware. However, their extraction and use can have negative environmental impacts. To address this, this study aims to investigate the substitution of calcite with bio-calcite, a type of calcite naturally produced by living organisms such as bivalves. So, this work aims to reduce the environmental impact associated with the extraction and use of natural calcite and promote the development of more sustainable and environmentally friendly ceramic products. First, the residue was characterized and pre-treated. The ceramic compositions were then prepared by replacing calcite with different levels of bio-$CaCO_3$. Prototypes were produced and characterized through specimen characterization. No significant differences were observed, and all values were within industrial limits. Thus, this study successfully demonstrated that bio-calcite can replace mineral calcite in ceramic products. The development of ceramics using bio-calcite is expected to reduce the amount of waste deposited in landfills and the consumption of virgin raw materials. In conclusion, the findings of this study contribute to the advancement of sustainable waste management and the development of more environmentally friendly ceramic products, promoting a circular economy and reducing the environmental impact of industrial activities.

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VANADIUM RECOVERY FROM ALKALINE STREAMS USING LA-DOPED LAYERED DOUBLE HYDROXIDES

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Layered double hydroxides, also known as anionic clays or hydrotalcite (HT) compounds, are composed of positive layers and exchangeable anionic interlayer species. The material is generally described by the chemical formula $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2]^{x+}$ $(A^{n-}_{x/n})\cdot mH_2O$, where M^{2+} are divalent cations such as Mg^{2+}, Zn^{2+} and Ca^{2+} and M^{3+} are trivalent cations like Al^{3+}, Fe^{3+} and Mn^{3+}. The A^{n-} are the exchangeable anions (carbonates, nitrates, chlorides…) located in the interlayer gallery together with the water molecules. The state of the art indicates a large possibility of LDHs with various compositions related with different combinations and ratios between the M^{2+} /M^{3+} and various interlayer anionic species.

The possibility to tune the brucite-like layers or the interlayer composition makes this category of clays very attractive for many applications, e. g. as stable and recyclable adsorbents, heterogeneous catalysts or catalyst supports for a variety of reactions with high industrial and academic importance. LDH-type materials are recognized to provide eco-friendly and low-cost solutions for today's problems related to pollution or energy requirements. One innovative application of LDHs represent their use as ionic exchangers to recover critical elements from complex and difficult streams, by-products or wastes.

Here, we report for the recovery of vanadium from alkaline solutions (pH ≥ 13) by designing an LDH-based adsorbent with innovative structure doped with La^{3+} cations within the brucite-type layers. The alkaline stability of the developed LDH-based adsorbent is ensured by the La doping. Further, this study investigates both the adsorption and the desorption steps which enable an efficient and eco-friendly vanadium recovery process directly from alkaline solutions.

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GRANULATED CLAY-TYPE SORBENT MATERIALS FOR CHROMIUM (CR3+/CR6+) CONTAINING WASTEWATER TREATMENT

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Due to the widespread industrial applications, large quantities of chromium compounds are released in the environment. These compounds are most abundant as Cr^{3+} and Cr^{6+}. Cr^{3+} is less harmful to the environment than Cr^{6+} because it is only weakly soluble in water and has a poor ability to permeate the cell membranes of organisms. However, in presence of atmospheric oxygen or organics, it can oxidize to Cr^{6+} which is 500 times more toxic than Cr^{3+}.

Water pollution by chromium can occur for example in mining, leather tanning, textile dyeing, electroplating, metal finishing, nuclear power plant, chromate preparation, among others.

Adsorption processes using materials with high binding capacities and fast kinetics represent one of the best performing and economical technologies for the treatment of wastewater containing a complex composition of metals and nutrients. It is especially suited for effluents containing low amounts of contaminants, but above the accepted limits for maximum contaminant level, where other techniques (such as precipitation) may not work.

In this work attention is given to the adsorption process, making use of structured clays-based adsorbents. Clays are known for their ability to effectively uptake heavy metal species by specific adsorption and ion exchange depending on their structure.

The present study focuses on the application of the granulated clay-based adsorbents for heavy metal uptake (such as chromium, as both Cr^{3+} and Cr^{6+}) from the Jajmau municipal wastewater treatment plant (STP). The contaminant concentrations of the STP Jajmau influent are high due to mixing of municipal wastewater with industrial wastewater from tanneries resulting in increased COD, Cr and salt concentration. Analysis of the sewage water show high concentrations of chromium (Cr) originating from the tanneries. Other large industries in the area are textile, jute and chemical manufacturers who are linked to the prevalence of heavy metals.

This work is part of the H2020 EU-India PAVITRA GANGA project which focuses on improving existing wastewater treatment systems. Within the project, the composition of the structured clay-based sorbents is adapted to the specific conditions of the Indian test-case, considering the chromium speciation (Cr^{3+} and/or Cr^{6+}) relevant concentrations and the competitive ions. Sorption performance with regard of capacity, kinetics, selectivity and desorption procedure are studied. The final goal is to ensure that wastewater loaded with Cr can be re-used for irrigation after the sorption treatment.

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TUNGSTATE SOLID PHASE EXTRACTION USING LAYERED DOUBLE HYDROXIDE FIBERS

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During the extraction of tungsten from ores highly alkaline streams are generated. Therefore, the present study focuses on the solid phase extraction of tungstate (WO_3^{2-}) from alkaline streams by ion-exchange with layered double hydroxides (LDHs) powders and shaped into fibers.

Layered double hydroxides (LDHs), are a family of anionic clays having positive layers and negative exchangeable interlayer species. SoA LDH compositions, e.g. MgAl-LDH or ZnAl-LDH, are not stable in such alkaline environments, and when used for recovery of W from alkaline leachates, metals are leached from the LDH structure. Therefore, LDH with new compositions were designed to be able to withstand the high alkaline conditions and enhance their exchange features for W recovery. In particular, La-doped-LDHs were synthesized. Sorption tests were conducted to study the leaching and adsorption behavior as a function of LDH composition and alkalinity of the W containing solutions. The results showed that the La doping provides the necessary alkaline stability during sorption testing and additionally increases the sorption capacity towards W recovery.

For practical handling the synthesized powder were extruded into fibers with different diameters and the sorption kinetics indicated the occurrence of some diffusion limitations in the first stage of adsorption, while the desorption step is overall not affected by the fiber thickness. The study demonstrates the applicability of the newly developed LDH-containing fibers for W recovery in a continuous adsorption/desorption process.

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ABSTRACT WITHDRAWN: LAST MINUTE CANCELLATION

Name Surname* (1)

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Scientific Research Abstracts
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ALKALI ACTIVATION OF FINE CLAY WASHING RESIDUES AS-RECEIVED FROM THE MINE

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The possibility of reusing residues deriving from mining processes without any calcination treatment to obtain more sustainable binders is the aim of this contribution. In particular, a washing residues deriving from quartz sand processing and containing halloysitic clay has been used in this work for producing dense alkali activated solid materials. Such residue has been classified as a mining by-product; it is composed mainly of halloysite (35wt%), a-quartz (22wt%) plagioclase (24wt%) and illite (ca. 10%) and present an average grain size between 5 and 10 mm and coarser grains inferior to 40 mm. The challenge has been to alkali activate the as-received clayey mine residues without any firing pre-treatment. To reach a satisfactory degree of geopolymerization another mine by-product from quartz sand processing was added as silica source. This second component of the geopolymeric mix is in the form of a fine sand (67wt% of quartz and 27% of mica/illite) with the coarse grain size lower than 30 mm and an average diameter around 8 mm. A sodium silicate with SiO_2/Na_2O molar ratio around 2 was added to the untreated clay plus sand mixture to obtain a fresh paste that was cured in climate chamber at 40°C, 60°C and 70°C and 50% of relative humidity for 1, 3 and 7 days and then at room temperature till testing at 28 days. The results showed a clear difference in chemical stability for samples containing sand compared to those without sand. Low percentages of metakaolin (5-15%) were also added in same formulations to achieve improvements in terms of chemical and physical properties of samples and reducing the curing time. For mixtures consisting of untreated clay and sand only NaOH was added as alkaline activator. The effect of curing temperature on the microstructure of geopolymers were analysed by different techniques: measure of pH and ionic conductivity of the eluate of the chemical stability test in water, X-ray diffraction (XRD), scanning electron microscopy (SEM), bulk density, and compressive strength. Finally, a statistical approach was adopted to rationalize the effect of the curing conditions on the consolidation of the fresh pastes of samples with untreated HC, sand and metakaolin. To test whether the parameters of the curing process as well as the MK content had an influence on the ionic conductivity and/or density values, a 3-way ANOVA followed by Tukey-Kramer post hoc test ($p<0.05$) were performed. It was evidenced how the addition of fillers, an easily controllable industrial step, can maximize the consolidated material’s performance, rather than controlling the curing time and temperature conditions. The results collected during this study indicate that these two mine by-products, halloysitic clayey residues and fine quartz sand, are suitable aluminosilicate precursors to obtain more sustainable high-performance binders.

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C-S-H PRECIPITATION AND ALTERATION VIA SIMULTANEOUS DISSOLUTION OF CHALCEDONY

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In radioactive waste disposal facilities, bentonite is used as an engineered barrier to inhibit radionuclide migration because of its low permeability. Montmorillonite, the main component of bentonite, is dissolved by the alkaline solution generated by reaction between cementitious materials and groundwater, which is concerning because it increases the permeability of the bentonite. The kinetics of montmorillonite dissolution during cement-bentonite interaction can be affected by dissolution of accessory minerals and precipitation of secondary phases. These complex processes should be understood to evaluate bentonite performance.
To understand the cement-bentonite interactions better, a simpler reaction, C-S-H precipitation by simultaneous dissolution of chalcedony, was investigated in a two-step flow-through experiment. In the first step, to evaluate chalcedony dissolution kinetics, a 10.2 mM NaOH solution was injected into a reaction cell including a chalcedony fragment at a flow rate of 0.07 mL/min, after which 0.1 mM of Si was added to the solution and the flow rate was reduced to 0.02 mL/min. In the second step, to evaluate both chalcedony dissolution and precipitation of secondary phases, 5.2 mM NaOH was injected with addition of 2.3-2.5 mM $Ca(OH)_2$ and 0.1 mM of Si. The initial flow rate was 0.02 mL/min, but it was later reduced to 0.002 mL/min. The dissolved ion concentrations and pH of the output solution were monitored during the experiment. At each step, the change in height of the solid surface was determined using a 3D laser scanning microscope. The solid phase after the experiment was analyzed using XRD, IR, and SEM-EDX.
In the first step, a higher Si concentration of output solution and lower height of chalcedony fragment confirmed that chalcedony was dissolving. Aqueous Si concentrations increased with decreasing flow rate in this step. The height reduction of the chalcedony fragment in the second step indicated continued dissolution of chalcedony. In addition, XRD and IR analyses revealed precipitation of C-S-H and calcite in this step. The calcite likely formed from CO_2 gas, which was present as an impurity. Higher aqueous Ca concentrations of output solution than input solution when decreasing the flow rate suggested that initially formed C-S-H dissolved and different Si-bearing precipitates formed. This was attributed to an increase in Si supply due to chalcedony dissolution as a result of the lower flow rate. Cross-sectional chemical mapping of the specimen containing secondary phases showed that C-S-H with lower Ca/Si ratio covered C-S-H with higher Ca/Si ratio. This study revealed the effect of flow rate on alteration of C-S-H precipitates during the dissolution-precipitation reaction.

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REGIOSELECTIVE APPROACH TO CHARACTERIZING INCREASED EDGE AVAILABILITY IN LAYERED INORGANIC SOLIDS BY LAYER EXPANSION: REACTION OF KAOLINITE WITH OCTADECYLTRIMETHYLAMMONIUM SALTS

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Layered inorganic solids possess both layered and edge surfaces, while their characteristics have been hardly separated since interactions of these surfaces with ions/molecules are generally identical. Meanwhile, edge availability can be increased by expanding each stacked layer upon layer expansion induced by an intercalation reaction. Therefore, the edge reactivity is worth focusing on and characterizing to elucidate a reaction mechanism including layered inorganic solids. Kaolinite, a layered aluminosilicate clay mineral with the formula $Al_2Si_2O_5(OH)_4$, comprises stacked asymmetrical layers, each composed of an AlO2(OH)4 sheet of octahedra and a SiO4 sheet of tetrahedra. These neutral layers allow the intercalation of salts and neutral polar molecules [1]. In addition, the layer surfaces cannot exhibit ion exchange reactions. In contrast, kaolinite edges are crystal fracture surfaces at which cation-exchange sites are present [2,3]. Thus, kaolinite is the best candidate to show regioselective reactions of layered and edge surfaces. Therefore, this study devoted special attention to the comparative reactions of pristine kaolinite and expanded kaolinite with octadecyltrimethylammonium chloride. The expanded kaolinite used in this study is methoxy-modified kaolinite (MeO-Kaol), an organically-modified kaolinite swollen by methanol; the interlayer distance is 0.40 nm [4]. Notably, pristine kaolinite never expands by methanol. This study mainly conducted the reactions of kaolinite or MeO-Kaol with octadecyltrimethylammonium chloride in methanol [5] and, subsequently, an exhaustive washing. Based on X-ray diffraction patterns, no intercalation of C18TAC between pristine kaolinite layers was evident. In addition, intercalation and subsequent deintercalation of C18TAC proceeded in the product using MeO-Kaol was revealed. In the Fourier-transform infrared spectra, the product prepared using MeO-Kaol displays a drastic increase in the intensities of CH_2 stretching bands compared with that prepared using pristine kaolinite. The CH_2 stretching bands in the product using pristine kaolinite were hardly observed without enlarging the spectrum eight times. The thermogravimetric curve of the product using MeO-Kaol displayed a mass loss in the 200–300 °C, which was greater than that of pristine kaolinite. The nitrogen content of the product using MeO-Kaol was estimated to be 0.15 mass% using the CHN analysis. The results mentioned above demonstrated that kaolinite edge availability increased upon expansion of each stacked layer. Thus, the increase was successfully characterized using kaolinite, a regioselective layered inorganic solid [2]. Therefore, this study is the pioneer to briefly characterize increased edge availability of layered inorganic solids following layer expansion, and paves the way to assess the contribution of edges depending on the degree of expansion of layered inorganic solids.

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POZZOLAN ACTIVITY OF LOW-QUALITY CLAYS BY FRATTINI TEST

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Cement is one of the most used materials in the world, including the Czech Republic. Its role in the construction industry is irreplaceable, but its production contributes to 5-8% of global CO_2 emissions[1]. One of the possibilities to reduce the amount of emissions is the production of mixed cements that contain pozzolans, such as fly ash, slag, microsilica and, recently, the increasingly discussed calcined clays[2]. The work was focused on the characterization and study of the pozzolanic activity of low-quality clays from the Bílina lignite mine in the Czech Republic. A very variable composition of clays was found from the point of view of XRF and XRD analysis, while the amount of kaolinite in the 9 investigated samples was in the range of 5-20 wt.% and the amorphous phase was in the range of 23-63 wt.%. By calcination the clays at a temperature of 850°C, it was found that all calcined clays reliably exhibit pozzolanic properties using the Frattini test[3]. By lowering the firing temperature to 650°C, the pozzolanic activity of some samples decreased significantly.

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PAPAIN IMMOBILIZED IN LAPONITE/CELLULOSE ACETOPHTHALATE FILMS AND THEIR ANTIBACTERIAL ACTIVITY

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Papain (PAP) is an enzyme that has pharmacological action as an anti-inflammatory, healing, exfoliating, immunomodulatory and antimicrobial agent. However, PAP can degrade under certain conditions of temperature, pH, and humidity. Therefore, the aim of this study is to immobilize papain in laponite® clay mineral (LAP) for the formation of acetophthalate cellulose (CA) and pluronic® (PF-127) films for complementary therapy for contaminated wound healing. For the nanostructured hybrid systems (NHS) PAP/LAP, adsorption isotherms were performed with PAP solubilized in phosphate buffer under 5, 6, and 7 pH values), varying the concentration from 4,500 to 25,500 mg L^{-1} in 0.1 g of LAP. Adsorption kinetics were also carried out at pH 7.0, 25,500 mg L^{-1} PAP , 0.1 g of LAP, and for 1 to 2880 min. Films (WNHS) was prepared by solubilizing CA:PF-127 at 7:3 w/w in acetone for 60 min, adding the NHS, which was obtained using 25,500 mg L^{-1} PAP, 1440 min, and pH 7.0 in a Petri dish under agitation, and then dried at 8°C. Same procedure was adopted for obtaining White films (WF) without use of the NHS. The NHS obtained in different times, WF and WNHS were evaluated by XRD, and FT-IR. WF and WNHS were also subjected to swelling degree evaluation. The antibacterial activity was performed on standard strains of *Staphylococcus aureus* sensitive and resistant to methicillin, *Escherichia coli*, and *Pseudomonas aeruginosa*. The samples were dispensed into sterile Falcon tubes containing Mueller Hinton broth and incubated in a shaker operating at 200 rpm for 24 h at 35°C. After incubation, colony enumeration was performed after contact with the films and compared to the untreated control. Higher PAP adsorption was observed in all pH values with increasing concentration. The maximum PAP adsorbed was at pH 7.0 (1,961.9 mg g^{-1}), due to the ionization of the enzyme. The reaction had a faster adsorption rate in ≤ 60 min and higher capacity at 1440 min (1,291 mg g^{-1}). The basal distance for raw LAP (d_{001}) in the NHS at 60 min of reaction was 1.34 nm, which was higher than d_{001} for raw LAP (1.25 nm), suggesting the intercalation of PAP in LAP. With the increase in reaction time, the loss of the *001* reflection occurred indicating occurrence of exfoliation. WNHS exhibited amorphous characteristic. The 1540 cm^{-1} band of PAP amide II (N-H vibration) shifted in intensity with increasing time, suggesting interaction with the silanol groups of LAP. In WNHS, the bands of the CA were predominant. WF and WNHS swelled over time, and the presence of LAP increased swelling capacity, at 480 min, by 57.1% and 76.84%, respectively. WNHS showed antibacterial activity for all strains, with the ability to reduce growth by 2 log_{10} compared to the positive growth control (untreated), which is equivalent to a bacteriostatic effect of WNHS, with a highlight for the action of the film against the *S. aureus* ATCC 33591 strain (methicillin-resistant). In this way, the film formed from PAP/LAP can be an alternative for the treatment of wounds contaminated with bacteria, especially bacteria resistant to conventional antibiotics.

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MINERALOGY AND GEOCHEMISTRY OF LACUSTRINE CLAYEY SEDIMENTS: EVALUATION OF POSSIBLE NATURAL AND ANTHROPOGENIC CAUSES OF ENVIRONMENTAL CONTAMINATION.

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This study focuses on the compositional characterization of fine sediments of the Pietra del Pertusillo Lake (PPL, Basilicata Region), one of the largest man-made water dams of southern Italy, located in an area with a strong touristic and naturalistic vocation, the Agri Valley. This area is also important for the presence of the largest onshore hydrocarbon field of Western Europe, the exploitation of which has led to the development of industrial activities mainly consisting of the extraction and first treatment of crude oil at the Val d'Agri Oil Centre (COVA). Furthermore, in this area hydrocarbons mixed with water naturally rise to the surface and, inevitably, pour into the dam. The main aim of the research is to detect sedimentological, mineralogical and geochemical features of the PPL lacustrine sediments, also considering the types and contents of heavy metals and hydrocarbons present in them, in order to understand if in the study area the land quality has declined over time and possibly what about the natural and anthropogenic causes of this decline. Two sediment cores, intercepting the whole sedimentary record of the lake, were collected within the inlet area of the Agri River in the dam where the material from the areas most affected by human activities and natural sources of crude oil is drained. The sediments mainly consist of clayey silts, whose mineralogical composition is largely represented by the quartz and feldspar and subordinately by phyllosilicates (especially illite/smectite), without significant variations along the stratigraphic columns. The contents of heavy metals of environmental interest in the sediments are comparable with the outcropping rocks in the area, here considered as local bedrock. As to the organic component of the PPL sediments, the study focused on the detection of the 16 polycyclic aromatic hydrocarbons (PAHs), considered the most dangerous by the WHO and US-EPA. The PPL sediments show a low total content of PAHs whose values vary from 40 to 180 μg/kg, falling in the compositional range of lake and lagoon sediments of the literature. The PAHs distribution along the cores seems to be influenced by the sediment grain-size and, in particular, by the <2 μm fraction contents with which they positively correlate. Contrariwise, heavy metals show a mostly constant trend along the cores, without correlation to any specific grain-size fraction. The compositional homogeneity of the samples along the cores suggests that, within the lacustrine deposit, there are no evidences of compositional discrepancy attributable to the presence of the most important anthropic activities of the Agri Valley (COVA). In order to identify the possible sources of the hydrocarbons found in the sediments, fingerprinting techniques were used by means of molecular diagnostic ratios (MDRs) and C stable isotope by compound specific isotope analysis (CSIA). The MDRs displayed contrasting values for the study case that leave some concerns about the identification of "petrogenic" and "pyrogenic" PAHs. The CSIA results revealed similar δ13C values in the analysed sediments suggesting that during their deposition no significant changes in the PAHs sources were recorded.

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VIBRATIONAL STUDY OF THE DEINTERCALATION OF KAOLINITE

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Intercalation in kaolinite involves the spontaneous self-assembly of small molecules (e.g. N-methylformamide, NMF) in the interlayer space of the mineral leading to an expansion of its structure from 7 Å to 10-14 Å. Recent kinetic studies by near-infrared spectroscopy (NIR) and X-ray diffractometry (XRD) over a broad temperature range [1, 2] have indicated that intercalation involves switching to the fully intercalated state, which does not distort the layers and does not induce interstratification. The opposite process, i.e. deintercalation, is known to induce stacking faults disorder [3-5] and the appearance of partially hydrated interlayers [6]. This work aims at studying the kinetics of the NMF deintercalation process by vibrational spectroscopy complemented by XRD and TGA.

KGa-1b and KGa-2 kaolinite samples, pre-intercalated with NMF, were subjected to isothermal deintercalation (30-80 ºC) under a flow of wet (~70 RH%) or dry N_2. Synchronous NIR measurements showed that the NMF content (intensity of the 2νNH mode) decreases to almost zero. Layer distortion (proxied by the width of the 2ν inner AlAlOH stretch) appeared independently of the presence of H_2O in the purging gas and had a non-monotonic evolution, first increasing and then decreasing with time. Interestingly, this transient distortion was manifested by a bimodal distribution of 2νOH oscillators, because a part of the original population remained unaffected in position and width.

In all cases, the final material had residual layer distortions depending on the conditions of deintercalation. As a result of these distortions, the as-obtained deintercalated kaolinites re-intercalate much faster than the original material, with decreased or no incubation period, to approximately the same degree of intercalation. Layer recovery was observed during the re-intercalation process. 'Hole' water was detected only in samples deintercalated in the presence of H_2O and did not seem to be a prerequisite for accelerated reintercalation.

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INTERACTION OF CS+ WITH DIOCTAHEDRAL SWELLING CLAYS

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Since the 1940s the artificial isotope of 137-Cs has been released into the natural environment as a result of nuclear weapons testing and nuclear plant accidents. Because 137-Cs is a strong gamma emitter having a half-live time of ~30 years, it constitutes the main environmental concern. After the Russian invasion of Ukraine, the potential risk of further release of 137-Cs into the environment increased dramatically and there is a clear need for an efficient and cheaply available adsorbent that could be used to immobilize 137-Cs.
The present study aimed to investigate the Cs adsorption/immobilization potential of dioctahedral swelling clays from a smectite-vermiculite family.
Nearly 30 clay samples including the CMS standards, different bentonites, and natural soil clays were used in the study. Studied clays were saturated with Cs and re-saturation with Na (CsNa samples). Adsorption of Cs from “natural” Cs-contaminated waters by the clays was studied in static adsorption experiments. The degree of fixation of Cs within CsNa samples was evaluated using XRD, EDS, ICP MS, ICP OES, and ICP MS methods. The mean layer charges (LC) of studied samples were determined using OD – method. The adsorption of Cs and the selectivity were studied using the ICP MS method.
All studied samples showed significant fixation of Cs even under wet conditions (i.e. without drying of Cs-saturated samples). In most cases, the fixation of Cs led to a reduction in the mean LC values. This indicated that the component having likely the nature of dioctahedral vermiculite was responsible for the fixation. Cs- adsorption was more pronounced for the clays containing the high layer charge component compared to the other ones. Those high-charge swelling components also seemed to adsorb Cs selectively from the studied waters. Cs – fixation potential and the selectivity concerning Cs observed for high-charge smectites and vermiculites were high enough to consider the clays as promising materials for decontamination of 137-Cs-contaminated waters.

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THEORETICAL AND EXPERIMENTAL STUDY OF THE ADSORPTION OF TOXIC PERCHLORATE AND PERIODATE COMPOUNDS WITH TETRAHEXYLPHOSPHONIUM-MODIFIED BEIDELLITE

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Perchlorate (ClO_4^-) and periodate (IO_4^-) oxyanions belong to the group of hazardous and toxic compounds. For example, ClO_4^- is detected widely in many food products in surface and groundwater sources [1]. Moreover, inside the human body, ClO_4^- anions can affect the thyroid gland of mammals, disrupting thyroid hormone production and metabolism of the human body [2]. Therefore, the presented work investigates the adsorption of ClO_4^- and IO_4^- anionic species into the interlayer space of tetrahexylphosphonium-modified beidellite (THP-Bd) with a theoretical DFT-D3 and experimental methods.

The main aims of this study are to provide detailed information about the structure and structural stability of studied systems and hydrogen bond interactions to anchor the ClO_4^- and IO_4^- oxyanions on the surface of the beidellite layers. Moreover, the calculated vibrational modes using *ab initio* molecular dynamics were analyzed in detail and compared with measured FTIR spectra. The calculated projected vibrational density of states was used to identify the individual vibrational modes and overlapped bands in the measured FTIR spectra.

Acknowledgements

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NANOCOMPOSITE PHOTOACTIVE FILMS DEPOSITED ONTO POLY(CAPROLACTONE) SURFACE VIA MELT FUSION

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Clay minerals are used as filler materials for incorporation into polymer matrices. They must be modified with surfactants to change their properties to achieve better compatibility with polymers and to improve in this way the mechanical, physicochemical, thermal, and optical properties of composites. So far clay/polymer nanocomposites have been used as fillers dispersed in polymer bulk. Nowadays there is an increasing demand, especially in the biomedical field, for the modification of surfaces tuning their physical and chemical properties. Therefore, in this work, the surface modification of poly(caprolactone) (PCL) with saponite (Sap)-based photoactive film functionalized with phloxine B (PhB) organic dye was investigated. The modification was achieved via melt fusion of the polymer into thin organoclay film and remained limited to the surface of a few μm.

Sap was firstly modified with a cationic surfactant and subsequently functionalized with PhB (0.01-0.1 mmol/g). XRD patterns of the precursor films containing organoclay and PhB confirmed the successful intercalation of these components by increasing d_{001} from 1.36 nm to 2.22 nm. PCL melt fusion led to the polymer intercalation followed by increasing d_{001} to 3.21 nm. Infrared and X-ray photoelectron spectroscopy and water contact angles confirmed PCL intercalation and surface hydrophobic properties. The optical properties of the precursor films and nanocomposites confirmed the photoactivity of the materials. The highest emission was achieved for the samples with the lowest PhB amount and higher led to the concentration quenching. Nanocomposites exhibited slightly higher fluorescence than organoclay precursors. The trends were confirmed by time-resolved spectroscopy and fluorescence quantum yields. The composite with the highest PhB content exhibited antibiofilm properties (*S. aureus*). Photoactivity was important since the irradiation significantly contributed to the enhancement of the antimicrobial effect.

Melt fusion at the interface of polymer and organoclay film is one of the effective ways to modify polymer surfaces. This work presents the method for the formation of antimicrobial surfaces in the form of a nanocomposite layer with a thickness of only a few micrometers.

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PHYSICO-CHEMICAL PROPERTIES OF POLY(2-ETHYL-2-OXAZOLINE) MODIFIED MONTMORILLONITE

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Clay minerals, especially from the smectite group, are ideal candidates for modification by organic polymers [1]. Materials modified in this way represent new materials with improved utilization. In this work, powder samples consisting of montmorillonite (Jelšový Potok, Slovakia) and a unique and novel polymer poly(2-ethyl-2-oxazoline) (PEtOx) were prepared at different loadings (100, 200, 300, 400 and 500 mg/g). Their structural characterization was carried out by using XRD and mid-infrared (MIR) spectroscopy. The thermal stability of the functional montmorillonite-polyoxazoline (Mt-PEtOx) nanocomposite was carried out by TGA/DSC and the surface characteristics by using BET-N_2 adsorption. Based on XRD, the d_{001} value for pure montmorillonite (Mt) was determined to be 1.22 nm, confirming the presence of partially hydrated sodium cation. After the intercalation of PEtOx using a loading level of 100 mg/g, a weak diffraction emerged at 4.5°2θ (1.93 nm), indicating the incorporation of the PEtOx into the interlayer space of montmorillonite. During the intercalation of PEtOx using the highest loading level 500 mg/g, the *d*-spacing increased further up to 2.11 nm, corresponding to the pseudo-trimolecular arrangement. The MIR spectrum of Na-Mt shows the absorption assigned to the characteristic groups of the montmorillonite layer [2]. After modification of Mt with polymer, absorption bands belonging to poly2-ethyl-2-oxazoline appeared in the MIR spectrum. Vibrations of typical CH3 and CH2 of PEtOx are located at 2983, 2944, 2886 and 2855 cm^{-1} and a dominant band of the C=O group is located at 1640 cm^{-1}. The FTIR spectra clearly show that the intensity of these vibrational bands increases with increasing loading of PEtOx. TGA/DSC results showed Mt-PEtOx thermal stability in the range of 250-550 °C. With increase of polyoxazoline concentration, the intensity of the second mass loss peak gradually increased and at a loading level of 400 mg of PEtOx/1 g Mt this peak was split into two mass loss steps around 380 and 520 °C . BET-N_2 adsorption isotherms of all Mt-PEtOx samples can be classified as the II IUPAC group, with a type H3 hysteresis loop. This group is characteristic of unrestricted monolayer-multilayer adsorption and aggregated particles with mesopores. Environmentally friendly PEtOx derivatives of montmorillonite have future prospects as nanofillers in non-traditional polymer matrices and in environmental applications as adsorbents of inorganic and organic pollutants.

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COBALT-CARBON-SMECTITE CATALYSTS IN OXONE® INDUCED OXIDATIVE DEGRADATION OF TARTRAZINE: THE ROLE OF THE NAHCO3 IN THE SYNTHESIS OF THE CATALYST

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Catalytic degradation of tartrazine in the presence of Oxone® was investigated. Oxone was activated by nanocomposite catalysts consisted of cobalt supported on smectite with chitosan-derived carbon loading. The catalyst was synthetized using an impregnation-carbonization procedure and $NaHCO_3$ was used as green porogen. Smectite rich bentonite clay from Bogovina, Serbia was used as started material. After milling, sieving and hydroseparation the fractions containing particles up to 2 μm in diameter were separated (denoted as S). The intercalation of chitosan into the smectite was performed according to the previously described procedure [1]. Obtained chitosan-smectite nanocomposite (Ch-S) was submitted to the wetness impregnation method by Co^{2+} ions [1]. The impregnation was performed by slow addition of $Co(NO_3)_2$ solution to Ch-S powder resulting in 0.03 g Co^{2+} per 1 g of Ch-S. After drying, the sample was mixed with $NaHCO_3$ in a mass ratio 1:3, placed in a tube furnace and carbonized in a stream of N_2 at 500°C for 1 h. The potassium peroxymonosulfate (Oxone®, i.e. $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$) was used as a source of sulfate radicals generated by cobalt from the catalysts. The catalytic activity of the N/Co/cCh-S was compared with catalyst Co/cCh-S obtained by the same synthesis procedure without activation by $NaHCO_3$. The degradation of tartrazine was monitored using UV–Vis spectrophotometry at wavelength of 426 nm within 60 minutes. It was found that N/Co/cCh-S reached 100% of dye degradation after 30 minutes, while degradation in the presence of Co/cCh-S was 77% for the same reaction time. The results of the catalytic tests were fitted by different kinetic models and the first-order-kinetic model showed the best correlation. The first-order constant (k_1) values for N/Co/cCh-S and Co/cCh-S were 0.1286 min^{-1} and 0.0561 min^{-1}, respectively. The results of this study confirmed that the presence of $NaHCO_3$ in the catalyst synthesis led to increased catalyst activity and accelerated tartrazine degradation in the presence of Oxone®.

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CLAY NANOSHEETS AS PERMSELECTIVE COATINGS TO IMPROVE SAFETY AND PERFORMANCE OF HIGH ENERGY BATTERIES

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To ensure the safety and performance of lithium-ion batteries (LIBs), a rational design and optimization of suitable cathode materials is crucial. Lithium nickel cobalt manganese oxides (NCM) represent one of the most popular high-energy cathode materials for commercial LIBs applied in electric vehicles. However, they are limited by several critical issues, such as transition metal dissolution, formation of an unstable cathode-electrolyte interphase (CEI) layer, chemical instability upon exposure to air, and mechanical instability.

Coating with colloidally stable nanosheet suspensions turned out to be an affordable and technically benign[1] approach for the fabrication of permselective membranes (CEI) as needed to improve the safety and cycling stability of cathode materials. Clay-based coatings may simply be made by self-assembly of osmotically delaminated sodium fluorohectorite (Hec, $[Na_{0.5}]^{inter}[Mg_{2.5}Li_{0.5}]^{oct}[Si_4]^{tet}O_{10}F_2$) nanosheets onto NCM (Hec-NCM) by an aqueous wet-coating process. Complete and continuous wrapping of NCM by high aspect ratio (≈ 10000) nanosheets[2] is facilitated by strong electrostatic attraction between Hec nanosheets and NCM as well as by the superior mechanical flexibility of Hec nanosheets.[3] The coating significantly suppresses mechanical degradation while forming a stable and functional CEI layer. Consequently, Hec-NCM delivers outstanding capacity retention for 300 cycles (a capacity decay of as little as 0.11% per cycle).

Furthermore, coatings of large aspect ratio nanosheets have long been established as barrier materials for gas diffusion due to producing a tortuous path.[4] In this line, Hec nanosheet coatings offer a diffusion barrier not only for the electrolyte but also for water vapor and CO_2, which greatly improves the shelf-life of NCM cathode materials that tend to deteriorate by the formation of $LiCO_3$ and LiOH. Hec-NCM, after 6 months of exposure to ambient atmosphere, still exhibits an excellent electrochemical performance (70% capacity retention after 250 cycles at 1.0C), while pristine, uncoated material at this point lost capacity completely. This conservation of capacity even in the ambient atmosphere can be ascribed to the unique chemical, structural, and physical characteristics that Hec nanosheets offer.

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SUPERIONIC CONDUCTIVITY IN MONODOMAIN FILMS OF NEMATIC CLAY GELS

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The study of superionic conductivity and its relation to pore confinement is highly relevant for potential applications in various fields, such as energy storage, sensors, and electrochemical devices.[1] Mass transport in confinement (<100 nm) differs significantly from the transport in a bulk volume. It is decisively influenced by the properties of the interface and can be orders of magnitude higher than the bulk conductivity. Extensive research has been conducted on different pore geometries, including zero-dimensional (0D), one-dimensional (1D), and three-dimensional (3D) channels, to characterize key parameters that govern superionic conductivity. Recent research has focused on investigating the superionic conductivity of confined ion transport in slits as provided by self-assembly of 2D materials such as graphene-oxide, hexagonal boron nitride, transition metal (hydr-)oxides, and natural clays into textured films. Because of material-inherent limitations and the lack of availability of strictly monolayer nanosheets of appreciable aspect ratio, a precise and systematic variation of key parameters of 2D confinement, such as the slit height, the solvent, the layer charge, and the confined ion type, has not yet been achieved.[1]

Sodium fluorohectorite $[Na_{0.5}]^{inter}[Mg_{2.5}Li_{0.5}]^{oct}[Si_4]^{tet}O_{10}F_2$ is a synthetic 2:1 layered clay material that exhibits 2D confinement. One of its rare properties is the ability to undergo crystalline and osmotic swelling, forming a nematic gel, thus allowing for precise and continuous control of the slit height in the range of the Debye-length, which was previously postulated to be the critical length scale.[2] Moreover, the material possesses exchangeable interlayer cations[3] and can be synthesized and swollen with different but homogeneous layer charges,[4] enabling the tuning and investigation of ion selectivity and transport properties. Fluorohectorite is also capable of swelling with various organic solvents and their mixtures,[5] allowing for developing a deeper understanding of the influence of solvents on ion-transport behavior in a 2D confined space.

Given the current demand for lithium-ion battery technologies, our initial focus is on the study of lithium-ion transport in lithium fluorohectorite slits. Lithium fluorohectorite can be synthesized in two steps, by replacing Na^+ with an alkylammonium cation, which is subsequently removed by deprotonation with LiOH. We observed a confinement-governed ionic conductivity (≈ 0.04 S/m) in thin films. As the confinement is sensitive to the variation of ionic strength we designed an in-situ prototype that allowed us to simultaneously control the slit height in a continuous range, determine it with X-ray diffraction, and measure the ionic conductivity with impedance. This setup allows the systematic characterization of the key parameters that govern superionic conductivity.

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EFFECT OF ZEOLITES ON THE HYDRATION PRODUCTS OF THE MAIN COMPONENT OF CEMENT - ALITE

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Globally, cement production has a negative impact on the environment[1,2]. This is related to the use of a huge amount of geological natural resources in the form of limestone rocks, and the large consumption of energy in the process of firing clinker, and thus the emission of a large amount of CO_2 into the atmosphere. The production of one ton of this raw material, is associated with the emission of 0.5-1 ton of carbon dioxide into the atmosphere, as well as a huge consumption of energy, which causes significant environmental pollution. Recently, investigators have been looking for mineral additives to cement that could partially replace it and at the same time improve the physical-mechanical parameters of pastes, mortars or concretes [3,4].
In the present study, the effect of the addition of zeolites (high-silicon and low-silicon) on the process and products of allite hydration was investigated. For the purpose of achieving the stated goal, components of the allite-zeolite system were obtained by synthesis. The effectiveness of the synthesis was evaluated on the basis of chemical and phase composition analysis and textural studies. The effect of pozzolanic additives on the hydration process was evaluated by XRD analysis, SEM, microcalorimetric and conductometric studies. Slurries with 15%, 35% and 50% zeolite additives were analyzed after 7, 28 and 90 days of curing. The results showed that each amount of additive reduced the heat release rate and total heat of hydration. The hydration products formed are affected by the curing time and the type of zeolite. The use of zeolite additive in the right amount in the production process of cementitious composites can positively affect its physical and mechanical properties. Zeolites reduced the ratio of CaO/SiO2 in the C-S-H phase, which for pastes with the addition of the Na-A ranged from 1.61 to 1.37, and for the ZSM-5 from 1.91 to 0.47. This ratio changed with the amount of addition and the maturation time of the pastes.

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VNIR-SWIR SPECTRAL RESPONSE OF THE LI-RICH MICAS DEPOSIT OF VALDEFLÓREZ (CÁCERES, SPAIN)

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The Li deposit of Valdeflórez (Cáceres province, Spain) is related to the alteration of Paleozoic metasediments due to the circulation of hydrothermal fluids linked to the intrusion of the nearby Cabeza de Araya pluton (Pesquera et al., 2020). Li-rich micas mainly, and other Li-rich minerals like amblygonite-montebrasite occasionally, appear as consequence of this hydrothermal alteration. The aim of this study is to find the spectral signature of the Li-mineralization to be able to apply it during the exploitation mining works and to the Li prospection in similar areas.

For that, 335 samples coming from cores have been studied by X-ray Diffraction (XRD) and reflectance spectroscopy in VNIR-SWIR wavelength. Each sample corresponds to 1 m of core. Mineralogical data and different parameters obtained from the spectra and from the second derivative of the reflectance curves have been statistically treated together to the chemical compositions of the rocks, previously studied. Statistical analysis were done with SPSS and PAST software. In addition, a classification of the spectra has been done to compare with the chemical and mineralogical composition of the samples.

The mineralogical composition of the samples is similar, and most of them are composed of mica, tourmaline, and quartz in different proportions. In occasions, chlorite and smectite also appear, and therefore tourmaline is less abundant. A good correlation was obtained between tourmaline and Li-content. This is because both, the Li-enrichment in micas and the formation of tourmaline, are related to the hydrothermal process, and therefore micas in samples with high tourmaline content are richer in Li.

Samples were classified in six groups according to the intensity of the main absorption features in the SWIR which, in turn, is related to the mineralogy. Nevertheless it is not useful to classify the samples according to the Li content. However, some data obtained from the second derivative curve of the spectra are strongly correlated with Li-contents and allow us to predict Li contents with low percentage of error.

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EXPERIMENTAL CONSTRAINTS ON SMECTITE ALTERATIONS IN THE PRESENCE OF ACCESSORY MINERALS AT 180°C WITH AND WITHOUT ORGANIC ACIDS

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The UMB2 (Mechanisms of Transformation in Bentonite Barriers) batch reactor experiments aim to investigate the thermal and chemical stability of smectites relevant to the underground disposal of high-grade radioactive waste. The smectite used for this study was extracted from the Moosburg (Bayern) bentonite from Germany and purified by Na-cation exchange and repeated size separation of particles to obtain a 1 μm fraction. The experiments involved subjecting synthetic mixtures of purified smectite with 10% accessory minerals (calcite, pyrite, gypsum, and pyrite-calcite mixtures) to varying solution chemistries and temperatures of 180°C for a month in a rotary oven with and without rotation (20 rpm). All the mixtures were treated with and without organic acids in different concentrations. After the experiments, the smectites were analysed using various techniques, including XRD, TEM, and EDS-SEM. The main focus of the study was to determine the possible alterations that occurred in the smectites and the mineral dissolution-precipitation mechanisms involved. The results show extensive alteration occurring in smectites in the presence of K-oxalate by forming 2:1 mica celadonitic-smectite mixed layered structures. However, in the absence of K^+, only incipient alteration of the smectites was observed. Overall, the UMB2 batch reactor experiments evaluate the feasibility of using bentonites as buffer materials in high-level radioactive waste repositories. The results of the study provide insights into the long-term stability of smectites under extreme conditions, which can improve the design and management of radioactive waste repositories.

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SOLVOTHERMAL GROWTH OF CU/CU2O/NIFE LAYERED DOUBLE HYDROXIDE AS PHOTOCATALYST FOR HYDROGEN PRODUCTION

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Layered double hydroxide has been widely used as photocatalyst for dye degradation and water splitting reactions. Their activity was limited by low transportation and fast recombination of the charge carriers, which could be suppressed by the formation of the heterostructures. *Herein*, the Cu/Cu_2O/NiFe-layered double hydroxide was synthesized by facile solvothermal method. The aid of glycerol could reduce Cu^{2+} and Fe^{3+} to Cu^{0}/Cu^{+} and Fe^{2+}. The presence of Fe^{2+} resulted in the increase of absorption in visible-light region. Glycerol could also increase the specific surface area of layered double hydroxide. The Cu/Cu_2O/NiFe-layered double hydroxide could generate hydrogen from water with the presence of methanol as a sacrificial reagent (apparent quantum yield of 0.53% at 400 nm). The activity of Cu/Cu_2O/NiFe-layered double hydroxide heterostructure increased about 2.5 times compared to that of bare NiFe-layered double hydroxide. This work presents the use of inexpensive metals and low toxic reducing reagent that may provide a facile strategy for loading metal co-catalyst on two-dimensional materials as well as enhancing of the photocatalytic activity.

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ADSORPTION OF 23 COMMON PHARMACEUTICALS TO MONTMORILLONITE: AN ADVANCED MOLECULAR DYNAMICS STUDY

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Free energy calculation techniques are powerful tools for understanding the underlying mechanisms of chemical reactions, such as hydration and surface adsorption. However, only a handful of molecular dynamics (MD) simulation studies have employed the techniques[1].

In this work, the free energy of perturbation (FEP), biased umbrella sampling (US) MD simulations, and energy decomposition were applied to investigate the relationship between the hydration and adsorption free energies of small pharmaceutical compounds of varying charge and hydrophobicity on sodium montmorillonite (Na–MMT) clay surface.

Despite repulsive coulombic interactions, the US free energy results showed that favorable adsorption energy between the negative pharmaceutical compounds and the negative MMT surface can still exist. The energy decomposition results further showed that some negative compounds adsorb on the MMT surface mainly by Van der Waals (vdW) interactions. These weak vdW interactions correlated positively with the short residence time of the negative compounds on the MMT surface compared to the positive ones. On the other hand, in addition to the vdW interactions, the positive compounds adsorbed on the MMT surface via a much stronger attractive coulombic contribution, resulting in fast and stable adsorption. Overall, the negatively charged compounds had lower adsorption energy than the positive ones.

The FEP results showed that all compounds registered higher hydration energies near the MMT surface than when they were far away. The FEP hydration results were also used to predict the water-octanol (log K_{ow}) partitioning coefficients[2].

The results of this work can be used to advance the development of new technologies that use clay minerals to remove pharmaceutical compounds that are of emerging concern in aquatic systems[3].

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EVALUATION OF ANTIOXIDANT ACTIVITY OF MANGO ALMOND PALYGORSKITE MIXTURE FOR A BEAUTY MASK DEVELOPMENT

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Clays have been used for long time in cosmetology like regenerant and sebum absorbent. With age, an excess of free radicals seems to lead to skin aging, which is problem especially for women.
To enhance natural resources, this study focused on Mbodiène palygorskite and mango kernel (*Mangifera indica*, Anacardiaceae).
It consisted in the evaluation of the antioxidant properties of palygorskite – mango kernel mixture (*Pahiri* variety) (1/1 by mass). This is in view of preformulation tests for the development of a beauty mask for anti-aging purposes.
Thanks to the spectrophotometric method using 2,2diphenyl -1picryl hydrazyl (4% concentration), according to a protocol described by Scherer R. et al., (2009), the methanolic extracts gave inhibitory concentrations of 50% of the oxidizing activity (IC50), equal to 0.31 mg/ml mango kernel, 130 mg/ml palygorskite, 7 mg/ml palygorskite – mango kernel mixture at the start, 6.7 mg/ml at 1 month and 6.5 mg/ml at 2 months. Compared to ascorbic acid used as reference which had an IC50 of 0.16 mg/ml.
These results show that the antioxidant activity of the mixture is higher than that of palygorskite alone. Moreover, this antioxidant activity of the mixture increased slightly over time.
Thus, these tests seem encouraging for the development of a beauty mask.

Keywords: palygorskite, mango kernel, antioxidant activity, mask

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OPTIMIZATION AND MINIMALIZATION OF THE EFFECT OF CROSS HEATING OF SAMPLES DURING IR-LASER ARGON EXTRACTION

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Among many methods of heat generation, laser heating is a very process-efficient method of heating. It allows to achieve relatively very high power density and therefore allows to achieve very large temperature gradients in a short time. It is one of the reasons why lasers are commonly used for heating of samples for K-Ar dating. Melting the samples by defocused IR laser beam allows to perform measurements with a low contribution of atmospheric argon. However, there are possible problems due to cross heating of neighboring samples. In order to analytically address this issue, cross heating of samples in various types of holders was studied using a non-contact optical pyrometer supported with K-Ar age dating tests on GLO standard.

A standard holder for the samples used for the laser heating process is usually made of copper. In this study, a total of six different holders were constructed, analysed and tested: standard copper, copper with cuts between sample holes, titanium, titanium with cuts, and two holders made of titanium rods with copper thermal shields at different distances between samples.

The research results allowed for precise determination of heat distribution mechanisms in a heated set of samples, and then iterative optimization of both: the shape of the holder and its material modification, as well as to implement additional elements. Consequently, this allowed for the formulation of design guidelines for this type of container and the construction of an optimal solution that was presented.

The experimental results show also that the decrease in thermal conductivity of the holder (from 400 W/mK for copper to 22 W/mK for titanium) leads to a small decrease in cross heating of neighboring samples. It indicates that the main mechanism of heat transfer between samples is by conduction. Additional cuts did not lead to a significant decrease of cross heating, either for copper or titanium holders. Therefore thermal radiation is also an important contributor to heat transfer.

Holders made of titanium rods with thermal shields made of copper allow to minimize thermal conductivity and radiation between the samples, therefore, allowing to heat the samples at a maximal optical power of 18 W for 5 minutes without the release of any radiogenic argon from neighboring GLO samples.

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ORIGIN AND CLIMATIC IMPLICATION OF A FIBROUS CLAYS OCCURRENCE IN THE LATE LUTETIAN-EARLY BARTONIAN (EOCENE) OF THE PARIS BASIN

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Fibrous clay minerals associated to Mg-rich environments have been well recognized and sporadically studied in some Cenozoic units of the Paris Basin from decades (e.g. Cavelier, 1963; Trauth *et al*., 1968). However, their occurrence in the Basin has been little discussed in relation to the palaeoclimatic and tectonic contexts. Eocene has been recognized as the last very warm interval and records major climatic events known as hyperthermals (Westerhold *et al*., 2020 and references herein). Therefore, fibrous clay formation may have been controlled by climatic factors. Recent investigations based on detailed sedimentological and bio, chemo and sequence stratigraphy studies allow to refine the palaeogeographic evolution of the basin and to better constrain 3D geometric reconstructions (RGF program led by BRGM).

This study focuses on two cores (Le Tillet and Ussy-sur-Marne) and two outcrops (Saint-Maximin and Isles-les-Meldeuses) distributed along an E-W transect. Both the timing and spatialization of a fibrous clays episode are investigated. All these sections present an equivalent episode within the 'Marnes et Caillasses' Fm. (late Lutetian-early Bartonian), often associated with syn-sedimentary dolomite. Due to its stratigraphic position, this episode most likely encompasses the Late Lutetian Thermal Maximum (LLTM), previously recognized in the deep ocean and associated with extremely high insolation values resulting in arid conditions (Westerhold *et al*., 2018). Using a new dataset based on XRD, electron microscopy (TEM and SEM imaging) and petrography, we aim to discuss the formation processes of these fibrous clays in the Paris Basin. Elemental geochemistry was also carried out using Laser Induced Breakdown Spectroscopy (LIBS) on bulk sediments and compared to XRF measurements on the same sample sets.

Our results seem to provide evidence of a transformation from Mg-rich smectite to palygorskite under arid environmental conditions as proposed by some authors (e.g. Trauth, 1977 and Chen *et al*., 2004). An arid climate combined to a basin confinement in relation with a major Pyrenean tectonic event (Briais, 2015) might have been the key factors that favored fibrous clays sedimentation in the Paris Basin.

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INVESTIGATION ABOUT IRON(III) INCORPORATION INTO LAYERED DOUBLE HYDROXIDES: COMPOSITIONAL AND STRUCTURAL PROPERTIES OF $MG_2FE_YAL_{(1-Y)}(OH)_6$-CL AND $ZN_2FE_YAL_{(1-Y)}(OH)_6$-CL

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Layered Double Hydroxides (LDH) and related nanocomposites have attracted much attention for biomedical applications and the development of LDH drug carriers composed by endogenous metals, such as iron, is of obvious interest. However, most of the studies reported so far on iron-containing LDH, mainly focusing on the applications, suffer from insufficient data about the synthesis and the characterization of these materials. In this study, it is addressed compositional and structural properties of two series of LDH materials, $Mg_2Fe_yAl_{(1-y)}$-Cl and $Zn_2Fe_yAl_{(1-y)}$-Cl with a M^{2+}/M^{3+} molar ratio equal to 2 and $0 \leq y \leq 1$. By combining crystal-chemical reasoning, Rietveld refinements and pair distribution function analysis (PDF), it was possible to differentiate between contributions from crystalline and amorphous components. Concerning Mg-series, for $y > 0.5$, the compositions were found to slightly deviate from those expected with an increase in the value of R tending to 3. For Zn-series, more heterogeneous samples were obtained with the presence of amorphous 2-line ferrihydrite clearly demonstrated by PDF analysis. As well as providing a reliable approach to the characterization of Fe-LDH, this study gives useful elements for better understanding and interpreting the results reported in the literature regarding these phases.

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PIROXICAM ADSOLUBILIZED IN PILLARED LAYERED DOUBLE HYDROXIDES AS A PROMISING STIMULI-RESPONSIVE LUMINESCENT MATERIAL

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The successful adsolubilization of piroxicam (PIR), a common non-steroidal anti-inflammatory drug of the enolic carboxamide class, in organically modified Zn_2Al-layered double hydroxide is described for the first time. Dodecyl sulfate anions (DDS) and different amounts of piroxicam were co-intercalated by the coprecipitation method using water/acetone mixtures as the reaction medium. With the help of dodecyl sulfate anions, the obtained pillared LDH structure (Zn_2Al-DDS) showed the incorporation of 5, 10 and 20 % of piroxicam. The presence of the above drug was verified by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), solid-state ^{13}C MAS NMR, and thermal analysis (TGA-DSC). In addition, photoluminescence characterizations not only confirmed the co-intercalation of the drug, but also allowed us to estimate the location of piroxicam within the carrier system. The obtained results highlight the potential of the prepared nanohybrids (Zn_2Al-DDS@PIR) to be used as potential biomarkers in biomedical and biological fields.

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ELECTRODE SYNTHESIS OF AN ALL IRON LDH, MößBAUERITE, AND ITS APPLICATION AS WATER SPLITTING CATALYST

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A simple, industrially benign electrodeposition of mößbauerite directly onto an electrode allows for an efficient, cheap, sustainable, and scaleable way to prepare an efficient electrocatalyst for electrochemical water splitting in an alkaline enviornment.[1] The advantages of electrosynthesis of mößbauerite are low production costs, excellent scalability, a good binding to the electrode. Moreover, an abundant, non-toxic metal is applied as catalyst that bares no environmentally hazards rather than rare or noble heavy elements.[2,3]
Simply by submerging steel plates in an alkaline $NaHCO_3$ solution and cycling the applied potential from 0 to 0.2 V vs. RHE for 90 cycles, first the multivalent iron compound green rust is formed on the surface of the steel substrate. As this transient intermediate is highly susceptible to oxidation in air yielding a variety of iron (oxy)hydroxides, instant oxidation to the active catalyst mößbauerite is required.[3] This may be occomplished by different procedures. One being chemical oxidation by immersing the coated steel plate in H_2O_2 solutions. Alternatively electrodepostion of mößbauerite may be directly followed by electrochemical oxidation by cyclization at a higher voltage (1.10 to 1.47 V) as compared to initial green rust synthesis. Both reaction routes yield phase pure brownish mößbauerite. X-ray diffraction, however, showed slightly different basal spacings, which indicate varying degrees of interstratification for the two products. This in turn can be attributed to varying volume ratios of simply intercalated and carbonate grafted (i.e. chemical bonded carbonate species) interlayers.[4,5] Chemical oxidation yielded the higher volume contents of grafted interlayers. The ratio of grafted to ungrafted (intercalated) carbonate turned out to significantely influence the electrochemical performance of the two types of mößbauerite catalysts. A higher content of grafted interlayers yields higher activities and thus a lower overpotential ($\eta(10\ mA/cm^2) = 440\ mV$). Additionally, this compound possesses a larger electrochemical surface area than the electrochemically oxidized mößbauerite.
In summary, direct electrochemical synthesis of a sustainable catalyst for water splitting by corrosion engineering provides a cheap and highly scaleable route for the direct deposition of OER catalyst onto a current collector.

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GLASS/STEEL/CLAY INTERACTIONS IN A SIMULATED RADIOACTIVE WASTE GEOLOGICAL DISPOSAL SYSTEM

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Nuclear energy is one of the safest and cleanest forms of electricity generation. To achieve sustainability, a great significance must be placed on the treatment and disposal of high-level radioactive waste generated during operation [1]. The multi-barrier system is responsible for long-term safe storage by isolating the radioactive waste from the biosphere in deep geological repositories. Achieving this goal requires both natural geological barriers and engineered barrier system with complementary safety functions, creating a robust system [2].

The aim of our work was to study the chemical evolution of a glass/steel/clay system held under conditions that could be predicted in a deep geological repository. Our model engineered barrier system comprises a sodium borosilicate glass [3]; modelling the waste matrix, iron; modelling the steel canister and claystone; modelling the low permeability buffer. A triplicate setup was kept at 80 °C for 3, 7 and 12 months and post-mortem characterization was performed. The main goal was to understand characteristics, applicability, and stability of the whole system, from the structural properties of the vitrified waste to the clay response in the repository.

No alteration products were observed with scanning electron microscopy energy dispersive X-ray spectroscopy measurements on the surface of the glass and Fe or in the clay after the end of the experimental period. Along the glass, the surface and borders do not vary. The main elements contained in borosilicate glass are Si, O, Na, Zr, Ba, and all of them with EDX analysis were detected after 3, 7 and 12 months. Additional surface analysis was carried out with XPS directly on the matrix glass to observe changes and possibly secondary phases formation. The results showed that the atomic composition remained rather the same in the case of Si and O after 3 months, while Na and Ba decreased. The most significant finding was the precipitation of Mg and Ca on the surface of the borosilicate glass resulting from the synthetic porewater. The formation of the passive layer can be observed, which takes on an increasingly homogeneous structure as time progresses. Based on the elemental analysis of the leachates, the released amount of B, K, Si and K increases over time, while that of Ca and Mg decreases. The concentrations of Cl^- and SO_4^{2-} did not change significantly.

According to the results, we can conclude that under the applied conditions the used components of the engineered barrier system do not have a significant effect on each other, they individually preserve their integrity, which is the basic principle of Defense in Depth.

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FROM VINEYARD TO BOTTLE: TRACING THE WINEMAKING PROCESS USING 87SR/86SR RATIOS. A CAMPANIA (ITALY) CASE STUDY

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Wine is an important commodity with a rich history and cultural significance that spans across many civilizations. The wine industry is characterized by a complex distribution network that includes multiple stages of production, from grape growing to wine production, packaging and labeling.
Ensuring the authenticity of wine products is critical for maintaining the reputation and economic value of the industry. In recent years, there has been a growing demand for wine traceability systems that can provide a comprehensive understanding of its origin, quality and authenticity.
One traceability system accounts for the use of $^{87}Sr/^{86}Sr$ ratios in wine. Strontium isotopes (^{88}Sr, ^{87}Sr, ^{86}Sr and ^{84}Sr) form in variable abundances the natural strontium, that is present in the soil and water of a vineyard and can be used to determine the geographical origin of wine. Indeed, the $^{87}Sr/^{86}Sr$ ratio of a wine reflects that in the soil and water of the vineyard where the grapes used to produce the wine were grown. The $^{87}Sr/^{86}Sr$ ratio is characteristic of each geographical area as its value is affected by the geological features of the inorganic material forming the soil, and by the weathering processes that take place. This means that the value of a specific area can be used as "fingerprint" to determine the origin of food products grown in that area. Studies have shown that the $^{87}Sr/^{86}Sr$ ratios of wine samples are unique to specific vineyard regions and can be used to distinguish between wine products of different origin (e.g., Mercurio et al., 2014; Tescione et al., 2020).
This study aims at confirming the close connection between the wine product and the specific origin region, necessary to establish its unique identity, to differentiate it from similar products, and also safeguarding it against potentially fraudulent activities or adulteration. To achieve this, the $^{87}Sr/^{86}Sr$ systematics were employed to analyze the whole winemaking chain (consisting of soil, grape and wine samples) from seven different vineyards of the Campania region (Italy), in the municipalities of Guardia Sanframondi and Castelvenere (Benevento, Italy). This characterization, based on the study of environmental matrices, enables a careful investigation of the geochemical processes occurring along the entire wine production chain.

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CATALYST AND POROUS MATERIAL DESIGN FROM LAYERED SILICATES HUS

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Layered silicates, having reactive neighboring silanol (SiOH and SiO^-) groups regularly located in the interlayer surface, are easily functionalized by various modifications such as cation exchange, silylation, and pillaring [1]. Furthermore, the layered precursors can be transformed into 3D-porous structures by various post treatments such as topotactic conversion and interlayer silylation [2]. The arrangement of neighboring silanol is defined by the crystal structure of the silicate layer and it can act as a starting connection point for constructing porous or catalytic superstructures. Thus, a novel layered silicate is a source for advanced and innovative material and its synthesis have been attracted attention. This presentation shows the potential of novel layered silicates, Hiroshima University Silicates (HUSs), as the precursor for designing new types of catalyst and porous materials [3]. Layered silicates HUSs were synthesized using various alkylammonium cations [3a,b,d]. Interlayer silyaltion of HUS-2 with trichloromethylsilane and subsequent calcination gave a new type of IEZ like material HUS-10 with an unique structure composed of methyl or hydroxyl moiety in the pore [3f]. The surface silanol group of HUS can be modifed with the titanium complex to form isolated tetrahedrally coordinated TiO species with defined structure and high sruface dencity [3e,h,i]. The titanosilicate layered catalysts obtained here exhibited promissing catalytic performance for several partial oxidation reaction of hydrocarbon. The surface silylation with silane coupling agent with catalytic moiety also provide unique acidic and basic catalytic reaction space in the in the HUS where interlayer space enhance the accesibility of reactants into the catalytically active site on the silicate layer [3g,h,j].

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STRUCTURAL AND THERMAL PROPERTIES OF NA-MODIFIED CLINOPTILOLITE EXCHANGED WITH CD2+ CATIONS

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Cadmium is one of the most toxic heavy metals even at low concentrations. It is regarded as a pollutant of global concern and forms major hazard to human health. Clinoptilolite, as a low-cost sorbent has been intensively investigated for the removal of heavy metals including cadmium. The variability of the exchange properties of clinoptilolite depends on the Si/Al ratio, the contents and the type of the extra-framework cations within the structure, their coordination by H_2O molecules.

In this work, the kinetics, structural features and the thermal behavior of Na-modified clinoptilolite exchanged with Cd^{2+} cations from the Beli Plast deposit (Bulgaria) were investigated. The main objective is to prepare a sorbent for detoxification of living organisms. The initial and exchanged samples were studied using X-ray powder diffraction (XRD), differential scanning calorimetry and thermogravimetry (DSC-TG), The structure refinements of the samples were performed applying the Rietveld approach (Topas v. 4.0 software).

The clinoptilolite sample was exchanged into sodium form by stirring 50 g of the natural sample and 500 ml of 1 M NaCl solution at 60 °C for 12 days. The cadmium exchange experiments were performed using 100 mg of Na-clinoptilolite treated with 20 ml of aqueous solution of 0.005M $Cd(NO_3)_2 \cdot 4H_2O$, at room temperature and at different initial pH. The rate of Cd^{2+} uptake by the Na-modified clinoptilolite as a function of contact time (from 15 to 300 min) was studied. The Cd^{2+} amount sorbed by the Na-form increases rapidly and reaches an equilibrium value after 40 min with 80–94% effectiveness. The experimental data fit well with the pseudo-second-order model and the parameters q_e (meq/g) and k_2 (g/meq.min) for pH=2.6 are 0.451 and 0.098, respectively, and for pH=4.94 the values are 0.474 and 0.339.

DSC-TG analyses were performed for all studied samples. The effects in the DSC curves show differences with temperature due to release of weakly bound H_2O molecules and strongly bound ones. The endotherm minima temperatures were between 86 and 115 °C decreasing in the sequence Na- < Natural- < Cd-clinoptilolite. The hydrate complexes around the exchanged cations also influenced the DSC curves. The cation coordinating H_2O molecules and the non-coordinating ones were determined by XRD Rietveld structural refinement. The number of the nearest H_2O molecules around all cadmium positions as well as around the residual Na^+ and Ca^{2+} cations after the exchange process is 10.7. The difference between the total number of H_2O molecules – 23.7 (calculated from TG data) and the number of strongly bound H_2O – 10.7 (obtained by XRD structural refinement) is 13.0 H_2O molecules. This value is very close to the TG results for weakly bound H_2O molecules –13.1. In the Cd-exchanged sample four Cd^{2+} positions were structurally determined, namely Cd, Cd1, Cd2, and Cd3, in which the total number of refined cations is 2.13 Cd^{2+}. Mostly occupied are Cd (M4 position in the original structure) and Cd2 (M2 position). Small portions of its cations are dispersed in other less preferred locations Cd1 and Cd3. The occupation of these atypical positions depends not only on the charge and size of the cation but also on the distribution of aluminum in the framework.

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THE EFFECT OF BASALT AMENDMENT ON INORGANIC CARBON ACCUMULATION AND GROWTH OF RICE AND SOYBEAN

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The increase of atmospheric CO2 is considered as a major cause of climate change and urgent phase-down of CO2 emission is required. Enhanced rock weathering (ERW) has been attracting attention as one of the Negative Emissions Technologies that aims to sequestrate CO2 in soil by accelerating weathering of silicate minerals. In ERW strategy on farmland, not only carbon sequestration but also supply of elements such as Ca, Mg, and Si from mineral to plants is also expected, which means co-benefits leading to plant growth promotion [1]. On the other hand, since toxic elements may be supplied by weathering minerals and absorbed by crops, it is important to properly understand the impact of ERW on soil fertility and crop growth, but such knowledge is limited.

In this study, rice and soybean were grown in pots with the different amounts of basalt (equivalent to 0, 5, 10, 20, 50, 100 t/ha) mixing with grey lowland soil from a field in Hokkaido University. The growth, yield and elemental composition of each crop were determined after 3 months cultivation. We also investigated the accumulation of inorganic carbon and the concentration of exchangeable elements in the soil.

There was a trend toward increased biomass with basalt inputs in rice, but no significant difference in soybean. Concentrations of some elements were significantly different depending on the amount of basalt. In rice leaf, P increased but Ba, Ca, Sr, Co, Mo, Ni decreased, while Na increased but Ni, Cr decreased in rice stem with basalt application. In brown rice, increase of Ca and Mg, and decrease of B, K, Rb, Sr, and Ba were observed. Regarding soybean, P and Ba increased but Al, Co, Cd, V, and Zn decreased in stem, while Rb increased and P, Se, As, V, and Li decreased in seed with basalt application. Basalt application didn't increase the concentration of toxic elements in seeds of both crops.

Change of inorganic carbon sequestration in soil is under investigation. Also, further investigation of the effect of basalt weathering on growth and yield of crops is needed, considering the importance of co-benefits.

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INTERCALATION OF METAL NANOPARTICLES INTO OSMOTICALLY SWOLLEN HECTORITE

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Clay minerals have long been explored as supports for metallic nanoparticles that have been produced by reduction of appropriate interlayer cations and their catalytic performance has been tested. As the number of interlayer cations is low, this route yields only very few metallic nanoparticles, which mostly if not completely are expelled from the interlayer space and end up residing on external surfaces.[1] Truly intercalated nanoparticles would, however, be highly interesting for two reasons: First, sandwiching nanoparticles between two clay surfaces is expected to slow down particle motion and thus hamper Ostwald ripening via coalescence. Second, as the support surfaces carry a relatively high negative surface charge density, an electronic interaction between support and metal (EMSI) may push catalytic performance.[2]
Melt-synthesized sodium fluorohectorite (NaHec, $[Na_{0.5}]^{inter}[Mg_{2.5}Li_{0.5}]^{oct}[Si_4]^{tet}O_{10}F_2$) swells osmotically simply when immersed into water resulting in a nematic liquid crystalline phase.[3, 4] In this nematic state, the negatively charged nanosheets with a huge aspect ratio of up to 20.000 remain in coplanar orientation with uniform separation that can be controlled by the amount of water added. Adjusting this separation to ≈ 60 nm then allows for fast diffusion and intercalation of positively charged nanoparticles in a kind of colloidal cation exchange. Contrary to the above-sketched route, with this intercalation route very high loadings may be realized that moreover can be fine-tuned by varying the zeta potential of the nanoparticles (65 wt% to 72 wt%). The positively charged nanoparticles moreover repel each other generating a nanoporous interlayer space with catalytic particles firmly captured and sandwiched between nanosheets.[5] Intercalated Pd nanoparticles with a diameter of 3.5 nm showed no Ostwald ripening even after annealing for 40 h at 700 °C.[6] The catalytical performance of the metal/clay composite was tested in CO-oxidation where it showed superior performance compared to a variety of widely used supports. The temperature for oxidation, T_{90} was reduced from 198 °C to 156 °C compared to the standard support Al_2O_3. As suggested by XPS and CO-DRIFT spectroscopy, the performance push can be attributed to a positivation of Pd nanoparticles by the peculiar polyanionic sandwich support that weakens the CO chemisorption and thus improves turnover.[7] The intercalation of nanoparticles with positive zeta potential into nematic phases of osmotically swollen anionic nanosheets is a generally applicable route for producing temperature-stable catalyst systems with performance improved by EMSI.

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MINERAL AND CHEMICAL COMPOSITION OF BENTONITES FROM THE JASTRABÁ FORMATION (KREMNICKÉ VRCHY MTS., WESTERN CARPATHIANS)

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The most important bentonite deposits in Slovakia are in the Central Slovakia Volcanic Field, where they associate with rhyolite volcanics (Jastrabá Formation) in the southern part of Kremnické vrchy Mts. With an annual production of about 250 kt of bentonite, Slovakia belongs to the TOP 10 world producers. The aim of the contribution is to characterize samples from one of the largest bentonite deposits in Slovakia – Lutila I and compare the mineral and chemical composition of mined bentonites from the Kremnické vrchy Mts. A detailed lithological-petrographic analysis found that perlite is the dominant parent rock for bentonites. The highest Al-Mg montmorillonite content in bentonite from the Lutila I deposit, and two other deposits is from 70 to 80 wt.%. Cation exchange capacity of the measured bentonites with a montmorillonite content of 65-80 wt.%, according to XRD quantitative analysis, ranged between 91 and 123 mmol/100 g. Altered rocks that contained only 20 to 35 wt.% montmorillonite and opal-C or opal-CT as the main phase had CEC from 27 to 57 mmol/100 g. The major interlayer cations in the studied samples are calcium and magnesium with an approximate Ca:Mg ratio of 3:1. The chemical composition of the studied bentonites was compared with the chemical composition of the presumed source rocks, primarily perlites, but also rhyolites of the Jastrabá Formation. This comparison shows that high-grade bentonites were affected by the same transformation mechanism. There was leaching of excess Si and alkali (Na and K), which were released during the transformation of volcanic glass into montmorillonite. Samples with an increased content of opal-C (CT) were formed in a zone with worse flow conditions, probably in a semi-closed system, into which a solution enriched in Si entered and crystallization of the opal-C (CT) took place. Practically the same proportions of non-mobile elements La/Yb, Nb/Ta and Zr/Hf of bentonites and perlites from the Jastrabá Formation point to perlite as the parent rock for bentonite. It looks, however, that bentonitisation increased amount of REE in comparison with parent perlites (perlites: 171 ppm < bentonites: 249 ppm < clay fraction from bentonites: 318 ppm of REE).
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PVA AND NANOCLAY-BASED FIBERS AS NOVEL FOOD PACKAGING MATERIAL

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Food loss and waste (FLW) is one of the most serious social, economic, and environmental issues undermining our planet sustainability [*1*]. According to Food and Agriculture Organization (FAO), nearly 1.3 billion tons of food are lost along the food supply chain.The increasing demand for new food packaging materials, which satisfy people requirements, provided thrust for advancement of nanomaterials science. Inherent permeability of polymeric materials to gases and vapours, and their poor barrier and mechanical properties have boosted interest in developing new strategies to improve these properties [*2*].Nowadays, the application of clay materials in food packaging is getting attention due to their mechanical, chemical, barrier (against oxygen, carbon dioxide, ultraviolet, moisture, and volatiles) and thermal properties [*3*].Given these premises, the aim of this work was the design and the development of innovative and sustainable packaging materials to limit the food waste, prolong the shelf-life of food and reduce environmental pollution. At this purpose, PVA-based fibers loaded with different concentrations of montmorillonite (MMT), a natural clay, were manufactured by means of electrospinning. . Clay minerals were grounded in a mortar, sieved with a 75 µm sieve and the blends were prepared by the addition of MMT to the polymeric blend. The systems were obtained using an electrospinning apparatus (STKIT-40, Linari Engineering, Italy), equipped with a high-voltage power supply (40 kV), a volumetric pump (Razel R99-E), a 10 mL syringe, and a conductive static collector, covered by aluminum foil.The systems were characterized using a multidisciplinary approach including morphology, size, solid state, thermal profiles, mechanical properties, ethylene scavenging activity and antioxidant properties. All the systems were characterized by fibers and a smooth morphology and preserved their structures upon hydration independently of their composition. The systems showed also distinctive properties as antioxidant and ferrous ion chelating activity.In future studies, these packaging materials will be loaded with antimicrobial compounds able to preserve the quality of food.

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MINERALOGICAL AND PHYSICAL-CHEMICAL CHARACTERIZATION OF RESIDUAL SMECTITIC CLAYS FROM SOUTH OF PORTUGAL

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Bentonite is a special type of clay very rich in smectites and presenting properties such as a high cation exchange capacity and specific surface, alkaline pH (> 7), as well as rheological and thermal characteristics, considered as positively relevant for therapeutic and cosmetic applications. Several residual clay deposits occur in south Portugal, resulting from weathering of feldspatic magmatic rocks (mainly diorites), some of them smectite rich and considered as “bentonites”.

This research work has as main objectives to characterize, from a mineralogical and physical-chemical point of view, 3 residual smectitic clays deposits from Beja (BEJA), Benavila (BENA) and Montargil (MONTA) locations in south of Portugal, and to assess if they show compositions and therapeutic and cosmetic properties commons to a typical bentonite. Thus, it was selected numerous laboratory analyses to characterize the designated samples: mineralogical analyses through X-ray diffraction of oriented (< 2 μm fraction) and unoriented aggregates (< 63 μm fraction), specific surface and scanning electron microscopy; and physicochemical analyses through X-ray fluorescence, pH, conductivity and cation exchange capacity.

Studied samples have in common high amount of fine particles fraction (>50%) and a predominantly smectitic composition (81%-88%), followed by calcite, feldspars, kaolinite, magnetite/maghemite and quartz, in smaller concentrations. Through the scanning electron microscope, it’s possible to notice the very small particle size of clay minerals with a laminar shape. BET analysis of specific surface area shows that BEJA has the highest value, 77 m^2/g, followed by BENA, 34 m^2/g, and MONTA with the lowest value,10 m^2/g. Due to the chemical composition of the samples, the presence of clay minerals as well as secondary minerals is confirmed, considering the occurrence of the following major elements: SiO_2 (48%-53%), Al_2O_3 (15%-20%), CaO (4%-6%), MgO (4%-6%) and Fe_2O_3 (3%-11%). BEJA, BENA and MONTA own alkaline pH values 8,3, 8,9 and 9,2, respectively, and electrical conductivity within the expected range for clayey materials, which means BENA has the highest conductivity, 503 μS/cm, and MONTA the lowest, 323 μS/cm. The samples exhibit high values of cation exchange capacity above 38 meq/100g (BENA) up to 70 meq/100g (BEJA). Thus, based on the results obtained, it’s possible to consider that they show the minimum acceptable values to use in therapy and dermocosmetic’s industry.

Nowadays, clayey materials are both employed in spas or thalassotherapy centres, to treat rheumatological or skin problems, or for cosmetic purposes, due to their adsorption and absorption properties. The significance of this research work remains in analysing and studying these properties, which are related to the cation exchange capacity and specific surface that provide to clayey minerals, specifically bentonites, anti-inflammatory, analgesic, healing and antitoxic characteristics.

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HUMAN LACTOFERRIN-CLAY NANOHYBRIDS LOADED ONTO BIOMIMETIC SPONGE-LIKE SCAFFOLDS FOR THE TREATMENT OF CHRONIC SKIN WOUNDS

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Since the emergence of antibiotic resistances to chronic wound infections is a growing problem, the use of non-antibiotic agents such as antimicrobial peptides has being receiving more and more interest [1]. Among these, human lactoferrin (hLF) stands out with marked bacteriostatic and bactericidal properties [2]. However, due to its peptide nature, its structure can be easily degraded by the highly proteolytic environment of chronic wound beds [3,4]. To avoid this drawback, hLF was recently loaded into montmorillonite and halloysite structures providing nanohybrid materials with great biocompatibility towards human fibroblasts cell culture **[5].** In the present work, hLF-clay nanohybrids were loaded into natural polymer-based freeze-dried sponges in order to design antimicrobial advanced biomimetic scaffolds intended to be applied on infected chronic wounds. Chitosan medium molecular weight (Cs; Merk Life Science, Spain) and hydrolyzed collagen powder (HC; Kelisema S.R.L., Italy) were used. Chitosan solution (2% w/v) was prepared by dissolving Cs in a 0.5 M aqueous solution of acetic acid under continuous stirring for 12 hours. Aqueous HC solutions (2% and 4% w/v) were prepared by dissolving collagen powder in distilled water under continuous magnetic stirring. Subsequently, CS and HC solutions were mixed in a 1:1 w/w ratio and hLF-clay nanohybrids were added to the Cs/HC mixtures under continuous stirring. The resulting mixture was poured into round polystyrene plates of 1.7 cm diameter and frozen at -80 °C. The frozen samples were subjected to sublimation (CoolSafe Touch 100-9, LaboGene; Denmark) for 24 hours operating under low vacuum (<4 hPa). The obtained sponge-like scaffolds were characterized for their mechanical properties using a TA.XT plus Texture Analyzer (Stable Micro Systems; United Kingdom) and morphological properties by means of a Scanning Electron Microscope (Hitachi S-510) and a Ultra-High Resolution Transmission Electron Microscopy (Titan G2 60–300, FEI Company, Thermo Fisher Scientific, Waltham, MA, USA). Results showed that the obtained materials exhibited mechanical and morphological properties suitable for their application as biomimetic scaffolds for wound healing purposes.

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IMPACT OF CLAY AND GYPSUM CONTENTS ON THE HYDRO-MECHANICAL BEHAVIOUR OF MARLS

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For the installation of a large facility in Spain a site was selected and the characterisation of the geological medium was undertaken, in particular concerning those parameters that affect the response of the bedrock to the thermal, hydraulic and mechanical impacts of the facility. A total of 73 cores coming from about 50 different boreholes drilled through a Neogene formation of the Tagus sedimentary basin in Cuenca (Spain) were characterised. The cores crossed three main formations, which could be described (in increasing depth) as: marly-gypsiferous claystone (LIB), gypsum with occasional claystone levels (YB),and gypsiferous-dolomitic claystones (LSB). All the samples had a gypsum content higher than 30% and a content of phyllosilicates mostly below 30%.

Properties showed a large variability inside each formation, but some trends were clear. Indeed, the clay minerals content was well and directly correlated with the plasticity, external specific surface area, water content and cation exchange capacity. For depths lower than 40 m the dry density was found to be inversely correlated with the content of phyllosilicates. The porosity values computed from the dry density and the density of solid particles agreed well with those obtained by mercury intrusion porosimetry, except for the samples with higher clay minerals content, probably because in these materials the volume of small pores that cannot be intruded by mercury is high, and the computation of porosity is underestimated.

Despite the fact that the samples were extracted below the water table, the degrees of saturation, computed considering the particular dry density and density of solid grains of each sample, were all lower than 100%. Although the decompression effects and some drying during manipulation could have some effect on this observation, many of the samples that came from swelling tests, which had been completely saturated in the oedometer, had also computed degrees of saturation below 100%. An inverse correlation between the gypsum content and the degree of saturation of samples supposedly saturated was clear.

Other properties were also affected by the predominance of a particular mineral. For example, the thermal conductivity decreased as the gypsum content increased (its thermal conductivity is very low, 0.5 W/mK) and increased as the dolomite content increased (the thermal conductivity of the pure mineral is 5.1 W/mK). As well, the density of solid particles was an indication of the predominance of one mineral or another: it was inversely related to the presence of gypsum, whose density of solid particles is very low (2.3 g/cm3), whereas a few samples containing anhydrite (2.97 g/cm3) had the highest density of solid particles.

The swelling capacity was analysed by means of three different kinds of tests. The swelling potential, both in terms of swelling under load and swelling pressure, was related to the total content of phylosilicates. The clay minerals identified in these samples were (in decreasing order) paligorskite, illite, smectite and kaolinite. Among these only smectite has swelling properties, and it was always found in proportions lower than 30% and on average of 8% in the less than 2 μm fraction. The particular kind of smectite found in these materials, saponite, has a very high swelling capacity, higher than that of montmorillonite, and this would explain why, despite its low content, some of the samples had high swelling potential. Other processes potentially causing swelling (such as the anhydrite transformation into gypsum and the precipitation of gypsum crystals) were ruled out. As expected, the swelling capacity was well related to the plasticity index and the liquid limit, since both increased with the phyllosilicate content. Also, the samples with a higher water retention capacity were those with the higher smectite content, even though this mineral was never present in large quantities. Samples with a higher plasticity and initial water content kept high degrees of saturation for a broader range of suctions.

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INTERCALATION OF SULFONAMIDES IN MONTMORILLONITE EXPERIMENTAL ALONG WITH MOLECULAR DYNAMICS AND DFT CALCULATIONS FOR BIOAVAILABILITY CONTROL

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The intensive use of antibiotics and especially sulfonamides in the livestock industry is getting an alarming level. The presence of these drugs in wastewaters, rivers and underground waters is increasing considerably in developing countries. At the same time, montmorillonite is a natural, low-cost, non-toxic, biocompatible clay with a high adsorption capacity. It is potentially useful as a nanocarrier to design sulfonamides dosage forms. In this work, the interaction between the drug and the clay mineral has been studied from an experimental and computational atomistic point of view to improve the drug's biopharmaceutical profile. The results showed the potential enhancement of the drug solubility due to the correct adsorption of sulfonamides in the clay interlayer space. The molecular interactions of these drugs with the surfaces of clay minerals can be interesting for evaluating their mobility in soils and for preparing composite complexes for optimal use. In this work, the intercalation of sulfonamides, such as sulfathiazole, sulfamethazine, sulfamethoxazole, sulfachloropyridazine and sulfacetamide, into the interlayer space of montmorillonite (MNT) is studied at molecular level by using computational modeling, molecular dynamics and DFT calculations. Most of these intercalations are energetically favourable, where the role of water molecules is critical. In general, the bioavailability of these compounds by intercalation in MNT is bigger than from the crystalline powder. The spectroscopic properties of these systems showed interesting frequency shifts in the bands of the IR spectrum produced during the intercalation in the confined space of MNT. These results predict that the IR spectroscopy as an interesting analytical technique for monitoring the intercalation of drugs in clay minerals.

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USE OF ALKALI ACTIVATED VOLCANIC ASH AS BINDER FOR CLAYEY SOILS TREATMENT

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The valorization of waste materials, such as natural and artificial materials with pozzolanic activity, for the synthesis of alkali activated binders represents a potential sustainable alternative to the use of traditional binders in the field of soil stabilization. Alkali activated binders are synthesized from the chemical reaction between an amorphous precursor, which is rich in alumina (Al_2O_3) and silica (SiO_2), with a sodium or potassium-based activator [1]. During alkaline activation processes, dissolution of aluminosilicate oxides in the alkali activator promotes a polycondensation reaction which results in the formation of a sodium aluminosilicate gel with cementitious properties [2]. There are several secondary by-products such as fly ash, ground granulated blast furnace slag, rice husk ash, crushed glass, etc., which are commonly used as precursor for the synthesis of alkali activated binders for geotechnical purposes [3,4,5]. Conversely, the use of alkali activation of natural pozzolanic materials as binders for soil stabilization has been quite limited. Valorization of natural aluminosilicate sources (i.e., pyroclastic deposits) is of practical interest since there is no needs for natural materials to be treated (i.e., calcination) before their use, with advantages in terms of lower cost, lower carbon dioxide emissions and easy access to the available resource.
In the present study, an insight into the mechanical improvement of a clayey soil, induced by the treatment with an alkali-activated binder (AAB) based on a volcanic ash, has been presented. The first attempt to an experimental multiscale analysis on the chemo-mineralogical evolution of the AAB and a deeper comprehension of its interactions with clayey soil particles has been developed. Mineralogical evolution of the AAB first and of the whole system later, has been monitored at increasing curing times by means of X-ray Diffraction (XRD) and Scanning Electron Microscopy (SEM). Test results shows a high reactivity of AAB treated soil (AABTS) to promote the formation of secondary mineralogical phases with cementitious properties. The evolution of mechanical performance of the AABTS has been investigated by performing unconfined compression tests on samples prepared with increasing binder contents and tested at different curing time. The addition of alkali-activated binder increases the shear strength of treated samples since very short term. Microstructural features and mechanical properties of AAB treated clayey soil highlight the strong correlation between the alkaline activation process and macroscopic evolution of soil behavior. The efficiency of treatment has been also highlighted by comparing the mechanical performance induced by alkaline activation with the one promoted by ordinary Portland cement.

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FABRICATION OF 2D/1D BI2WO6/HALLOYSITE NANOTUBES PHOTOCATALYST TOWARDS WATER PURIFICATION: A SUPPORT EFFECT ON IN SITU CONSTRUCTION AND ELECTRON-HOLE SEPARATION

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Water pollution caused by antibiotics has seriously harmed human health. Photocatalytic oxidation has been widely studied for the treatment of organic pollutants in water due to its sustainability, high efficiency, and no secondary pollution. However, the nano-photocatalyst is easy to agglomerate in water, which greatly limits the efficiency of pollutant degradation. To improve the activity of photocatalysts and attain desirable solar energy conversion, the mineral-supported photocatalysts have gained considerable attention in practical applications. Herein, a reusable and efficient 2D/1D heterogeneous structure photocatalyst based on amine-functionalized halloysite nanotubes (MHNTs) and Bi_2WO_6 nanosheet (BWO) was prepared using a facile hydrothermal method for decomposing antibiotics under simulated sunlight. The effects of composite catalysts with different preparation conditions on the degradation of tetracycline hydrochloride (TCH) were discussed. The results showed that over BWO/MHNTs with a mass ratio was 3:1, the synthesizing temperature was 120°C and the precursor pH value was 1, the TCH (10 mg/L) degradation efficiency reached 100% after 1 h irradiation of simulated sunlight. Moreover, BWO/MHNTs composites kept good recovery and stable photocatalytic activity after 5 cycles. The high activity and stability of the composite catalyst could be attributed to the good dispersion of Bi_2WO_6 on the surface of clay minerals and the facilitated electron-hole separation. In addition, the radical capture test revealed that the ·O- 2 played the most important role in the photodegradation of TCH. Thus, BWO/MHNTs composites exhibit a good application prospect in the field of natural light photocatalytic degradation towards antibiotics pollutants in water.

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HOW GOOD ARE CLAY MINERALS AS PROXIES FOR CLIMATE?

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Clay minerals formed or concentrated during surface weathering have long been suggested to provide a general proxy for climatic conditions (1). These assemblages accumulate in soils and sediments and may be preserved in rock lithologies that are not strongly overprinted by subsequent alteration after burial in the Earth's crust. The best insight into the relationship between clay minerals and climate is obtained by looking at soil profiles across the northern and southern hemispheres. Here, it is well known that kaolinite, halloysite and smectite chemically precipitate around warm equatorial latitudes whereas detrital illite and chlorite are more prone to alteration. In contrast, cold climates favour the physical enrichment of illite and chlorite over the precipitation of kaolinite or smectite. Similar trends in clay minerals and climatic zones are mirrored in the deep ocean sediments (2)

This contribution uses a recently published global clay mineral inventory (3) to assess just how well clay mineral assemblages reflect climate. The relative abundance of the main clay mineral groups (the 1:1, 2:1 and 2:1:1 hydrous phyllosilicates) is also used to evaluate the Clay Mineral Alteration Index (CMAI), which is compared with current latitudes and the Köppen-Geiger climatic zones. This CMAI relationship is defined as:

CMAI = (2:1LE+2:1:1LE) – (1:1LE+2:1HE)

(physically weathered – newly formed)

where, LE = Low to no expandability, HE = high expandability and CMAI values range between -100 (warm tropical) and +100 (cold polar).

For selected soil types, such as the alfisols, some general correlations do exist between CMAI values and distance from the equator. However, the database indicates that lithological controls on clay mineral assemblages introduce a large degree of heterogeneity to the system, which makes a direct interpretation based on numerical indices difficult to implement. Improved correlations can be made by selecting particular soils on the same types of host rocks (e.g. soils on Silurian shales, 4), where very good correlations can be attained if the climatic parameters of temperatures and rainfall are both considered. A refined correlation between CMAI and current climatic conditions is put to the test on palaeosols and shales from the geological record.

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CALCULATION OF SWELLING PRESSURES IN AQUEOUS CLAY SYSTEMS

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DLVO theory [1,2] treats intra- and interparticle forces in liquid media as an additive superposition of van der Waals and electric double layer forces. While van der Waals forces can nowadays be reliably calculated via Lifshitz theory [3], the calculation of electric double layer forces is often done on varying levels of sophistication. Even if the non-linear form of the Poisson-Boltzmann equation is used, it is often not obvious whether the double layers are entirely diffuse and which boundary conditions are appropriate for a given system (i. e. interaction at constant charge, constant potential or charge regulated).
For particulate clay minerals reliable information on parameters such as Hamaker coefficients or proper boundary conditions for the calculation of double layer forces is either scarce or virtually absent. Yet, many publications claim, for various reasons, that DLVO-theory would not be applicable in certain aqueous clay systems, see for instance [4,5,6]. Closer inspection of the calculations leading to such claims often shows that (i) electric double layers have not been treated in sufficient detail and (ii) that, at least for particulate clay minerals, Hamaker coefficients have been seriously overestimated. The latter derives from the fact that experimental Hamaker constants of the muscovite-water system have been used.
The aim is thus to provide a short overview on Hamaker functions for particulate clay minerals that were derived from the full Lifshitz theory and to outline the influence of double layer structure and different boundary conditions on the total interaction forces in clay systems. Comparison will be made against experimental force distance data (swelling pressures) in aqueous smectite suspensions.

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CALCINED CLAY MINERALS AS PRECURSORS FOR GEOPOLYMERS

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Calcined clays can be used as supplementary cementitious materials (SCM) or as precursors for alkaline activated materials (AAM) and geopolymers (GP). SCM replace only a certain amount of ordinary Portland cement (OPC), whereas AAM and GP are OPC free binders. AAM and GP are formed by the reaction of aluminosilicate precursors with a highly alkaline activator solution (NaOH or KOH) that results in the hardening of a 3-dimensional inorganic binder.
Calcined clay minerals seem to be well suited as precursors since they contain large amounts of silicon (Si) and aluminum (Al) with a molar ratio of 2:1 to 1:1. While nearly pure clay minerals are rare, common clays, that are heterogeneous concerning the phase composition, structure and particle morphology, are abundant and could be utilized as precursor after calcination.
The aim of this project was to study the relationship between clay mineral properties and process parameters (calcination temperature, adjustment of Si:Al, concentration of alkaline activator, solid:liquid ratio) during thermal and alkaline activation which influence the formation and properties of GP. Different dioctahedral clay minerals (a kaolinite, a smectite, an illite) were investigated with respect to calcination, stability after calcination, solubility and formation of GP. Furthermore, the micromechanical properties of the obtained GP were studied.
Optimum thermal activation is not only related to the dehydroxylation temperature of the clay minerals but also their composition. For both the cis-vacant smectite and the trans-vacant illite the highest solubility in 10.79 mol/L NaOH and thus the optimum thermal activation was obtained by calcination at 750 °C. All three studied clay minerals showed incomplete dissolution (< 90%). Thereby metakaolinite and metaillite dissolved congruently while metamontmorillonite dissolved incongruently. Stoichiometric mixing of the precursor and the alkaline activator resulted in excess Na^+ and the formation of trona and thermonatrite. With proceeding geopolymerization the amount of thermonatrite decreased. For calcined montmorillonite rehydroxylation at ambient conditions (22, 40 and 60 °C, 75% relative humidity) was observed after a few hours. Nanoindentation was used to determine Young's modulus and hardness of geopolymer discs prepared of the calcined clay minerals. Hardness up to 1.09 GPa were in the same order of magnitude as for cement.
Based on the knowledge gained from the investigations carried out, it was concluded that all three calcined clay minerals are suitable as precursor for geopolymers. Furthermore, it can be assumed that a mixture of the calcined clay minerals can be used as a precursor, too.

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DESIGN AND ASSESSMENT OF CLAY-BASED PRODUCTS FOR TOPICAL APPLICATION

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Clay minerals are used in many pharmaceutical and cosmetic formulations due to their unique properties, low cost, abundance and environmentally friendly character. The aim of this study was the evaluation of kaolinite and montmorillonite on occlusive properties and skin hydration.

Pharmaceutical grade kaolin and bentonite were used for the formulation of two different cosmetic semi-soli products, a facial mask and a paste. Both materials were analyzed using X-Ray Diffraction and the results demonstrated that the dominant phase in kaolin was kaolinite and in bentonite was montmorillonite. Both cosmetic products were prepared using each material resulting in a mask and paste with kaolin (*Mk, Pk* respectively) or bentonite (*Mb, Pb* respectively). The physicochemical stability of the prepared samples was tested by centrifugation and storage at 25 ^{o}C and 40 ^{o}C, for 30 days by weekly visual evaluation and measuring their pH and viscosity. All samples were stable for the tested period.

The occlusive properties of the facial masks were evaluated by monitoring their film forming capacity by Scanning Electron Microscopy after spreading them on a cellulose substrate and by calculating their occlusive index (F) *in vitro*. The *Mk* produced continuous and thicker film, covering completely the cellulose fibers. The F for both masks was similar ($p>0.05$), but *Mk* maintained its occlusion properties longer than *Mb* ($p<0.05$).

The effect of the pastes on skin hydration was tested *in vivo* in healthy volunteers calculating the skin conductivity change in predetermined intervals (30 min, 1 h, 2 h) after application of each paste on the volar forearm of each volunteer for a 2 h period. The perception of the volunteers on the use of pastes was also evaluated by asking them to fill out questionnaires. Both pastes demonstrated similar effects ($p>0.05$) on skin hydration that was elevated by about 30 ± 9 hydration a.u, 30 min post application of either paste, remaining at the same levels for at least 2h. Most of the volunteers replied that both pastes had excellent cosmetic properties and effectiveness.

Our results demonstrate clay minerals may contribute to the enhancement of cosmetic properties of topically applied products.

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MINERALOGICAL AND GEOCHEMICAL INDICATORS OF PALEOSOL WEATHERING ACROSS THE PALEOCENE-EOCENE BOUNDARY IN THE BIGHORN BASIN, WYOMING, USA

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Strong climatic warming led to increased abundances of detrital smectite in the Bighorn Basin during the Paleocene-Eocene Thermal Maximum (PETM) and Eocene Thermal Maximum 2 (ETM2) (Wang et al., 2017; Ji et al., 2023). Field observations show widespread and intensive soil formation possibly linking to mineral weathering. Alternating episodes of river avulsion/floodplain deposition and soil formation have obscured the authigenic clay signal, which was overlooked in previous quantitative clay mineral studies using broadly spaced (one-meter) samples. Here, we performed an integrated analysis of a pre-PETM and a PETM paleosol horizon collected at higher spatial resolution (5-20 cm) from Sand Coulee, Bighorn Basin, Wyoming, USA, and focused on the youngest paleosol horizons during the river avulsion/floodplain cycles, which were quickly covered by later avulsion deposits, to avoid the influence of aggradational pedogenesis. X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and X-ray fluorescence (XRF) spectrometry were employed to study the mineralogical and geochemical features of the paleosols. Bulk mineralogy consists of quartz, feldspar, calcite, dolomite, and phyllosilicates. Average contents of quartz decrease, and plagioclase increases from the B horizon to the C horizon, while K-feldspar abundance varied irregularly. A large increase of smectite and a decrease of mixed-layered illite-smectite (I-S) were observed over the same interval. The two paleosols exhibit different characteristics of the chemical index of alteration without potassium (CIA-K) and paleosol weathering index (PWI). In the PETM paleosol, CIA-K increased and PWI decreased downward from 64 to 74 and 44 to 31, respectively, whereas in the pre-PETM paleosol, no changes in CIA-K and PWI were observed. We are still studying the minerology and geochemical indicators, and the first results point that the increase of smectite may reflect decomposition of feldspar and weathering of the edges of I-S crystals to smectite. Neoformed honeycomb smectite and dissolution of feldspar along cleavage planes were observed, while the genetic relationship between smectite and feldspar needs to be further confirmed. The alkaline and seasonal dry conditions with soil pH ranging from 8.6 to 9.4 may favor feldspar dissolution and smectite crystallization. The contrasting changes of CIA-K and PWI in the PETM and Pre-PETM paleosols may indicate different chemical weathering intensities owing to changes in climate conditions over time.

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EFFECT OF GRANULATION PROCESS ON SWELLING AND HYDRAULIC BEHAVIOUR OF GRANULAR BENTONITE

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Bentonite clays are used as engineered barrier material in waste containment facilities, like tailing ponds and landfills. These bentonite materials show very low hydraulic conductivity, high swelling capacity, and high retention capacity upon hydration [1]. Granular bentonites (GB) are generally preferred as it is primary product in bentonite processing, and it produces less dust during transportation and installation process. The final mean effective grain size of GB varies in wide range (i.e., 0.25mm – 1mm) due to various factors like initial moisture content, plasticity, and mechanical processes [2-4]. The process of hydration lead to development of repulsive forces which lead to the disintegration of granules of GB. These repulsive forces lead to the development of a pressure on the surroundings if kept under isochoric conditions. The influence of different granule size on development of swelling pressure and hydraulic conductivity under constant volume conditions by maintaining the mineralogy and plasticity is not available. The present study will evaluate the swelling pressure using constant volume method for GB with different grain sizes. Hydraulic characteristics will also be evaluated simultaneously by attaching the burette with pore-fluid using falling head method. The rate of development of the swelling pressure also varies with granulation of GB. The higher rate of development of pressure was observed in coarse grained GB due to higher water permeation initially and swelling progresses in complete sample simultaneously. Moreover, finer GB shows slower rate of swelling pressure development as its process progresses from direction of permeation. But finer GB achieved higher swelling pressure at equilibrium as compared to coarse grained GB. The mechanisms governing the swelling and hydraulic behaviour will be discussed in detail.

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DESIGN OF THE MOLECULARLY THIN AMORPHOUS SILICA NANOSHEETS UTILIZING SOLID-STATE LAYERED SURFACTANTS

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Amorphous silica is one of the most widely used silica-based materials, and there are various chemical protocols for creating diverse nanostructures with controlled morphology. In particular, amorphous silica nanosheets have been researched for several decades, and the design of the thickness at a molecularly thin level has been progressively revealed to be crucial.[1] However, amorphous silica cannot be accessed by conventional layer exfoliation because of the nonexistence of its bulk layer counterpart. Recently, we found the rational approach for synthesizing molecularly thin amorphous silica nanosheets (0.9 nm thickness) utilizing surfactant silica lamellar hybrids[2]. Although this novel method allows to obtain monolayer silica nanosheets selectively and fabricate the precisely assembled film, the thickness control is still challenging because of the lack of understanding on the formation mechanism. Here, we clarified the essential factors for synthesizing layered hybrids suitable for the exfoliation of amorphous silica nanosheets[3] and succeeded in accurately controlling the thickness of the nanosheets.

The silica-surfactant lamellar hybrids were prepared by adding tetraethoxysilane into the dispersion of the non-ionic surfactant Brij52 ($C_{16}EO_2$). The critical factor to obtain the lamellar hybrids suitable for exfoliation was the synthetic temperature, which was lower than the Krafft point of surfactant. Although the surfactants have been generally used after dissolving in the solution, our method required the solid-state surfactant without forming micelles as templates. In fact, XRD patterns showed that the lamellar hybrids were successfully formed when we synthesized hybrids below 50 ºC, which is the Krafft point of $C_{16}EO_2$. On the other hand, the SEM image showed that no obvious mesostructured silicas were obtained when we applied over 50 ºC. Then, we synthesized lamellar hybrids below Krafft point using various kinds of non-ionic surfactants with different hydrophilic head group lengths ($C_{18}E_2$, $C_{16}E_{10}$, and Tween40). The lamellar hybrids were successfully obtained below Krafft points, as shown by XRD patterns. The obtained lamellar hybrids were exfoliated into the ethanol, and the thicknesses of nanosheets were investigated by the AFM measurement. The thicknesses of nanosheets synthesized using $C_{18}E_2$, $C_{16}E_{10}$, and Tween40 were 1.0, 1.5, and 2.0 nm, respectively. The thickness of the nanosheets corresponds to the length of the hydrophilic head groups, which indicates that we can control the thickness of the nanosheets by the design of solid-state surfactant lamellae. Therefore, this solid-state surfactant templating method is potentially useful for the general design of amorphous nanosheets.

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INSIGHT INTO THE SPIRAL GROWTH OF DISORDERED KAOLINITE NANOCRYSTALS

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The mechanism of spiral growth driven by screw dislocation in disordered nanocrystal kaolinite, which leaves growth spirals on the (001) face of high-defect kaolinite nanocrystals when the growth unit encounters internal or external stresses that cannot be compensated by self-adaptive deformation. A large amount of substitution of AlIV for Si in the tetrahedral sheet destabilizes the kaolinite structure significantly, triggering screw dislocations introduced by the Burgers vector and resulting in the breaking through of the corrugated tetrahedral sheets. Compared with the radius ratio of RSi4+ : RO2- =0.331, the RAlIV3+ : RO2- =0.438 is too high for the ideal tetrahedron hole created by the closest packing tetrahedral oxygens, which implies a radius ratio of 0.155. Increasing AlIV: Si will further destabilize the distorted kaolinite, which can not be compensated by the self-adaptive deformation, leading to the overall fit being considerably dissatisfied for the kaolinite structure. Local stress also generates a horizontal vector due to the higher ionic radius of Al3+ than Si4+ in fitting the tetrahedral hole, as supported by the SAED and HRTEM lattice patterns with a small angle staggering between the adjacent layers.
Keywords: Kaolinite, Spiral growth, AlIV for Si substitution, Lattice patterns, SAED

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ALTERATION OF COMPACTED BENTONITE PERMEATED WITH NAOH AND CA(OH)2 SOLUTIONS AT 50 °C

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Bentonite is used as an engineered barrier in radioactive waste disposal facilities to inhibit radionuclide migration. Bentonite reacts with the alkaline solution generated by the reaction between the cementitious materials and groundwater. The physicochemical properties of bentonite change with mineralogical alterations under long-term exposure to alkaline conditions. Therefore, the evolution of bentonite alteration under alkaline conditions is important for long-term performance assessment.

In this study, the permeability and mineralogical alteration of compacted Na-type bentonite (Kunigel V1), with a dry density of 1.6 Mg/m^3, was investigated by permeability tests using NaOH (300 mmol/l, pH = 13.4) and $Ca(OH)_2$ (5 mmol/l, pH = 12.0) solutions at 50 °C for 8.6 years. The hydraulic conductivity of the specimens were measured using a constant-volume permeameter. Dissolved ion concentrations of the solution were monitored during the permeability test. The solid samples after 3.7 and 8.6 years were analyzed to evaluate alteration behavior.

In the NaOH solution, the hydraulic conductivity decreased slightly until approximately 700 d and remained constant until 1500 d; after which, the permeability exhibited a slightly increasing trend. For the $Ca(OH)_2$ solution, the hydraulic conductivity remained nearly constant during the permeability test. For both NaOH and $Ca(OH)_2$ solution, leaching of Si due to mineral dissolution was observed. Furthermore, some of the Na ions and almost all Ca ions in each input solution were consumed in the specimens during the permeability test. This consumption of cations may be due to ion-exchange reactions and the precipitation of secondary products.

Based on the powder X-ray diffraction (XRD) measurements, although the peak intensity of cristobalite was weaker in the sample permeated with NaOH solution for 8.6 years, the mineral composition did not change significantly after all solutions was permeated for both 3.7 and 8.6 years. The montmorillonite content ratio in the NaOH solution increased with time in the lower part of the specimen because of the preferential dissolution of associated minerals such as cristobalite. In contrast, in the $Ca(OH)_2$ solution, the montmorillonite content ratio was not altered. The composition of the exchangeable cations in the NaOH solution showed an increase in the percentage of exchangeable Na over 3.7 years, regardless of the position of the specimen. For $Ca(OH)_2$, the percentage of exchangeable Ca increased with time, although it did not differ with the position of the specimen.

From the results of long-term permeability tests, the common alteration reactions were the dissolution reaction of associated minerals, cation exchange reaction, and possibly precipitation reactions of secondary products. The extent of these reactions and their effects on the hydraulic conductivity varied significantly depending on the type of solution and pH.

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BULGARIAN ZEOLITE CLINOPTILOLITE FOR CATALYSTS CARRIER FOR REACTION OF ENVIRONMENTAL PROTECTION

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Volatile Organic Compounds are one of the major air pollutants. Catalytic oxidation is recognized as one of the most efficient methods employed to VOCs eliminations.

Among the metal oxides, cobalt and manganese oxides has been shown to be one of the most efficient in the total oxidation of VOCs [1]. An effective principle in the practice of heterogeneous catalysis is the application of the active phase to a chemically inert support. The extremely high activity and selectivity of zeolites in a number of catalytic reactions, the high thermal stability of their crystal lattice and their molecular sieve effect make them very suitable as catalyst carriers.

The zeolite used in this work was obtained from a deposit located near Beli Plast village, Eastern Rhodope Mountains, Bulgaria. Mineralogical composition of parent material is Clinoptilolite (88-89%). Two methods of modification of clinoptilolite before deposition of active phase was used: ion exchange and acid treatment. The prepared catalysts were obtained by the wet impregnation method. The studied samples were calcined at 500°C for 3 h. The experimental techniques that were used for characterization of the so prepared catalysts are: XRD, TPR, XPS and adsorption properties. Catalytic activity was examined in the reaction of complete oxidation of n-hexane. In air, n-hexane participates in radical reactions, which are involved in the formation of photochemical smog.

The modification performed by ion exchange leads to partial or almost complete removal of the interfering cations. The acid treatment of the starting natural clinoptilolite for its use as a carrier leads to a decrease in the size of the crystallites and an increase in the specific surface area.

A phase of Co_3O_4 is formed in cobalt catalysts. Several oxide phases are formed in manganese catalysts on clinoptilolite: MnO_2, Mn_3O_4, and Mn_2O_3. The oxides formed are highly dispersed and easily reduced, which determines the high catalytic activity in the oxidation reaction of n-hexane.

Samples with a lower concentration of active phase (10%) show higher catalytic activity. This is due to a more uniform distribution of the active phase on the carrier surface, smaller size of the crystallites and easily reducible Co- and Mn-oxide phases.

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CLAYS FOR THE CERAMIC TILES INDUSTRY

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The ceramic tile industry is a dynamic sector whose technological innovation and market trends paint a complex picture both in terms of products and processes. The commercial success of ceramic tiles is due to a continuous increase of product quality from both technical performance and aesthetic appearance viewpoints. Such a quality improvement stems from the intensive product (for example the advent of large slabs) and process innovation (dry- granulation)that took place during the last decades and is now widespread in every tile-making country. The raw materials have been and are always deeply involved in this evolution: the flexibility of current processing cycles allows the use of a very wide range of clays, whose chemical and mineralogical composition, granulometric distribution and ceramic properties are always in constant evolution. Moreover, in the contingent period, the recent geopolitical events have also highlighted critical issues in the approval of imports of ceramic raw materials, in particular as regards clays. As a consequence, a paradigm shift occurred in the formulation, also due to the use of waste of various kinds, of ceramic bodies and in the selection of raw materials. The purpose of this work was to outline the evolution of the ceramic use of clay materials in terms of types of clays (chemical composition, granulometry, etc.) and the consequent technological evaluation as well as their relative future prospects.

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ABSTRACT WITHDRAWN: LAST MINUTE CANCELLATION

Name Surname* (1)

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ECO-FRIENDLY AMINO FUNCTIONALIZE CLINOPTILOLITE@ HAP AS AN ADSORBENT FOR SIMULTANEOUS REMOVAL OF CR(VI) AND F-

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Nowadays, water contamination with heavy metal ions and anions has become a burning issue and significant concern due to the economic and industrial development. In aqueous phase, chromium exists in two forms, namely, the trivalent (Cr(III)) and the hexavalent (Cr(VI)) chromium. While Cr (III) acts as a nutrient to control the protein metabolism, C(VI) is carcinogenic and mutagenic and also cause a great threat to human health, even at trace concentration. In addition, the presence of Fluoride in water depending on the concentration between 1.0 and 1.5 mg /L can be useful, especially for calcination of the dental enamel of children. In contrast, high concentration of F^- is harmful to human health and lead to some problems [1] . In this prospective, an attempt has been made for the synthesis of Amino-functionalized Clinoptilolite @ Hydroxyapatite (Clino @ HAP/NH_2) for removal of Cr(VI) from aqueous environment. In the present study, the physochemical properties of the synthesized adsorbent were extensively characterized utilizing various instrumental techniques including FT-IR, XRD, SEM and the specific surface area by N_2 adsorption-desorption isotherms. Surprisingly, the synthesized Clino @ HAP/NH_2 not only detects Cr(VI) but also recognizes fluoride anions, remarkably. Expectedly, in all cases with functionalized amino group, the percent of removal of pollutants was increased. Furthermore, the mechanism for detection of Cr(VI) and fluoride ions was evaluated. Subsequently, batch adsorption studies were implemented to consider the effect of parameters such as the contact time, pH, temperature, and initial concentration of pollutants, types of adsorbent and adsorbent dosage. In accession, regeneration and reusability studies were carried out to enable the effective utilization of the Clino @ HAP/NH_2 nano composite. A pseudo-second order model is the best described the kinetic mechanism and the isotherm data were fitted well by the Langmuir isotherm and Freundlich model [2].

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VARIABILITY OF CLINOPTILOLITE CONTENT AND CONTAMINANT ADSORPTION PERFORMANCE OF CLINOPTILOLITE FROM A LARGE MINE IN SEMNAN PROVINCE (IRAN)

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Clinoptilolite is a naturally occurring zeolite mineral which is commonly used in various industrial and agricultural applications, including water purification, gas adsorption, and soil amendment. Iran is one of the countries that has significant deposits of clinoptilolite some of those being located in the Semnan province. The Semnan clinoptilolite deposits have been already studied for their potential use in water treatment, as the mineral has demonstrated high efficiency in removing various types of heavy metals and organic pollutants from contaminated water. In order to accurately assess the clinoptilolite content within a given deposit, samples taken at different locations and depths from a large mine in the Semnan province has been analysed by XRF and XRD for chemical and mineral phase compositions. Other physical and adsorption properties were also characterized by TGA, BET, SEM observations and N_2 adsorption-desorption isotherms. Samples were also tested for removal of different kind of contaminants from water. The results of Rietveld quantitative phase analysis (QPA) showed that clinoptilolite content varies from up to 80 wt% in agreement with the TG analyses. The N_2 isotherms showed a hysteresis loop between 0.5 to 0.9 for the 1-4 and 6. The specific surface area of samples was found about 29-118 m^2/g . SEM images showed rounded morphology of clinoptilolite aggregates with size in the 40-200 nm range. The adsorption experiments of Pb (II), Cd (II), Cr (VI), NH_4^+, Methylene blue (MB) and Gentamicin in water performed on the clinoptilolite samples confirmed the great potential of these materials to be used for water remediation [1]. As expected, the adsorption performances for all contaminants scale with the clinoptilolite content in the samples. However, distinct linear or polynomial relationships were observed.

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SILICATE WEATHERING AS A THERMOSTAT FOR RECONCILING THE LATE MIOCENE CLIMATE-CARBON CYCLE TRANSITION

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Earth's climate has been regulated over millennia by the solubilization of atmospheric carbon dioxide ($[CO_2]_a$) through silicate mineral weathering [1-3]. Although this powerful feedback mechanism is wildly known, it remains an open question how the thermostat coordinates the climate-carbon cycle, particularly when non-temperature related climate events occur. In this study, we analyze a set of continental silicate weathering records from a drill core in eastern China covering the past 8 million years, using clay mineral, spectral, and geochemical methods. Here, we validate the clay-mineral-structure-related spectral parameter D_{1400}/D_{1900} as a proxy indicator for the $[CO_2]_a$ consumption via silicate weathering.

We find that around 6 Ma, both long-term and orbital scale switches occur, signaling a reorganization of the climate-carbon cycle system. The similarity in timing between the crustal production reduction and continental weathering CO_2 sink contraction suggests a dominant CO_2 source forcing of the late Miocene climatic and ecosystem change. Two distinctive climate states emerge with different orbital variations imprinted on the silicate weathering signals: the monsoon-driven state (after 6 Ma) and the glacial-dominated state (prior to 6 Ma). In the monsoon-driven phase, eccentricity-band (i.e., ~200-kyr and ~100-kyr rhythm) dominated the silicate weathering records, indicating a strong influence of monsoon-related low-latitude processes on climate and carbon cycles. After 6 Ma, the distinctive ~1.2-Ma and ~173-ka rhythm are stemmed from Earth's long-term obliquity modulation, suggesting a strong imprint from the high-latitude glacial variations and hence the emerge of the glacial-dominated state. After the major climate-carbon cycle shift occurs, the silicate weathering reconciled the balance between climate and carbon cycle variations. Proxy records indicate that the Earth's $[CO_2]_a$ did not plunge to extremely low values following the CO_2 degassing shrinkage at 6 Ma. The falling $[CO_2]_a$ produces a colder, drier climate that retards weathering, whereby the strong negative feedback mechanisms inhibited further $[CO_2]_a$ drawdown. Silicate weathering work as a geologic thermostat that coordinates the climate-carbon cycle on both long-term and orbital scale, playing a major role in maintaining the habitability of our planet.

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MO–V–O/MONTMORILLONITE CATALYSTS FOR GAS-PHASE OXYDEHYDRATION OF GLYCEROL

Chun Hui Zhou* (1), Alfin Kurniawan (1), Ke Jin Li (1), Da Jian Li (1), Wei Jun Huang (1)

(1) Zhejiang University of Technology

The catalytic gas-phase (oxy)dehydration of glycerol represents a promising industrial process for the sustainable production of acrolein and/or acrylic acid [1]. Several types of solid acid catalysts based on supported mixed metal oxides have been developed [2-4] and among them molybdenum–vanadium oxides (Mo–V–O) supported on montmorillonite (MMT) could afford 52% selectivity to acrolein at an initial conversion of 92% [2]. However, the practical applications of MMT and MMT-supported catalysts in the above conversion process are still hindered by the build-up of coke deposits that causes progressive deactivation and thus loss of catalytic activity and/or selectivity [3]. In this study, the coke formation on the acid-treated MMT (HMMT) supported Mo–V–O catalysts during gas-phase glycerol (oxy)dehydration of glycerol was investigated in detail to elucidate the nature and formation pathways of carbonaceous compounds as a function of time-on-stream (TOS) by multiple characterization techniques. The effects of acid modification and the impregnation-deposition of Mo–V–O particles on the MMT layer structure were examined by X-ray diffraction, Fourier transform infrared spectroscopy, and scanning electron microscopy. Total coke content, as well as soluble and insoluble coke fractions formed on the deactivated catalysts were characterized by multiple techniques, such as GC-MS, 13C solid-state magic-angle spinning nuclear magnetic resonance, and X-ray photoelectron spectroscopy. The major chemical constituents of soluble coke were mononuclear aromatic derivatives (e.g., xylenes, 2,4-di-tert-butylphenol, and 1-hydroxycyclohexyl phenyl ketone) and long-chain paraffins with 12-18 carbon atoms. The aldol condensation reactions of acetaldehyde and ketone lead to the formation of light monoaromatic hydrocarbons, which further react with light olefins to form insoluble polyaromatic coke species at higher TOS. A picene-like structure of insoluble coke containing various oxygen-bonded groups, such as –OH, –CHO, and –COOH is proposed based on the ^{13}C solid-state NMR analysis. Acknowledgements: The authors wish to acknowledge the financial support from the National Natural Science Foundation of China (22072136; 41672033).

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INFLUENCES OF MICROPORES AND WATER MOLECULES IN THE PALYGORSKITE STRUCTURE ON THE COLOR AND STABILITY OF MAYA BLUE

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Maya blue is an ancient hybrid pigment composed of indigo and microporous palygorskite, with a fantastic hue and outstanding stability [1]. Its color-causing and stabilization mechanism are unsolved problems. Previous work implied that water molecules in clay micropores might be related to the formation of Maya blue pigment [2]. However, the influences of different water molecules and micropores on the color and stability of Maya blue have not been clarified.

In this work, palygorskite materials containing different water molecules were obtained by heating at 180, 300, and 570°C. Maya blue-like pigments were prepared from these palygorskite materials and solid indigo by grinding. The microporous structure of palygorskite and the status of inside water molecules were investigated by thermal analysis, X-ray diffraction, Fourier transform infrared and microporous analysis. The color properties, chemical resistance, and photostability of pigments were characterized by reflectance spectra, CIE color parameters, and color differences after the attack of concentrated nitric acid, dimethyl sulfoxide, and visible light exposure equaling about 100 years.

It was confirmed that the stable greenish-blue hybrid pigment could only be prepared when indigo molecules were inserted into the micropores of palygorskite. Zeolitic water molecules inside the micropores should be removed because they hindered the insertion of indigo molecules. The key to immobilizing indigo molecules inside micropores was hydrogen bonds between indigo and coordinated water [3]. This study emphasized the important role of micropores and hydrogen bonds in the synthesis of organic-inorganic hybrid pigments.

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FUNCTIONALIZED HYBRID MATERIALS BASED ON CLAY MINERALS FOR CO2 SORPTION

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Excessive use of fossil fuels, rapid industrialization, and urbanization are raising increasing concerns about climate change. As many indications point out, it is associated with an increase in greenhouse gas emissions into the atmosphere, and carbon dioxide has been identified as a major cause of global warming and climate change. Therefore there is a continuous need to minimize the level of CO_2 emission and create novel materials that can be used for CO_2 capture. When designing such materials their production costs, long-term stability, and the highest performance should be crucial in broad manufacturing, however, in the global application, the safety of the environment in which we live also should be taken into mind. In this regard, clay mineral-derived materials can be considered strong candidates for CO_2 removal, the advantages of which are easy accessibility, susceptibility to modifications, and high sorption potential without the need to apply amines that are toxic to humans and the environment.

The aim of this work focused on the enlargement of the base properties of parent smectite, with a small basic character resulting from the presence of Mg in its structure and evoking the release of magnesium ions from the octahedral sheet of the clay mineral resulting in the auto-transformation of the structure of the clay-derived composite. The templating methods were applied to produce porous hybrid composites based on layered hydrous magnesium silicate, Laponite, and amorphous silica. A series of composites were functionalized by mechano-chemical Fe doping and microwave irradiation in the slightly acidic salt solution. It resulted in a benign proton attack on the layers of clay mineral, intense leaching of Mg^{2+} cations from the octahedra, and their forced migration to the surface upon treatment. It was confirmed by the XPS and FTIR technics, which show the increase of Mg/Si ratio accompanied by the decline of the (Mg_3OH) absorption bands intensity attributed to Laponite. The results showed that the leached-out Mg cations are captured on the surface of the composites grain and constitute the source of cations for nucleation of nanostructured MgO moieties with weak base properties capable of adsorbing CO_2. CO_2-TPD investigation and DFT calculations revealed that the sorption of CO_2 molecules on MgO basic centers is closely related to the coordination of oxygen sites in the MgO lattice while edge and corner O^{2-} sites facilitate the interaction with CO_2 molecules. Doping of clay-derived composite by microwave modification resulted in the crystallization of the α-Fe_2O_3 nanoparticles able to capture CO_2 molecules with the strength and quantity higher than on MgO centers and different kinetic of sorption. In this work, the mechanisms leading to nucleation and formation of basic centers on the porous clay-derived composite surface are described in detail with the use of advanced XRD, SEM/BSE/EDS, FTIR, XPS, TG/DSC, CO_2-TPD methods and ^{57}Fe Mössbauer spectroscopy supported by DFT calculations. The one-pot synthesized porous composites equipped with Me^{x+} (where $Me^{x+} = Ca^{2+}$, Zn^{2+}, Zr^{4+}) were prepared and comparatively investigated towards application as sorption materials. The difference in surface basicity and contribution of surface species in the efficient sorption of CO_2 molecules as well as the mechanism of CO_2 sorption on these centers are discussed. This study shows that the application of solvothermal synthesis under microwave irradiation results in significant development of the surface basicity as part of the transformation of Laponite structure and confirms the importance of clay minerals in the uptake and retention of CO_2 as available, cheap, and environmentally safe, thus “green solid sorbents”.

[1] 1. M. Zimowska, M. Śliwa, H. Pálková, J. Gurgul, R. P. Socha, Applied Surface Science 619 (2023) 156768

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INFLUENCE OF FULVIC AND HUMIC ACIDS ON THE UNDRAINED SHEAR STRENGTH OF CLAYEY SOILS

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In engineering, soil organic matter is considered detrimental for engineering properties. This is especially relevant in the case of clayey soils, as this challenging material shows unpredictable soil mechanical behavior. Although this issue has received little attention in the scientific community, recent studies showed that organic material alters indeed the soil mechanical properties (e.g. Varghese et al., 2021; Zeng et al., 2017). However, results are contradictory and difficult to interpret, because they focus purely on physical parameters, and they lack sample characterization of clay and organic used. In this study, the influence of organic matter on the shear strength of different clays was investigated. For the mixtures, commercial humic- (HA) and fulvic acid (FA) were mixed with the four different clays kaolinite, illite, Ca-, and Na-bentonite. HA and FA were chosen because they are the two most prominent proxies for soil organic matter and have been used for over two centuries. Results of the vane shear tests on organic-clay mixtures showed that the outcome strongly depends on the clay used. Overall, HA increases shear strength of Ca-bentonite and illite, while it decreases the shear strength of kaolinite and Na-bentonite. The addition of FA decreases the shear strength of all clay samples but to a different extent. This intuitively implies that the results depend very much on direct interaction between organic used and clay mineral type. However, further physicochemical investigations revealed that the influence of organic matter on the shear strength of clayey soils was not always a result of a direct reaction between organic and clay. More often, it is a secondary interaction which involves i.e. impurities (soluble cations) in the organic used or accessory mineral phase in the clay used. Such secondary interactions are often a result of an altered soil pH due to the mixing of clay and organic. This shows further that seemingly less important properties of clay or organic matter may be key parameters for the mechanical behavior of organic-rich clayey soils. But it also shows that even simplified organic-clayey soils are by no means a binary system. Future research should carefully assess its samples and consider a paradigm shift away from HA/FA towards more natural organic matter (Lehmann and Kleber, 2015).

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INDEX OF AUTHORS

NOTICE. THE NAMES OF SOME OF THE AUTHORS WERE NOT ERRONEOUSLY OMITTED BUT THEY WERE NOT AVAILABLE SINCE THEY HAD NOT BEEN INSERTED DURING THE ABSTRACT SUBMISSION PROCEDURE.

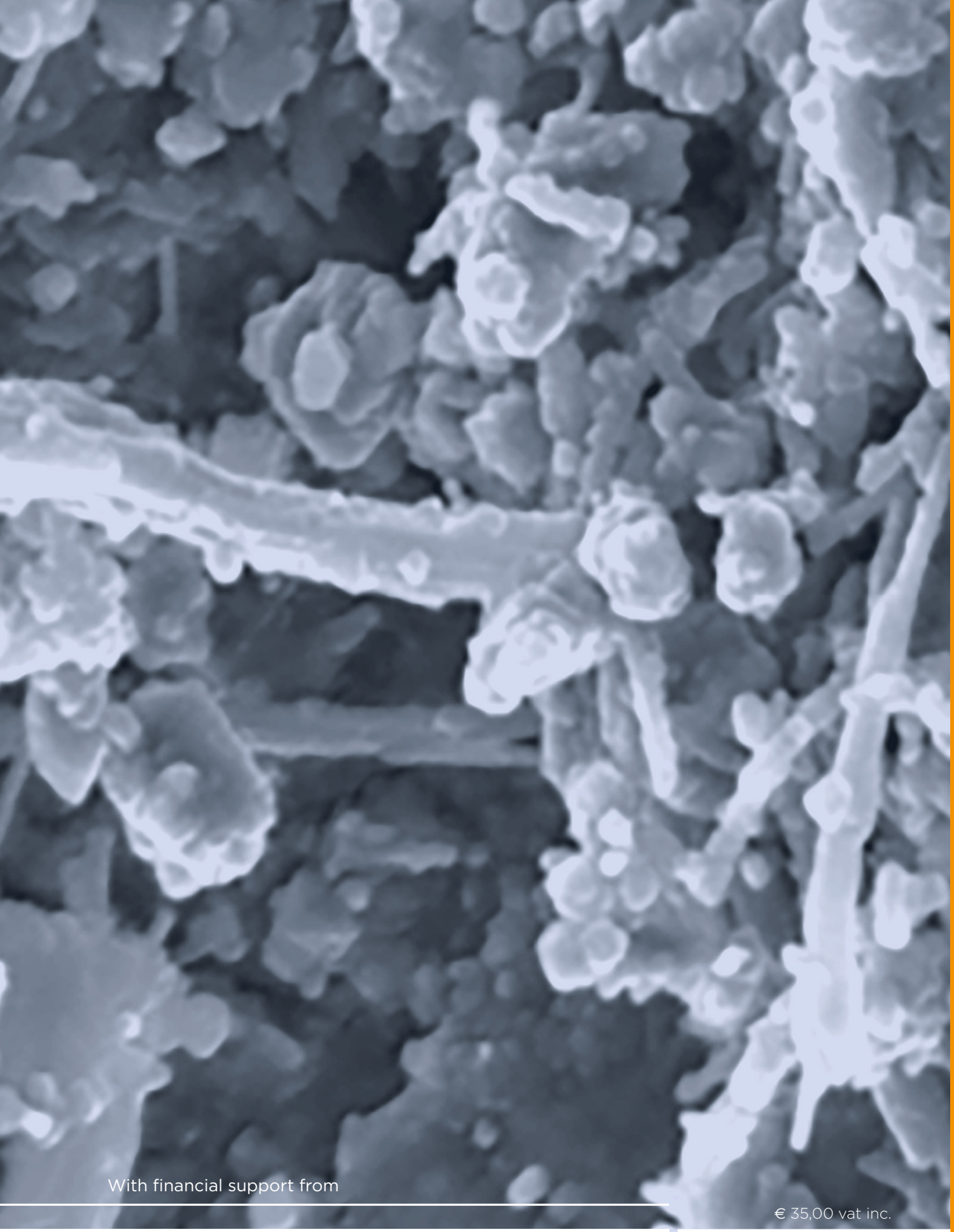
ABDELSATER MOHAMMAD 1
ABDOLRAHIMI MARYAM 22
ABELS HEMMO A. 311
ADATTE THIERRY 50
AEPPLI MERET 77
AGUZZI CAROLA 168,302
AHRENS LUTZ 165
AJDUKOVIĆ MARIJA 279
ALAYA YOSRI 189
ALBUQUERQUE ELAINE 114
ALCÂNTARA ANA C.S. 2
ALGEO THOMAS J. 311
ALLARD THIERRY 3,14,13,192
ALMARZA-CIFUENTES PABLO 118
ALMEIDA FERNANDO 258
ALMEIDA MARIANA M. 99
ALOMAYRI THAMER SALMAN 132
ALONSO URSULA 4,5,184,185
ALOUPI ELENI 142
ALTIMARI FABIANA 6
ALVERÀ GRETA 7
AMALIN DIVINA 212
AMENT KEVIN 298
AMICONE SILVIA 142
ANDREJKOVICOVA SLAVKA 176
ANDREJKOVIČOVÁ SLAVKA . . . 8,248,258
ANDREOLA FERNANDA 9,6
ANDREOU FEVRONIA T. 45,274
ANGELICA ROMULO 10
ANGIOLETTI-UBERTI STEFANO 203
ANSART CLAIRE 3
ANSOE-TAREAU CLARISSE 130
APARICIO CLAUDIA 255
ARANDA PILAR 167,232,2
ARCHER P. DOUGLAS 176
ARDIT MATTEO 68
ARENAS CONCHA 20
ARGENZIANO MONICA 84
ARLETTI ROSSELLA 83,84
ARMBRÜSTER MARC 298
ARREBOLA VARGAS FRANCISCO . 168,302
ASAAD ALI 12,11
ASSADI M. HUSSEIN N. 70
ATAYTÜR ÖYKÜ 14,13
ATSUO YASUMORI 270
AUQUÉ LUIS 20
AURELL MARCOS 150
AVERSEG FRÉDÉRIC 192
AZEVEDO JOYCE 114
AZUMA KAZUKI 204
B. HUNVIK KRISTOFFER W. 92
BA NDIAYE DIANGA 287
BÁDENAS BEATRIZ 150
BADJI MAMADOU 15
BAELE JEAN-MARC 289
BAEYENS BART 140
BAI YUQING 220,299
BAILLE WIEBKE 11
BAKKER ELEANOR 76
BALAN ETIENNE 3
BALASSONE GIUSEPPINA 52
BALDE MAMADOU 287
BANAŚ MICHAŁ 288
BANDURA LIDIA 95
BANKOVIĆ PREDRAG 279
BARAKAT YARA 16
BARATELLA VANESSA 233
BARBIERI LUISA 6
BARBORA BÖSERLE HUDCOVÁ 17
BARBOSA RAQUEL DE MELO 177,114
BARLOG MARTIN 18,162,226,277
BARON FABIEN 170,77
BARRE PHILIPPE 61
BARRION ALBERTO 212
BARRIOS SANTOS 283
BASCHINI MIRIA 200
BASHIR SANAM 19
BASTIDA JOAQUÍN 20
BATBAATAR MUNKH-ERDENE 33
BAUDIN FRANÇOIS 197
BAUER ANDREAS 151
BAULUZ BLANCA 150,149
BAYON GERMAIN 50
BEAUVOIS ANTHONY 242
BECCALETTO LAURENT 178
BEDRNOVÁ EVA 69
BELAROUI LALA SETTI 31
BELLOTTO MAURIZIO 21,106
BELVISO CLAUDIA 22,165
BEN HAJ YAHIA NOUR 147
BENASSI PIER PAOLO 6
BENMAHDI LAHCENE 31
BENNING LIANE 77
BENTABOL MARIA 23,118
BERGAMASCO ROSÂNGELA 172,173
BERNAL LOPEZ SUSAN 136
BERNIER FRÉDÉRIC 16
BERRAUD-PACHE ROMAIN 158
BERTOLINO ANA VALÉRIA FREIRE ALLEMÃO 26
BERTOLINO LUIZ CARLOS 24,26,25
BHOWMICK SUBHAMOY 264
BIAŁOSZEWSKA MONIKA 95
BICKMORE BARRY 27,79
BIDE TOM 136
BILLON SOPHIE 229
BILSKÁ KATARÍNA 28,35
BIRD CLARE 194
BIROŇ ADRIÁN 299
BISHOP JANICE L. 29
BISWAKARMA JAGANNATH 77
BISWAS BHABA 30
BIZIEN THOMAS 115
BLACK LEON 136
BLATMANN THOMAS 325
BLONDET JUSTINE 50,289
BLUKIS ROBERTS 77
BOCEIRI NADIA 31
BOCHICCHIO DOMINGA 273
BODIAN MALANG 15
BOHÁČ PETER 277,239,299
BÖHM LEONARD 32,103
BONNET MARINE 33
BORREGO-SÁNCHEZ ANA 169,304
BOSBACH DIRK 140
BOSE PURNENDU 265
BOUCHEZ JULIEN 3,14
BOUHEBDALLAH MARWA 242
BOURBON ELORA 192
BOURBON XAVIER 74
BOURQUIN SYLVIE 178
BRAGIĖ EMILY 48
BRANDT FELIX 140
BRČEKOVÁ JANA 299
BREU JOSEF 225,262,111,85,281,93,292,92,171,224,280,298
BRIAIS JUSTINE 289
BRIENZA MONICA 179
BRIGANTE MARCELLO 91,90,242
BRIOIS VALÉRIE 242
BRITO PAULO HENRIQUE MICHELS . . . 92
BRIZZOLARA STEFANO 256
BROOKBANKS ADAM 134
BRUNEAU LUDOVIC 178,289
BUDZÁK ŠIMON 239
BUGYNA LARYSA 277
BUJDÁK JURAJ 34,28,226,35,239,277
BUJDÁKOVÁ HELENA 35,28,277
BÜNNING KAMILLA THINGHOLM 36
CAGGIATI MARCELLO 7
CAI MINJUAN 90,91
CALMELS DAMIEN 3,14
CALVINO MARTINA MARIA 37
CAMPOS GEMMA 303
CAPELA MARINÉLIA 38
CAPPELLETTI PIERGIULIO 52,190,305,104,294
CARBONE CRISTINA 39
CARDINALE ANNA MARIA 39
CAREME CHRISTEL 62,61
CARNEIRO JORGE 148
CARRIER XAVIER 192
CARUSO MARIA RITA 37
CARVALHEIRAS JOÃO 40,211
CAUTERUCCIO SILVIA 169
CAVALCANTE FRANCESCO 22
CAVALCANTI GRAYCYELLÊ R. S. 41
CAVALLARO GIUSEPPE 37
CAVALLI ROBERTA 84
CENGIZ OZGÜR 132
CEREZO PILAR 102
ČERNOCHOVÁ KATEŘINA 255
CHA GIHOON 280,281
CHARDON-NOBLAT SYLVIE 243
CHEESEMAN CHRIS 136
CHEONG JUN 280
CHIKANDA FRANCES 113
CHLIARAS ATHANASIOS 43
CHOUDHURY TANUSHREE 42
CHRISTIDIS GEORGIOS 44,43,311
CHRYSSIKOS GEORGIOS D. . . . 45,274,141
ČIČKAN MICHAL 46
CIESIELSKA ZUZANNA 288
CINELLI CAMILLA 256
CISSE KHALY 15
CITLI PINAR 47
CLARET FRANCIS 108
CLARK JOANNA 176
CLAUSI MARINA 238
COLETTI CHIARA 48
COLLICO STEFANO 49
CONFALONIERI GIORGIA 84
CONSTANTINO VERA REGINA LEOPOLDO 78
CONTE SONIA 83,317,68,189
COOL PEGIE 266,264,265
CORENTIN PAULINE 50
COSENZA PHILIPPE 51,180
COSTA CRISTIANA 250
COSTA LETIZIA TERESA 305
COSTENTIN CYRILLE 243
COTICELLI SEBASTIANO 52
COTTONE FRANCESCO 231
COUASNON THAÏS 77
COURTIN ALEXANDRA 130
CRESPO-LÓPEZ LAURA 53
CRISTIANI CINZIA 107,106
CRUCIANI GIUSEPPE 54,320,7,68
CUEVAS JAIME 56,55,57
CUI YUJUN 16
CULTRONE GIUSEPPE 53
CUNHA SILVIO 177
CZERWIENIEC RAFAŁ 171
CZOMPOLY OTTO 58,80,221,293
D'ANGELO ARIANNA 59,60
D'ANTONIO MASSIMO 122,294
DABAT THOMAS 12
DADI NITIN TEJA CHANDRA 35
DAL CORSO JACOPO 7
DALCONI MARIA CHIARA 48
DAMASCENO BOLÍVAR PONCIANO GOULART DE LIMA 216,272
DANIEL FURKA 166
DANOVA SVETLA 207
DANZER MICHAEL 280
DAOU IMANE 153
DARDER MARGARITA 2,167
DARRACQ GUILLAUME 62,61
DATHE WILFRIED 63
DAWSON JONATHAN 247
DAZAS BAPTISTE 229,12
DE GEEST MITRA 265
DE GENNARO BRUNO 217
DE OLIVEIRA LUÍS HUMBERTO 218
DE VIGUERIE LAURENCE 158
DEBELLE AURÉLIEN 74
DEHN FRANK 309
DEL REAL GUSTAVO 167
DELL'ANNO MATTEO 107
DELLA VECCHIA GABRIELE 199

DERKOWSKI ARKADIUSZ . . .64,131,45,274
DESCOSTES MICHAEL 229,249
DESCOTES MICHAEL. 33
DI GENNARO SPARTACO. 273
DI MICHELE ALESSANDRO 231
DI RENZO FRANCESCO 84
DI RENZO VALERIA. 122,294
DI ZHANG 182
DIALLO ALIOUNE. 287
DIEDEL RALF 65,76
DIEDHIOU ADAMA 287
DIEGUEZ MIKEL. 5
DIETEL JAN 66
DIMOWA LOUIZA 296
DIOUF NGONE. 287
DJEBIHA SARA. 72
DJOUDER HOCINE 288
DOBREVA LILI 207
DOHRMANN REINER 67,206,66,131
DOLEŽAL TOMÁŠ 271
DOMINICI FRANCO 231
DONDI MICHELE 68,83,317,189
DOTELLI GIOVANNI 106
DOUSOVA BARBORA 69,156
DOUSTKHAH ESMAIL 70
DUDKO VOLODYMYR 171,281,93
DUPLAY JOELLE. 72
DUPUIS CHRISTIAN. 289
DYREK JULIA 275
DZIEWIĄTKA KLAUDIA 71,174
EIGENBRODE JENNIFER 8
EL BERRICHI FATIMA ZOHRA. 72
EL HAFIANE YOUSSEF 109
EL KHOMSI ANASS 74,73
ELLIOTT JOSHUA 75
EMMERICH KATJA 76,11,159,309
ENTWISTLE JAMES 77
ERASTOVA VALENTINA 240
ERTL MICHAEL 292
EULALIO DENISE 78
EVANS EMILY 79,27
EVANS NICHOLAS. 247
EYMAR ENRIQUE 57
FABIAN MARGIT 80,293
FACHINA YASMIN JAQUELINE 172
FAGEL NATHALIE. 81
FAKHFAKH EMNA. 124
FALL DJIBRIL 287
FALL MODOU 15
FANG QIAN. 82,321
FANTINI RICCARDO 83,84
FARDJAOUI NOR EL HOUDA 72
FARIA DALVA LUCIA ARAUJO DE 78
FEDDAL IMENE 179
FEDERER LUKAS 85
FEKIACOVA ZUZANA. 3,14
FERNANDES FREDERICO COLÃO 25
FERNÁNDEZ ANA MARÍA . . . 86,184,4,185
FERNÁNDEZ DÍAZ ANA MARÍA. 154
FERNÁNDEZ RAÚL 55,57
FERNANDEZ ROMERO ANA 219
FERNÁNDEZ-JIMÉNEZ ANA 238
FERRAGE ERIC 12,108
FERRARI FRANCESCO 268
FERRIERO FLAVIA 87
FIALHO ROSANA 177,114
FIGUEIREDO MARIANA PIRES 78
FINDLING NATHANIEL. 151
FINOCCHIO ELISABETTA 107,106
FIORE AMBRA M. 88,164
FIORE SAVERIO 164,23
FISCHER MICHAEL 84
FLÉHOC CHRISTINE 289
FODIL CHERIF NAWAL 291
FOGARASSY ZSOLT. 58
FONSECA MARIA GARDENNIA . 41,218,272
FORANO CLAUDE. 90,91,89,208,129,242
FORMÁČEK PETR 271
FORMIA ALESSANDRA. 268
FORTUNATO MARCO 39
FOSSUM JON OTTO 93,92,225,224
FRACCICA ALESSANDRO 49
FRANÇA DENISE B. 41
FRANCISCA VÁSQUEZ 263
FRANUS MALGORZATA 94
FRANUS WOJCIECH. 96,95,125,97
FRANZ HEATHER 176
FRIEDRICH DANIEL. 280
FRONCZYK JOANNA 97,125
FUJII NAOKI 137
FUKUMOTO TAKASHI 195
FURKA DANIEL 46
FURKA SAMUEL. 46
GALÁN ANA BELÉN 237,200
GALICIA-ANDRÉS EDGAR. 98
GAMEIRO TÂNIA 99,211
GARCÍA-DELGADO CARLOS 57
GARCÍA-GUTIÉRREZ MIGUEL 100,4,184,185,5
GARCÍA-ROMERO EMILIA. 101,257,160,283
GARCÍA-VICENTE ANDREA 101
GARCÍA-VILLÉN FÁTIMA 102
GARRALÓN ANTONIO 55
GASMI BRAHIM 72
GASSAMA DIADOLY 15
GASTALDI CÉDRIC 89
GAUTHERON CÉCILE. 14,13,3
GAUTIER ARNAUD 89
GAYE NANGO 287
GEON YOUNG KIM 183
GERZABEK MARTIN H.. 103,98,32
GHARZOUNI AMENI 74,73
GIANNI ELENI 260
GIANOLLA PIERO 7
GIER SUSANNE 146
GIL ANDRÉS 20
GIL IRENE 232
GILDOR OFIR 246
GILI MON BRYAN 213
GIMENO MARÍA JOSÉ 20
GIORA BRUNO. 153
GIOT RICHARD 180,51
GÓMEZ PALOMA 55
GONÇALVES NUNO P.F. 211,99
GONZÁLEZ RODRIGUEZ MARÍA LUISA 219
GONZÁLEZ-ALFARO YOREXIS 2
GÖTSCH THOMAS. 298
GRANČIČ PETER 103,32
GRANITZIO FABIO 52
GRANT NEIL 134
GRATHOFF GEORG 284
GRAZIANO SOSSIO FABIO. 305
GREAD FAISAL 299
GREGOIRE BRIAN. 12
GREGOROVÁ EVA. 105,223
GRGIC DRAGAN. 215
GRO NIELSEN ULLA 129
GRÖGER-TRAMPE JENS 67,66
GRONEWOLD LAURA 57
GROZEVA NIYA 33
GRYPAIOU-ISKENTERIDOU GEORGIA. . 43
GUAGLIANO MARIANNA 107,106
GUALTIERI ALESSANDRO F. 83
GUARINI GUIA. 189
GUARINO CARMINE 294
GUERARD-HELAINE CHRISTINE 89
GUERIN LOÏC 108
GUILLEMIN FLEUR 109
GUINOISEAU DAMIEN 3,14
GUIRAUD MICHEL 50
GUO HAOZHE 110
GUTIÉRREZ-ÁLVAREZ CARLOS 303
GUYOT MÉLANIE 243
HAMON CYRILLE 115
HANUSOVÁ IRENA 255
HARADA TAKUMI. 111
HARJUPATANA TERO 214
HATZIANTONIOU SOPHIA 310
HEARD CHRISTOPHER 298
HEDAN STEPHEN 51,180
HEIN ANNO. 48
HENRIQUE MICHELS BRITO PAULO . . 224
HERNÁNDEZ BENAVIDES PABLO . . . 302
HERNÁNDEZ-BENAVIDES PABLO . . . 168
HERNÁNDEZ-LAGUNA ALFONSO . . . 304
HESSER JUERGEN. 245
HEUSER WERNER. 65
HILL ERIC 112
HILLIER STEPHEN 144,141
HKAUNG HTUT SAN 113,138
HOFFMANN MARTIN 76
HOFSTETTER THOMAS. 77
HOLMBOE MICHAEL 286
HONG HANLIE. 321,311
HONTY MIROSLAV 222
HORBE ADRIANA 14,3
HORIUCHI LUCAS. 114
HOTTON CLAIRE 115
HOU DIANWEI. 298
HRISTOV STANISLAV. 316
HU QINHONG 116
HUANG WEI JUN 322
HUBERT FABIEN. 12
HUDEC PAVOL. 220
HUERTAS F. JAVIER 23,117,118,164
IDE YUSUKE 70
IGLESIAS RUBÉN JAVIER 303
INÊS VILARINHO 263
INNOCENCIO NETTO VAGNER 173
ISHIWATA TOBIMARU 119
ISRADE-ALCANTARA ISABEL. 81
ITO KENTARO 120
IWANO HIROYUKI 188
IZMIROVA NEDYALKA 121
IZZO FRANCESCO. 122,104,294
JABER MAGUY 123,314,41,158
JAEGGI DAVID. 86
JAHN LEONARD 280
JAKOB ALEXANDRA 61
JAMOUSSI FAKHER 124
JANEK MARIÁN 46
JANEK MARTYNA. 125,97
JANKOVIC LUBOS 162,276,278
JĘDRAS ANNA 126
JELAVIC STANISLAV 127
JIN-SEOP KIM 183
JOÃO LABRINCHA 263
JOMMI CRISTINA 198
JOSÉ LUCAS URBANO 128
JOSÉ SILVA 263
JOURDAIN ALEXANDRA. 129
JOUSSEIN EMMANUEL. 130,170
JOVIĆ-JOVIČIĆ NATAŠA 279
JROUNDI FADWA 4
JUAN ANTELO 17
JUAN MIGUEL ESGUERRA. 212
K. SELJELID KONSTANSE 92
KALAGRI OLYMPIA. 44
KALINICHEV ANDREY G. 201,47
KALO HUSSEIN 262
KAMSEU ELIE 155
KANCZLER JANOS 247
KANIK NADINE 131
KANTIRANIS NIKOLAOS. 228,143
KAŠPAR VLASTISLAV 255
KATO RIKI 188
KATO TAKASHI 188
KAUFHOLD STEPHAN 308,67,66,131
KAWAKITA RYOHEI. 119
KAWAMATA JUN. 205,111
KAZE CYRIAQUE RODRIGUE 132
KAZUHIRO SHIKINAKA 133
KELADINOS ALVERTOS 44
KELLY OSCAR 134
KEMP SIMON. 136,135
KEN-ICHI KATSUMATA. 270
KHAORAPAPONG NITHIMA 285,241
KHIARI IMEN 124
KIEŁBASA DANIEL 275
KIKUCHI RYOSUKE. 137,119,138,113
KIMOTSUKI NONO 138,113
KINOSHITA REIRA. 139
KISIEL MARTA. 275
KLEMENT RÓBERT 46,239
KLINKENBERG MARTINA 140
KNAPP HENNING 65
KNIES JOCHEN 261
KNUDSON CHRISTINE 8,176
KOBAYASHI MAKOTO 120,313

KODĚRA PETER 222
KOHOUTKOVÁ MARTINA 244
KOKKARI ANASTASIA 143
KOLDITZ OLAF 245
KOLEV HRISTO 316
KOLONITS TAMAS 58
KOLOUŠEK DAVID 69
KÖNIGER FRANZ 76
KONRAD ALEXANDER 196
KORANYI TAMAS 221
KOULOUSSIS NIKOS 143
KOUSERI AIKATERINI A. 141
KOUTOUVAKI EIRINI 142
KOVAIOU SOULTANA KYRIAKI. 143
KÖWITSCH NICOLAS 298
KOZIEŃ DAWID 230
KRAKOW LUTZ 234
KRÁLOVÁ KAROLÍNA 271
KRISTIAN UFER 144
KRÖHN KLAUS-PETER 145
KRÖHN MICHAEL. 145
KRÖHNERT JUTTA 298
KRSTIĆ JUGOSLAV 279
KRUMOVA EKATERINA 207
KUBO KATASHI 204
KÜHN MICHAEL. 86
KULIGIEWICZ ARTUR 309
KUMAR SAHIL. 312
KUMM ZORA ALICE 146
KUREKOVÁ VALÉRIA 46
KURNIAWAN ALFIN. 322
KUS MONIKA 266,264,265
KUVA JUKKA. 214
KVALEM SELJELID KONSTANSE 224
LABILLE JÉRÔME 147
LABRINCHA JOÃO 40,38,148
LABRINCHA JOÃO A. 99,211
LABUTA JAN 34
LACALAMITA MARIA. 107,39,106
LAITA ELISA 150,149
LANCELLOTTI ISABELLA 6
LANG FRIEDERIKE 196
LANGELLA ALESSIO 104,122,294
LANSON BRUNO 151,181,127
LANSON MARTINE 1,151
LAPORTE LUCIE. 158
LASSINANTTI GUALTIERI MAGDALENA 155
LATRILLE CHRISTELLE 152,163
LATTA DREW. 77
LAUNOIS PASCALE 227,60,59,1
LAZZARA GIUSEPPE 37
LE PAPE PIERRE 192
LECOMTE-NANA GISÈLE 109
LECOMTE-NANA GISELE LAURE. 132,153,193
LEON FRANCISCO JAVIER. 86
LEÓN VICENTE FRANCISCO JAVIER. . 154
LEONELLI CRISTINA 155,268
LEONESSA CARMELA 273
LEROUGE CATHERINE 86,289
LETTINO ANTONIO 22
LEWIS AMY 135
LEWIS JAMES 176
LEXA JAROSLAV 299
LHOTKA MILOSLAV 156,69
LI DA JIAN 322
LI KE JIN 322
LI LI 157,323
LI MENGWEI 90,91
LI MENGYUAN 323,157
LI QIANG 158
LIAUDAT JOAQUÍN 198
LICANDRO EMANUELA 169
LICURSI ERNESTO ADLER. 24
LIHAREVA NADEJDA 296
LIS KINGA 175
LISUZZO LORENZO 37
LIU YI-YU. 159
LIULIU QINFU 314
LOCH PATRICK 92
LOPEZ GALINDO ALBERTO 124
LORENZO ADRIAN 160
LORENZO ALEJANDRO. 149
ĽUBOŠ BAČA. 166
LUCIANI GIUSEPPINA 217
LUCINI PAOLA. 22
LULU ZHAO 82
LUPPINELLI STEFANIA. 106
LUQUE PEREZ ANTONIO. 219
LUZI FRANCESCA. 231
MA JIAYU. 161,306
MACARIO INÊS 248
MADEJ JAROSŁAW 95
MADEJOVÁ JANA 162,278,299
MAGGIO ANDREA. 200
MAGNIN VALÉRIE. 1
MAHAFFY PAUL. 8,176
MAHIEDDINE DHIKRA 72
MAIA FREDERICO. 128
MAILHOT GILLES 242
MAILLET JEAN 163
MAILLHOT GILLES 91,90
MAJ-SZELIGA KATARZYNA 275
MAJDAN MICHAL. 299
MAKIEL MAGDALENA 275
MAKRI PAGONA. 43
MALESPIN CHARLES 8,176
MAMELI PAOLA 164
MANCINELLI MAURA 165,22
MANOLIS STAMATIOS 44
MAOUI AMMAR 72
MARASCHI FEDERICA 22
MARCHAND MATHILDE 62
MARCHET PASCAL 153
MARGRETH ANNINA 261
MARIAN JANEK 166
MARIÁN MATEJDES 166
MARINÉLIA CAPELA 263
MARINOVIĆ SANJA. 279
MARITAN LARA 233,142,48
MARQUES FERNANDES MARIA 140
MARQUES JOSÉ 248
MARSH ALASTAIR 136
MARTÍN-SAMPEDRO RAQUEL 167
MARTÍNEZ-RODRÍGUEZ TOMÁS . . 168,302
MARTUCCI ANNALISA 165,22
MARUYAMA HAYATO 297
MASCI LORELLA 1
MASINI COSIMO. 256
MASSARO MARINA. 169
MASSON DELPHINE 170
MASTRORILLI PIERO. 88
MATEJDES MARIÁN 46,171,224,278
MATOS DEMITI GABRIELA MARIA 172,173
MATTIELLI NADINE 81
MATUSIK JAKUB 174,175,126,71
MAURICE LAURENCE 130
MAZZOLI CLAUDIO. 48
MCADAM AMY 176,8
MCCAMMON CATHERINE 292
MCDERMOTT CHRISTOPHER 194
MEDEIROS KALINE DE ARAÚJO 272
MEDEIROS PETTERSON CORREIA . . . 177
MEDHIOUB MOUNIR 124
MEDINA CARRASCO SANTIAGO . . 218,219
MEDINA PÉREZ MARÍA DEL MAR . 168,302
MEFTEH SAMIR 124
MEKHLOUF HAMDI. 72
MELÓN ANA MARÍA 56
MERCURIO MARIANO 104,294,122
MERCUZOT MATHILDE 178
MERROUN MOHAMED LARBI 4
MESBAH ABDELHAK. 179
MESTO ERNESTO 39,107,106
METCALFE SARAH 81
MEYNEN VERA 264
MHAMDI ALAOUI HAMZA. 180
MICHAEL KOMÁREK 17
MICHAL ČIČKAN 166
MICHAU NICOLAS 74
MICHELS BRITO PAULO HENRIQUE . . . 93
MICHELS LEANDER 224
MICHIELSEN BART 266,265,264
MICHOT LAURENT 108
MIDER URSZULA 230
MIETTINEN ARTTU 214
MIGNON PIERRE 181,151
MIKUTTA CHRISTIAN 206
MILLAN MAËVA. 8
MILUTINOVIĆ-NIKOLIĆ ALEKSANDRA 279
MING DOUGLAS. 176
MINGARRO MANUEL. 100,5,4
MINGXIAN LIU 182
MINO LORENZO 84
MINSEOP KIM 183
MIRA NAFTALY 166
MISSANA TIZIANA . . . 184,185,100,154,5,4
MITCHELL CLIVE 136
MITEVA-STALEVA JENY 207
MITSUI SEIICHIRO 119
MIYAGAWA MASAYA 186
MIYAMOTO NOBUYOSHI 188,187,195
MIYOSHI MOMOKA. 188
MOKNI NADA 16
MOLINARI CHIARA 189,317,68
MOLNAR IAN 194
MON ALBA 55
MONDILLO NICOLA 52
MONET GEOFFREY 59
MONETTI VINCENZO 104
MONGELLI GIOVANNI 273
MONTENEGRO LUIS 55
MONTESANO GIOVANNA 190
MORAIS ALAN I. S. 218
MORALES-HIDALGO MAR. 4
MOREJÓN JESÚS 5,4
MORENO EUGENIA 304
MORENO-RODRÍGUEZ DANIEL. 191
MORIN GUILLAUME 192
MORRIS CALLUM 134
MORRIS RICHARD 176
MOTA CARLOS. 55
MOUAFON MOHAMED 193
MOUAT ELISE 194
MOURI EMIKO 195,205
MOUSTY CHRISTINE 243
MUDASHIRU ADAM 134
MULDER INES 196
MULLENS STEVEN 264
MÜLLER KATHRIN 234
MUNIER THOMAS. 197
MUNIS COSTA MARCOS ROGÉRIO . . . 173
MURARO STEFANO 198
MUSSO GUIDO. 199
MUSSO TELMA 200,237
MUTISYA SYLVIA M. 201
MYERS RUPERT 136
MYTIGLAKI CHRISTINA 228,143
NAIDU RAVI 30
NAKAGAKI TAKAO 202
NAKAMICHI YOHEI. 203
NAKAO ATSUSHI 204,297
NAKASHIMA YUJI. 188
NAKATO TERUYUKI 205,111,195
NDOYE IDRISSA. 287
NEUMANN ANKE 77
NEVES OLSEN SCALIANTE MARA HELOISA 172,173
NGWENYA BRYNE 194
NIEGISCH MAX 206
NIELSEN ULLA GRO 128,36
NIEMIEC PIOTR 324
NIETO PAULA 86
NIKOLAOU PANAGIOTA 310
NIKOLOV ALEKSANDAR. 207,296
NISHIMURA SHOMA 186
NITSCH ANTONIA. 11
NJIOMOU DJANGANG CHANTALE . . . 193
NJOYA DAYIROU 193
NOMICISIO CRISTIAN 208,209
NOTARBARTOLO MONICA. 210
NOVAIS RUI 40
NOVAIS RUI M.. 211,99
NOVO BRUNA LEMOS 25
O`SULLIVAN CATHERINE 203
ODONNE GUILLAUME 130
OHTOMO YOKO 138,113
OLEGARIO ELEANOR 213,212

OLIN MARKUS 215,214
OLIVEIRA FRANCISCO DE ASSIS SILVEIRA 216
OLIVERIA KEVIN DA SILVA 272
OOSTENBRINK CHRIS 98
OREFFO RICHARD 247
ORRICO MARIANNA 217
ORTA CUEVAS MARIA DEL MAR . . 218,219
ORTEGA ALMUDENA 56,55
OSÁCAR CINTA 20
OSACKÝ MAREK 220,299
OSADA MINORU 120,313
OSAJIMA JOSY A 218
OSAN JANOS 221,293,58
OSTERTAG-HENNING CHRISTIAN . . . 222
OTAKE TSUBASA 119,138,113
PABST WILLI 223,105
PACAKOVA BARBARA 225,224
PAGANO CINZIA 231
PAINEAU ERWAN 60,59,115,130
PAINEAU ERWAN-NICOLAS 227,12
PÁLKOVÁ HELENA 226,220,324
PALMA ACHILLE 273
PAN YIFAN 227
PANATTONI FRANCESCO 256
PANEK RAFAL 94,97
PAPADIMITRIOU DIMITRIOS 228
PAPOULIS DIMITRIOS 310
PAPPALARDO LUCIA 87
PARROTIN FLORA 229,249
PARTYKA JANUSZ 230
PASIUT KATARZYNA 230
PASTI LUISA 189
PATERNOSTER MICHELE 273
PAZ SIMONE 10
PEDDIS DAVIDE 22
PEDRAZ JOSE LUÍS 102
PELLENARD PIERRE 289,178,50
PERETZ-LAPID NERIYA 246
PÉREZ DE LA LUZ ALEXANDER 304
PEREZ DEL VALLE CARLOS 151
PÉREZ GUTIÉRREZ CARMEN LAURA . 231
PÉREZ-ABAD ALEJANDRO 200
PEREZ-CARVAJAL JAVIER 232
PÉREZ-MONSERRAT ELENA MERCEDES 233
PÉREZ-RIVARÉS FRANCISCO JAVIER . . 20
PERIOLI LUANA 231
PERRAUD ARTHUR 61
PERROTTA LAURA 87
PESCE PIETRO GIAN 235
PESCH KATJA 234
PETAVRATZI EVI 136
PETROVA NADIA 296
PETTI ROSSELLA 236,235
PETTINARI GISELA 237,200
PEYRATOUT CLAIRE 109,193,153
PILAŘ LUKÁŠ 69
PINTO CARLOS 148
PINTO DANIELA 238
PLANETOVÁ VIKTÓRIA 239
PLÖTZE MICHAEL 325,236,235
POLLAK HANNAH 240
POLLASTRI SIMONE 221
PONGKAN NIPAPORN 241
POSPÍŠIL MIROSLAV 260
PÔSSA JÉSSICA TINÉ 26
POVEDANO-PRIEGO CRISTINA 4
POZARYCKI CHAD 8
POZO MANUEL 237,200
PRÊT DIMITRI 180
PRÉVOT VANESSA . . . 36,90,91,129,242,243
PRIBUS MAREK 28
PUCÉAT EMMANUELLE 50
PUGLIA DEBORA 231
PULCOVÁ KLÁRA 244,271
PULKKANEN VELI-MATTI 214
PUXIANG ZHAO 182
PUZRIN ALEXANDER 236,235
PYZIK ADAM 125,97
QUESNEL FLORENCE 289
RAAEN STEINAR 224
RABASCO ÁLVAREZ ANTONIO M. . . . 219
RADEISEN EIKE 245
RADIAN ADI 246
RAGONE P. PASQUALE 273
RAMNARINE SANCHEZ ROXANNA SHARON 247
RANTALA MARTTIINA 81
RASHEV VIKTOR 207
RAUHALA OLLI-PEKKA 214
REBELO RAFAEL 248
REGGI SERENA 107
REGUER SOLENN 130
REIJONEN HEINI 214
REINHARD KLEEBERG 144
RENAUDAT LUCAS 141
RICKERT JÖRG 234
RIELA SERENA 169
RIESS MARTIN 85
RIQUIER LAURENT 197
RISPOLI CONCETTA 190,52,305,104
RIVAS MARÍA JESÚS 160
RÓBERT KLEMENT 166
ROBIN VALENTIN 249,170,33
ROCA-JALIL MARÍA EUGÉNIA 200
ROCHA FERNANDO 250,301,258,248,8
ROCHA WILMA RAIANNY VIEIRA . . . 272
RODRIGO IRENE 150
RODRIGUES FRANCISCO 41
RODRÍGUEZ-AMEIJIDE VANINA 200
RÖLKE CHRISTOPHER 76
ROLS STÉPHANE 1,60,59
ROMAGNOLI MARCELLO 9,155
ROMERO ENRIQUE 49
ROSENFELDT SABINE 262
ROSSI LUCIANA 107
ROSSI SILVIA 168,300,209,302,208
ROSSIGNOL SYLVIE 73,74
ROUZIÈRE STÉPHAN 227,60,59
RUDMIN MAXIM 251,252
RUGGERI MARCO 253,300,209,208
RUIZ ANA ISABEL 56,55,57
RUIZ-HITZKY EDUARDO 167,2
RUSHTON JEREMY 135
RUSSO GIACOMO 235,87,305
RYAN PETER 254
RYBKA KAROLINA 175
ŠACHLOVÁ ŠÁRKA 255
SAENZ-DEL-BURGO LAURA 102
SAFAIERAD REZA 81
SAINZ-DÍAZ IGNACIO 169,304
SALAMÈ ELIGE 256
SALGADO-CAMPOS VICTOR V.M.J. . . . 24
SAMPER JAVIER 55
SAMUEL FURKA 166
SÁNCHEZ MICAELA 200
SANCHEZ-ESPEJO RITA 114,169,177
SÁNCHEZ-SANTOS JOSÉ MANUEL . . . 160
SANDRI GIUSEPPINA . . 168,302,300,209,208
SANTAMARÍA-LÓPEZ ÁNGEL 257
SANTANIELLO DAVIDE 104
SANTOS ANDREIA 258
SANTOS KRIS LORD 212
SAPHY ADRIEN 57
SATO TSUTOMU 137,119,297,138,113
SAUVIGNET PHILIPPE 62
SAVOYE SÉBASTIEN 12,163,229
SCHÄFER THORSTEN 259
SCHAMEL MAXIMILIAN 280
SCHELLHORN MATTHIAS 65
SCHERER MICHELLE 77
SCHEWE NILS 159
SCHINGARO EMANUELA 107,106
SCHMIDT SABINE 81
SCHNEIDER ARNAUD 147
SCHOLTZOVA EVA 19,191,260,276,324
SCHÖNENBERGER JASMIN 261
SCHRECK EVA 130
SCHUCHARDT DOMINIK 262
SCHUHMANN RAINER 76
SCHULZE SIMONE ELISABETH 234
SCHWAIGER RUTH 309
SCIARRILLO ROSARIA 294
SEABRA MARIA PAULA 38,148,263
SEBASTIAN EDUARDO 53
SECK MATAR 287
SEFTEL ELENA 264,266,265
SEHANINE YASSINE 31
SEIGNEUR NICOLAS 33
SEKKAL WASSILA 267
SELLIN PATRIK 5
SENKER JÜRGEN 85
SEOK YOON 183
SETTI MASSIMO 208
SGARLATA CATERINA 268
SHAFRAN KIRILL 134
SHAO HUA 245
SHIMABUKU BIADOLA QUELEN LETÍCIA 173
SHIMBASHI MISATO 269,315,137
SHIN'ICHI ISHIMARU 139
SHINANO TAKURO 297
SHINGO MACHIDA 270
ŠÍDLOVÁ MARTINA 271,244
SIEGEL RENÉE 85,171
SIEMENS JAN 196
SILINA ANASTASIYA 61
SILVA DAYANNE TOMAZ CASIMIRO DA SILVA 216,272
SILVA EDUARDO 301
SILVA FERNANDA ARRUDA NOGUEIRA G. 25
SILVA FRANCISCO JOSÉ 24
SILVA-FILHO EDSON C 218
SILVESTRI BRIGIDA 217
SINISI ROSA 273
SIRANIDI EIRINI 274,141,45
SISTI MATTIA 84
SKAŁA ALEKSANDER 288
SKIBA MICHAL 275
ŠKORŇA PETER 276,19,171
SKOURA EVA 277
ŠKVÁRA FRANTIŠEK 244
SLANY MICHAL 162,278
SLATNI IBTISSEM 72
ŚLIWA MICHAŁ 324
SMITH AGNÈS 109
SMOLEŃ SYLWESTER 275
SOARES MÔNICA FELTS DE LA ROCA . 216
SOARES-SOBRINHO JOSÉ LAMARTINE 216
SOCHA ROBERT P. 324
SOFIA BAPTISTA 263
SOMFAI BARBARA 80
SORIANO-CORREA CATALINA 304
SOSSIO FABIO GRAZIANO 104
SOTO-RUIZ CARLA 4
SOUBRAND MARILYNE 130
SOUPRAYEN CHRISTELLE 158
SPAGNOLI GIOVANNI 49
SPOOREN JEROEN 266
STERN JENNIFER 8
STEVANOVIĆ GORDANA 279
STEVENSON MAX 281,280
STÖTER MATTHIAS 171
STURINI MICHELA 22
STUTZ KENTON 196
STYCZEŃ JOANNA 282
SUÁREZ MERCEDES 283,257,101,160
SUDHEER KUMAR RITWICK 284
SUEISHI KOKI 205
ŠULC ROSTISLAV 271,244
SUMMA VITO 273
SUPPASO CHOMPONOOT 285,241
ŠURKA JURAJ 299
ŠUTEKOVÁ MONIKA 34
SUTTER BRAD 176
SUZUKI YASUTAKA 111
SVOBODA JIŘÍ 215
SWAI ROGERS 286
SYLLA GUEYE ROKHAYA 287,15
SZABO FRUZSINA 58
SZCZERBA MAREK 288,274,275
SZRETER ANNA 64
TADIKONDA VENKATA BHARAT 312
TAKABA HIROMITSU 186
TAKAYAMA YUSUKE 119
TAKEZAKI YUMA 313
TAKUMI MATSUO 188

TALEN SAFIA 179
TALON JULIEN. 289
TANG RENHENG. 110
TANGNEY PAUL 203
TANINAKA KEISUKE 205
TARDANI MARIANNA 256
TAREAU MARC-ALEXANDRE. 130
TARHINI ALI 243
TASSIS GEORGIOS 261
TAVIOT-GUÉHO CHRISTINE 208,209,290,291
TEOBALDI GILBERTO 75,59
TERROSO DENISE. 301
TERTRE EMMANUEL 249,229,12
TESSIER-DOYEN NICOLAS 153,193
THANNER JANNIK 292
THIEBAULT THOMAS. 181
THISSEN PETER 159
TIJERO MARÍA. 57
TINE YORO 287
TODOROVA SILVIYA 316
TOLNAI ISTVAN 293,80
TOMA YO 297
TONUTTI PIETRO 256
TORRES ELENA 55
TORRES RODRÍGUEZ MIGUEL . . . 172,173
TOWLER GEORGE. 194
TOZAKI KEIGO 186
TRANFA PIERGIORGIO 294,122
TRCERA NICOLAS. 227
TRIGUEIRO NETO OSVALDO 93
TRUCHE LAURENT 222,1
TRUNSCHKE ANNETTE 298
TSUNOJI NAO 295,70
TSVETANOVA LILIYA. 296
TUNEGA DANIEL 98,32,276,103
TURRERO MARÍA JESÚS 55
TZVETANOVA YANA 296
UCHIBAYASHI HIROSHI 297
UFER KRISTIAN 66,206
UHLIG FELIX. 298
UHLÍK PETER 299,220
UNGOLO AMEDEO 300
VACCARI FRANCESCO EDOARDO . . . 268
VALDIVIESO PEDRO 4
VALENTE ANDRÉ 301
VALENTINO CATERINA 302,168
VALLS DAVID 283
VAN DER LELIJ ROELANT 261
VAN DRIESSCHE ALEXANDER E.S.. .23,118
VANTELON DELPHINE 227,130
VAROUCHAKIS EMMANUEL 44
VEČERNÍK PETR. 255
VELDE MÉLUSINE 151
VELOSO TELMA. 248
VENKATARAMANA RADHA. 292
VENNIN EMMANUELLE 289
VETEŠKA PETER 46
VEZZALINI GIOVANNA. 84
VIDALE MASSIMO 142,233
VIGANI BARBARA 300,209,208
VILARINHO INES 38,148
VILHELMOVA-ILIEVA NELI 207
VILLA LUIS. 200
VILLAR MARÍA VICTORIA. 303,56
VISERAS CÉSAR. . . . . .
. 304,300,209,102,177,114,208,169
VISÉRAS CÉSAR. 124
VISÉRAS IBORRA CÉSAR 231
VITALE ENZA 305,235,87
VITONE CLAUDIA. 236,235
VULLUM PER ERIK 225
WAGANER DANIEL 224
WALTER PHILIPPE. 41
WANG BIN 306,161
WANG CHAOWEN. 311
WANG QIANG 110
WANG WENQING 245
WARR LAURENCE. 307,30,284
WATANABE TOSHIHIRO 297
WATANABE YASUTAKA 315
WEBER CHRISTIAN. 308
WEISS SEBASTIAN 281,292,280
WELE ALASSANE 287
WELLS JUSTIN. 224
WERLING NADJA 309
WIDORY DAVID 122
WIECZOREK KLAUS 76
WONG HONG. 136
WOSZUK AGNIESZKA 96
WOZNIAK ROKSANA. 275
XENOU CHARALABIA 310
XIANGYU CHEN. 182
XU YANXIAO. 311
YADAV HIMANSHU 312
YAMAMOTO EISUKE 313,120
YAMASHITA NAITO 138,113
YANAI JUNTA 204
YANG YONGJIE 314
YERSIN HARTMUT 171
YOKOYAMA LÍDIA 25
YOKOYAMA SHINGO 315,269
YORDANOVA ILIYANA. 316
YOU ZHIXIONG 90
YUAN PENG 323,157
YUE FENG 182
YUICHIRO OTSUKA. 133
YUSTE ALFONSO 150,149
ZABALA ANA BEATRIZ. 56
ZADVERNYUK HALYNA. 275
ZAMORA SERGIO 57
ZANELLI CHIARA 317,68,83,189
ZAOUI ALI 318,267
ZENDEHDEL MOJGAN 319,320
ZHAO LULU 321
ZHOU CHUN HUI 322
ZHUANG GUANZHENG. 323,157
ZIMOWSKA MAŁGORZATA 324
ZIZAK IVO 221
ZUCHA WOLFGANG 325
ZUNA MILAN. 255
ZUZOLO DANIELA 294



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