

NORDIC CLAY MEETING

THE 3RD INTERNATIONAL & INTERDISCIPLINARY SYMPOSIUM

CLAYS & CERAMICS



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SYMPOSIUM PROGRAM

Copenhagen, Oslo, Stockholm, Berlin, Paris, Bratislava (UTC/GMT +1 hour)	Riga, Tartu (UTC/GMT +2 hours)	Moscow, Rostov (UTC/GMT +3 hours)	February 8	February 9	February 10
8h30	9h30	10h30	Welcome		
9h00	10h00	11h00	Plenary lecture	Plenary lecture	Plenary Lecture
9h45	10h45	11h45	Coffee Break	Coffee Break	Coffee Break
10h00	11h00	12h00	Scientific lectures	Scientific lectures	Scientific lectures
10h45	11h45	12h45	Coffee Break		
11h00	12h00	13h00		Coffee Break	Coffee Break
11h15	12h15	13h15			
11h30	12h30	13h30	Poster flash presentations		Scientific lectures
12h00	13h00	14h00		Scientific lectures	
12h45	13h45	14h45			Closing remarks and discussion



February 8 (UTC/GMT +2 hours)

	9.30-10.00	Welcome opening prof. Valdis Segliņš <i>Vice-rector for exact sciences, life and medical sciences of University of Latvia</i> Dr Reiner Dohrmann <i>President of AIPEA</i>
	10.00-10.45	Plenary lecture
		prof. Kalle Kirsimaä <i>Tartu University</i> Weathering indicators of the environmental change at the oxygenation of the Earth's atmosphere in Paleoproterozoic?
	10.45-11.00	Coffee Break
Scientific lectures		SESSION 1 Clays environmental aspects in geology and modern soils / Stephen Hillier
	11.00-11.15	Timing and interplay of faulting, hydrothermal alteration and weathering processes of the Rolvsnes granodiorite in southwestern Norway. <i>A.Margreth</i>
	11.15-11.30	Long term soil tillage system influence on loamy soil physical-mechanical properties and crop productivity. <i>I.Erdberga</i>
		SESSION 2 Clays in archaeology and arts / Sandijs Meškis
	11.30-11.45	Surveying and researching clay beds in the context of Bronze Age archaeological pottery research: A case study of Dole Island microregion. <i>V.Visocka</i>
	11.45-12.15	Coffee Break
Poster session	Poster SESSION / Juris Burlakovs	
	12.15-13.00	Subsurface drainage effect on clay-sized mineral content and mineralogy in two glacial till soils. <i>A.Boča</i>
		Yield of grass mixtures depending on the physical clay content in Luvisol soil. <i>L.Zarina</i>
		Do soluble organic acids bind to basal mica surfaces? <i>J. Dziadkowiec</i>
		Alkaline activation of Illite Clay. <i>M. Randers</i>
		Synthesis, Characterization, and Magnetic Properties of MA14(OH)12SO4·3H2O with M = Co ²⁺ , Ni ²⁺ and Cu ²⁺ : A Novel Class of 1D Spin Chains. <i>A. Bruhn Arndal Andersen</i>
		Composites of clay minerals and natural pigments: synthesis, characterization and potential in biocosmetics. <i>A. Salmina</i>
		Removal of Co (II) from aqueous solution using organically functionalized silica gel. <i>S.Bashir</i>
Mineralogical discrimination between authentic and recent imitations of pottery manufacture in Zlakusa, Serbia. <i>M.Milošević</i>		



February 9 (UTC/GMT +2 hours)		
	10.00-10.45	Plenary lecture
		Dr. Nicolas Michau <i>ANDRA Chemical behaviour of clay host rock and clay-based materials under repository conditions in the French context: main achievements and future development for HLW repository implementation</i>
	10.45-11.00	Coffee Break
Scientific lectures		SESSION 3 (1) Clay mineral properties / Ulla Gro Nielsen
	11.00-11.15	Investigation of the effect of γ -irradiation on Bentonite clay. <i>M.Holmboe</i>
	11.15-11.30	Cation exchange processes observed in the third excavated parcel of the Alternative Buffer Material test (ABM-V) in Äspö, Sweden, after heating to 250 °C. <i>R.Dohrmann</i>
	11.30-11.45	Dissolution mechanism of kaolinite in alkaline media: A DFT study. <i>G.Lazorenko</i>
	11.45-12.00	Development of yet another classical forcefield for molecular simulations of (clay-) minerals. <i>M.Holmboe</i>
	12.00-12.30	Coffee Break
Scientific lectures		SESSION 3 (2) Clay mineral properties / Michael Holmboe
	12.30-12.45	MgAl hydrotalcite-derived mixed oxides for CO ₂ adsorption. <i>S.Bennici</i>
	12.45-13.00	Insight into the phosphate uptake properties of layered double hydroxides. <i>U. Gro Nielsen</i>
	13.00-13.15	Computational study of diuron-smectite interactions. <i>M. Rodriguez</i>
	13.15-13.30	Evolution of Germanium-based Imogolite Nanotubes During Dehydroxylation. <i>E.Paineau</i>
	13.30-13.45	Relationships between structural and FTIR characteristics of kaolinites: new insight. <i>B.Zviagina</i>



February 10 (UTC/GMT +2 hours)

10.00-10.45 Plenary lecture

Solvita Kostjukova Ltd ALINA *Commercialization of clay technologies: technology transfer steps and practices in Latvia*

10.45-11.00 Coffee Break

SESSION 4 Clay mineral synthesis / Reiner Dohrmann

Scientific lectures

11.00-11.15 Influence of the precursor and the temperature of synthesis on the structure of saponite. *L.Dzene*

11.15-11.30 Optimization of iron-rich clay mineral synthesis via design of experiments and response surface methodology. *P.Dutournié*

11.30-11.45 Influence of the synthesis parameters on the formation and characteristics of organic-inorganic hybrids having a talc-like structure. *J.Brendlé*

11.45-12.00 Hybrid inorganic-organic lamellar materials containing Fe(III): effect of Fe(III)/Mg(II) ratio on the condensation state. *L.Cipriano Crapina*

12.00-12.30 Coffee Break

SESSION 5 Clay composite based materials / Liva Dzene

Scientific lectures

12.30-12.45 Research of lake clay use in medicine and aesthetic cosmetology. *S.M. Misiņa*

12.45-13.00 Humic substance - clay mineral composites as novel and ecofriendly sorbents for environmental remediation. *J. Burlakovs*

13.00-13.15 Novel pH-sensitive composites containing clay minerals and anthocyanins to monitor meat freshness. *R. Ozola-Davidāne*

13.15-13.30 Functional surfaces of polymer nanocomposites modified with organoclay and methylene blue. *E.Skoura*

13.30-13.45 Characterization of hybrid luminescent materials based on smectites, Rhodamine 6G and cationic surfactants. *M.Barlog*

Closing remarks *Dr. geogr. Juris Burlakovs Chairman of the Board of Latvian Clay Science Society*



PLENARY LECTURES



Are There Any Weathering Indicators of the Environmental Change at the Oxygenation of Earth's Atmosphere in Paleoproterozoic?

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Earth as a system is built on abiogenic and biogenic interactions that have been, at least at its near-surface environments, intimately linked in a co-evolution since the life appeared in geological history of Earth. Dynamic balance between these components, intertwined by complex negative and positive feedbacks, reflects in a temporal changes of Earth's ocean and atmospheric chemistry [1]. One of the key events in the development of Earth system was the shift from anoxic to oxic surface environments at Archean to Proterozoic transition [2]. This evolutionary step in Earth's redox state triggered progressive modification nearly of all biogeochemical cycles.

The disappearance of mass-independent fractionation (MIF) of sulfur isotopes in the sedimentary record between ca. 2.4 and 2.3 Ga marks the Great Oxidation Event (GOE) when free oxygen appears and remains in atmosphere at concentrations of at least 10^{-5} of the present atmospheric level (PAL) required to shut down the MIF [3]. However, though widely recognized, the triggering mechanisms behind the GOE and its timing are heavily debated and largely controversial [4]. As an evidence of major disturbances in (bio-)chemical cycles caused by the GOE are the largest-magnitude perturbation of the carbon cycle – the Lomagundi-Jatuli Event – immediately between 2.2-2.06 Ga [5] in parallel to build-up of a sizable sulphate marine reservoir [6], the ca. 2 Ga Shunga Event – an unprecedented accumulation of organic-rich sediments, and the first appearance of globally significant phosphorites [7].

It has been suggested that these major events were triggered by the oxidation of continental sulphides in the GOE leading to extensive sulphuric acid weathering liberating variety of nutrients, specifically phosphorous, and triggering a bloom of primary producers [8, 9]. However, if the oxygenation of atmosphere caused an intensive sulphuric acid weathering of the landmasses resulting in major disturbances in (bio-) chemical cycles, then it remains unclear if such boosted weathering event is recorded in the composition of the weathering crusts and sediments formed during and immediately after the GOE?

The aim of this work is to review and discuss the weathering indicators in early Paleoproterozoic weathering crusts and sediments as recording the environmental conditions across this important change in the Earth history.

Acknowledgments:

This study has been financed by the Estonian Research Council grant No PRG447.

References :

- [1] Holland H.D. (2006) The oxygenation of the atmosphere and oceans. *Philosophical Transactions of the Royal Society B-Biological Sciences*, 361, 903-915.
- [2] Lyons T.W., Reinhard C.T., Planavsky N.J. (2014) The rise of oxygen in Earth's early ocean and atmosphere. *Nature*, 506, 307-315.
- [3] Luo G.M., et al. (2016) Rapid oxygenation of Earth's atmosphere 2.33 billion years ago. *Science Advances*, 2.
- [4] Planavsky N.J., et al. (2014). Evidence for oxygenic photosynthesis half a billion years before the Great Oxidation Event. *Nature Geoscience*, 7, 283-286.
- [5] Karhu J. & Holland H.D. (1996) Carbon isotopes and the rise of atmospheric oxygen. *Geology*, 24,867-870.
- [6] Blättler C.L., et al. (2018). Two-billion-year-old evaporites capture Earth's great oxidation. *Science*, 360, 320–323
- [7] Melezhik V.A., et al. (2013) *The Palaeoproterozoic of Fennoscandia as Context for the Fennoscandian Arctic Russia - Drilling Earth Project. Reading the Archive of Earth's Oxygenation*. Vol 1. Springer, Heidelberg, 487 pp.
- [8] Bekker A., Holland H.D. (2012) Oxygen overshoot and recovery during the early Paleoproterozoic. *Earth and Planetary Science Letters*, 317, 295-304
- [9] Konhauser K.O., Lalonde S.V., Planavsky N.J., et al. (2011) Aerobic bacterial pyrite oxidation and acid rock drainage during the Great Oxidation Event. *Nature*, 478, 369–373.



Chemical Behaviour of Clay Host Rock and Clay-based Materials Under Repository Conditions in the French Context: the Main Achievements and Future Development for HLW Repository Implementation

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Andra is the French national agency for radioactive waste management. Its main goal is to design, implement and manage safe disposal facilities for long-term management of each kind of radioactive waste produced in France. For the most dangerous ones - High Level Waste (HLW) - an underground system of disposal tunnels is planned in a natural layer of clay located in a depth of around 500 m near Bure (East of Paris basin, in the Meuse/Haute Marne area). This deep geological repository project is named Cigéo (*Centre industriel de stockage géologique*).

In the Cigéo project, clays are present both in natural and engineered barriers: the host formation of the repository is a clayey rock, the Callovo-Oxfordian claystone, composed of the clay minerals, quartz and carbonates (~25-30% each) and of other minor phases (pyrite, feldspars...). Some of the repository structures also use clays as a material: shaft and tunnel closure structures are made of a bentonite-sand mixture to limit the transfer of fluids inside the disposal facility once it has been closed. Also galleries are to be backfilled with the excavated argillite at the end of the exploitation period to prevent them from collapsing and damaging the host rock. In addition, there is a need to develop materials with particular functions, using clays minerals in their composition. For example, to fill the space between the host rock and the steel casing in the HLW disposal cells, the use of an alkaline material based on cementitious grout, mixing cement and bentonite is being investigated. Finally, alteration processes occurring in the repository frequently lead to the clay neoformations, particularly at interfaces between clays (host rock or engineered components) and other materials, such as concrete, steel or vitrified waste.

The studies undertaken by Andra and its partners over the last thirty years have made it possible to characterise the elementary processes, which affect the Callovo-Oxfordian clay, clay-based engineered components or lead to the neoformation of clays during the different phases of repository life. Step by step, the results have enabled Andra to support the design of the repository, to demonstrate its safety during the operating phase and over a long-term period after its closure. Andra now has a significant knowledge base resulting from a wide range of studies: surface laboratory experiments, underground laboratory tests, analysis of ancient analogues, modelling and digital simulation on different scales. The presentation illustrates this strategy with examples from various contexts, where clay reactivity may play a role. It shows how Andra tried to achieve maximum efficiency with different experiments that have been carried on and that have increased in their complexity over the last ten years. The task for the current period is to implement this knowledge in the licence application process with regard to the underground radioactive waste repository.

In the future, R&D activities involving clays at Andra could be divided into different areas in order to meet the new needs and challenges: to support the consolidation of long-term performance and safety assessment, to improve the quantification of margins compared to the safety assessment conceptualization and to contribute to the design optimization of the disposal facility in the future. These areas will be addressed by: (i) making the results acquired on elementary processes more precise and consolidating them, (ii) integrating the knowledge acquired at the level of elementary systems to achieve a multiphenomenon-multimaterial description at the repository scale in time and space, and (iii) developing multi-coupled approaches (for example, the hydraulic, mechanical and chemical behaviour of clays). The development of innovative clay-based materials will also be investigated, in particular to limit interactions and to increase long-term performance management of the repository components. For example, geopolymer materials that could be used for the construction of both disposal cells and specific storage containers. These new materials also represent a way of valorizing the claystone excavated during the construction of the disposal site and thus reducing the environmental impact of the repository. The first available results on these different aspects will be part of this presentation.



SESSION 1:

CLAYS ENVIRONMENTAL ASPECTS IN GEOLOGY AND MODERN SOILS



Timing and Interplay of Faulting, Hydrothermal Alteration and Weathering Processes of the Rolvsnes Granodiorite in Southwestern Norway

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Old crystalline basement terranes are commonly pervasively dissected by dense networks of faults and fractures, so that previously formed brittle features are often reactivated. The resulting complex brittle deformation histories can only be deconvoluted by combining detailed structural analysis with the mineralogical and geochronological studies [1, 2]. Brittle fracturing is frequently accompanied or followed by fluid circulation causing the alteration of primary minerals into an assemblage of secondary clay mineral phases. The source of these fluids may be diverse and can include meteoric water percolating from the surface along with the fracture planes and fault damage zones. However, the secondary alteration products may also be formed during the hydrothermal fluid circulation or weathering processes, which are seemingly unrelated to tectonics. These can be very similar and difficult to distinguish from secondary phases forming in fault rocks during deformation. Being able to distinguish between a “structural”, “hydrothermal” or “weathering” origin of these phases is crucial in order to reconstruct the evolution of basement blocks, including pinpointing when a crystalline basement terrane reached near-surface conditions [3].

The 466 Ma-old Rolvsnes granodiorite, outcropping on a coastal archipelago of southwestern Norway, has been intensively investigated in the recent years, since it provides evidence of both i) extensive and complex brittle deformation [1, 2] and ii) saprolitization along fracture zones suggesting near-surface environmental conditions [3]. In order to distinguish between different alteration processes, a suite of detailed geochemical, mineralogical and isotopic analysis has been used. Subtle but clear variations in the geochemical and mineralogical composition of the bedrock and associated secondary clay assemblages in the altered granodiorite allow linking the measured K-Ar ratios to the specific geological events ranging from the Carboniferous to the Early Cretaceous periods.

Acknowledgments:

Funding has been provided through the BASE project (‘Basement fracturing and weathering on- and offshore Norway – Genesis, age, and landscape development) hosted by the NGU and jointly funded by Det Norske Oljeselskapet (now Aker BP ASA), Lundin Petroleum, Maersk Oil, Wintershall and NGU.

References :

- [1] Viola G., Scheiber T., Fredin O., Zwingmann H., Margreth A., Knies J. (2016). *Nat. Comm.*, **7**, 13448
- [2] Scheiber T., Viola G. (2018) *Tectonics*, **37**, 1030–1062.
- [3] Fredin O., Viola G., Zwingmann H., Sørli R., Brønner M., Lie J.-E., Grandal E.M., Müller A., Margreth A., Vogt C., Knies J. (2017) *Nat. Comm.*, **8**, 14879.



Long Term Soil Tillage System Influence on Loamy Soil Physical-Mechanical Properties and Crop Productivity

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Soil plays a key role in any biocenosis and its quality affects the sustainability of the ecosystem. Nowadays 15-20% of global CO₂ flux into the atmosphere are provided by the wrong choice of agriculture and deforestation. Since soil plays essential role in carbon management it is important to understand ways to reduce carbon mineralization during agrocenosis formation. Tillage is considered to be one of the main causes of carbon mineralization. Despite the fact that minimum tillage is considered preferable and is recommended for agricultural use, there is no unequivocal justification in the literature for the advantages or disadvantages of reduced soil tillage (RT), which is related to a number of factors: bedrock, climate, relief, rotation and selection of crops, as well as the duration of observations.

The physico-mechanical properties of the soil are an important factor influencing the fertility of the soil, however, the changes caused by the tillage are not immediately apparent, but takes a time for the soil to adapt to the new conditions. Therefore, the aim of the study is to evaluate the long-term soil tillage system influence on loamy soil physico-mechanical properties and crop productivity. Monitoring data are collected since 2009 to 2020. The field station is located in the central part of Latvia at the Zemgale lowland on research farm “Pēterlauki”, 56.50°N, 23.62°E. Soils are composed from glaciolacustrine silty loam and clays. Soil samples were taken annually from monitoring fields, which were continuously treated with ploughing (CT) and disk harrowing (RT) technologies. Nutrient uptake was calculated as total nutrient uptake by the crop (grain or seed, straw and plants roots). In crop rotation system three field crops – winter wheat (*Triticum aestivum* L.), spring barley (*Hordeum vulgare* L.) and faba bean (*Vicia faba* L.) were grown.

Soil compaction were observed after six years of uniform tillage in the whole soil profile in the fields with RT, which continues increase in the following years, while in the fields of conventional tillage (CT) where the arable layer is less compacted which provides better soil aeration, the soil compaction increases under 25 cm. Proportion of organic carbon stayed above 1% in the all monitoring fields, which is sufficient to ensure soil fertility. The effect of crop rotation on the accumulation of organic carbon in uniform tillage remains to be studied, as the current results only “mark” the heterogeneity of organic carbon stocks between fields with different crop rotation, where organic carbon stock variation by soil profile is small in the CT system, which could be explained with more even distribution of organic matter using CT. In contrast, in the fields of RT system, soil compaction processes and crop rotation are likely to affect the rate of decomposition of organic matter and stock heterogeneity. Long-term conventional soil tillage system compared to RT had a more favorable effect on soil agrophysical properties in the arable layer, such as water and air circulation, nutrient and organic matter accumulation. However, previous studies have shown that long-term ploughing can increase the plow sole formation.

Nutrient (NPK) uptake by spring barley was higher in RT in 2018 and 2019. In this period the nutrient uptake of winter wheat was not affected by the type of tillage but by crop rotation system. The lowest NPK uptake was identified in the repeated wheat sowings regardless of tillage. There is not certain effect of tillage on the nutrient removal of faba beans – the higher value was observed in the CT in 2018 while the uptake of N and K in RT system in 2020. Nutrient uptake of winter wheat, spring barley and faba bean has affected differently by RT and CT.

Crop grain yields in 11 – year long trial of soil tillage did not differ significantly (winter wheat – p=0.43, spring barley – p=0.80, faba bean – p=0.82). Average of harvested grain yield was 6.16 t ha⁻¹ for winter wheat, 4.97 t ha⁻¹ for spring barley, and 4.46 t ha⁻¹ for faba bean. Grain yield level were mostly influenced by the year’s meteorological situation and differed between seasons (p<0.05). The interaction between year and soil tillage were found for spring barley (p=0.03), and it was related with lower yield in RT in early tillage trial years, but higher – in RT fields in dry years after several years of tillage practice. Overall, the assessment of the whole monitoring period leads to the conclusion that using RT



is possible to harvest similar to CT yields of winter wheat, spring barley and faba bean. It must also be acknowledged that changes in soil physico-mechanical properties were observed during the monitoring period, but the studied eleven-year period does not yet show changes in winter wheat, spring barley and faba bean yields.

The study was made by financial support of the project of the Ministry of Agriculture “Impact of minimal tillage on the preservation of soil fertility, development and spread of harmful organisms, yield and its quality in permanent crops”.



SESSION 2:
Clays in archaeology and arts



Surveying and Researching Clay Beds in the Context of Bronze Age Archaeological Pottery Research: a Case Study of Dole Island Microregion

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Study of availability of the resources in the surroundings of the prehistoric settlements is crucial in order to understand various aspects of human lives in the past. One of the most important resources in prehistoric times was clay that had a wide range of application including pottery production. Therefore, study of available clay beds is crucial in order to study origin (imported or local?) and technological aspects (what kind of clay was used?) of the ceramic vessels [1, 2].

During the Bronze Age (1800-500 BC) in the present-day territory of Latvia active trade and exchange took place. One of the trade centres and most inhabited areas was the lower reaches of Daugava River, especially Dole Island and its surroundings [3, 4]. The aim of this paper is to present preliminary results from the ongoing research of clay bed availability and their chemical and mineralogical compliance to the Bronze Age pottery in this region.

The Dole Island and both coastlines of Daugava River until Nāvēssala, as well as three areas from inland were surveyed, overall a total of 12 clay samples were collected. Afterwards, clay briquettes were prepared and fired at 700°C (the average temperature of open pit-firing [5]). Then the chemical composition of clays and pottery were measured using WD-XRF and compared to the nearby Bronze Age settlement and grave pottery (Ķivutkalns, Reznēs, Vīnakalns etc.). Mineralogical study using petrographic analysis as well as Liquid and Plasticity Limit test will be carried out as well to determine the main tendencies of clay properties and similarities to the archaeological pottery.

This research is funded by LZP FLPP project “Sociālās transformācijas bronzas laikmetā Daugavas lejtecē” (grant No lzp-2018/2-0127).

References:

- [1] Paynter S., White H., Brown D. (2015). *Archaeological and Historic Pottery Production Sites: Guidelines for Best Practice*. Historic England.
- [2] Tsetlin Y. (2018). The origin of ancient pottery production. *Journal of Historical Archaeology & Anthropological Sciences*, Vol 3(2). 193 - 198.
- [3] Graudonis J. & Apals J., eds (2001). *Latvijas senākā vēsture 9. g. t. pr. Kr. - 1200. g.* Rīga: Latvijas Vēstures Institūta apgāds.
- [4] Vaska B. (2019). *Rotas un ornamenti Latvijā no bronzas laikmeta līdz 13. gadsimtam*. Rīga: Latvijas Nacionālais vēstures muzejs.
- [5] Dumpe B., Stunda-Zujeva A. & Vecstaudža J. (2014). Keramikas apdedzināšana vidējā un vēlajā dzelzs laikmetā - analīzes un eksperimenti. In: *Latvijas Nacionālā vēstures muzeja zinātniskie lasījumi, 2011.-2013: Latvijas Nacionālā vēstures muzeja raksti. Nr. 20*. Rīga: Latvijas Nacionālais vēstures muzejs. 33 - 43.



SESSION 3:
Clay mineral properties



Investigation of the Effect of γ -irradiation on Bentonite clay

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In the Swedish KBS-3 and similar repository concepts for nuclear waste disposal, certain radiolysis of the clay pore water is unavoidable due to the ionizing radiation from the canisters holding the nuclear waste. In view of the fact that iron is the major redox-active element in the Bentonite clay barrier (Wyoming Bentonite MX80 contains approx. 3w% Fe(III)), the structural Fe(II)/Fe(III) ratio and the overall redox conditions of the Bentonite adjacent to the copper waste canisters may change due to transient oxidizing and reducing species formed from radiolysis. Since mineral transformation/changes in the overall physicochemical properties of clays is of general concern in repository safety assessments, and since a fundamental understanding of the mechanisms of irradiation-induced structural Fe(II)/Fe(III) cycling in clays are lacking, this on-going research is focused on the effects of γ -radiation on the structural Fe(II)/Fe(III) in compacted Bentonite clay and montmorillonite.

It is well known that the ionizing radiation can cause several different effects in clay minerals and their surrounding chemical environment [1]. In the KBS-3 repository, the Bentonite clay barrier will be exposed to 40-200kGy of ionizing radiation (mainly γ -radiation from 137-Cs, $t_{1/2} \sim 30y$), where approx. 50% of the emitted γ -radiation energy would be deposited in the first 4 cm of the Bentonite barrier adjacent the copper canister holding the spent nuclear fuel. Any radiation-induced processes altering the native redox-chemical properties of saturated and compacted Bentonite, for instance off-setting the structural Fe(II)/Fe(III) ratio, could potentially affect the overall corrosion chemistry at copper canister interface, by reacting with dissolved solutes, such as H₂O₂ and different sulphur-species (HS⁻/SO₄²⁻).

Even at (low) doses comparable to the cumulative dose expected outside a copper canister in the KBS-3 repository, previous experiments with dilute clay suspensions has revealed that exposure to γ -radiation can *i*) enhance the colloidal stability of montmorillonite suspensions [2], *ii*) alter the sorption capacity for certain radionuclides [3, 4], as well as *iii*) cause an increase in the structural Fe(II)/Fe_{Tot} from ≤ 3 to 25-30% [5]. Because of these previously reported effects with dilute montmorillonite suspensions, the current study focuses on the effects on compacted Bentonite and montmorillonite, in order to investigate the possible implications from γ -irradiation under more realistic repository-like conditions, regarding water-saturation levels and anoxic/oxic conditions.

Acknowledgments:

This study has been financed by the Swedish Radiation Safety Authority, SSM (SSM2020-962).

References:

- [1] Allard Th, Balan E, Cala G, Fourdrin C, Morichon E, and Sorieul S. (2012). *Nucl. Inst. Meth. Phys. Res. Section B*. 277: 112–20.
- [2] Holmboe, Michael, S Wold, M Jonsson, and S Garcia-Garcia. (2009). *Applied Clay Science*, 43 (1): 86–90.
- [3] Holmboe, Michael, K Norrfors, M Jonsson, and S Wold. (2011). *Radiation Physics and Chemistry*. 80 (12): 1371–77.
- [4] Norrfors, K Karin, Åsa Björkbacka, Amanda Kessler, Susanna Wold, and Mats Jonsson. (2017). *Radiation Physics and Chemistry*. 144, 8–12.
- [5] Holmboe, M., Jonsson, M., & Wold, S. (2012). *Radiation Physics and Chemistry*. 81(2), 190–194.

Cation Exchange Processes Observed in the Third Excavated Parcel of Alternative Buffer Material Test (ABM-V) in Äspö, Sweden, After Heating to 250°C

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Bentonites are candidate materials for High-Level Radioactive Waste (HLRW) repositories and, therefore, have been investigated with respect to their 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]. The first cation exchange data of the lower blocks #1-15 of the package ABM-V dismantled in 2017 are reported. This was the third excavated parcel after ABM-I and II (first phase of the project). The blocks were heated in three steps starting with 1) a 2.5 years phase at approximately 50°C, followed by 2) a four months phase of up to 132°C and 3) a seven months phase of up to 250°C (Fig. 1a).

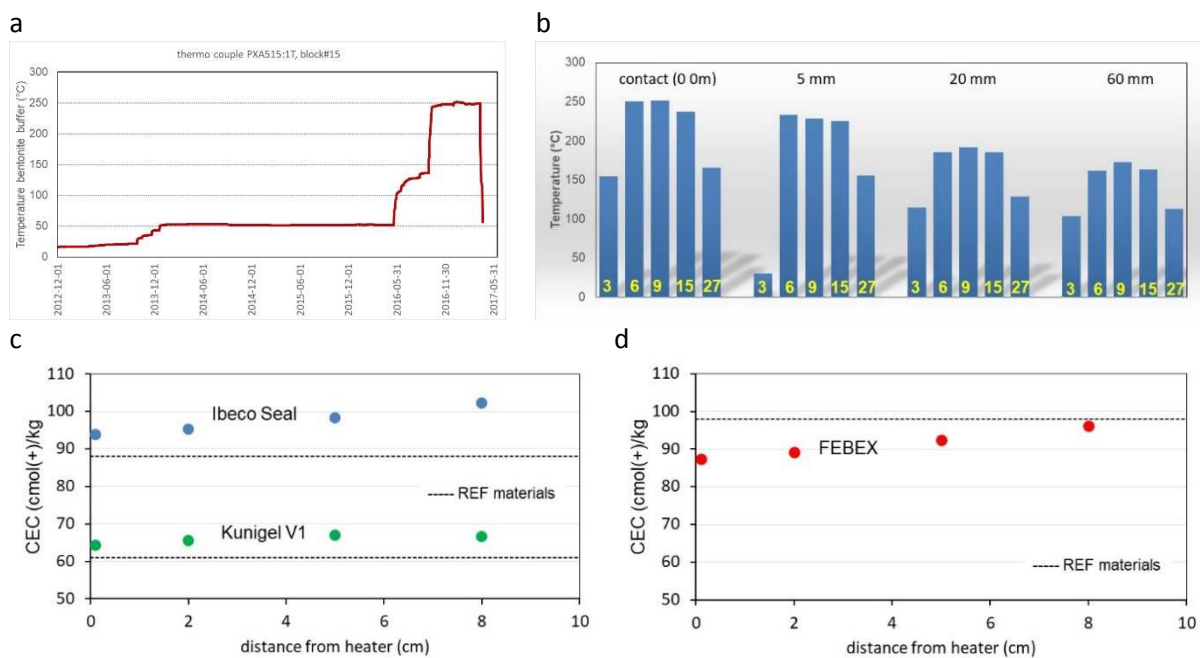


Figure 1a: Temperature development of ABM-V as detected by a thermocouple in block#15 positioned directly at the heater; 1b: development of max. temperature in blocks #3, 6, 9, 15, and 27 as function of the distance from the heater; data taken from SKB (2018); Development of c) increase and d) decrease of CEC values of ABM-V buffer materials as function of the distance from the iron heater. Note: all other bentonites showed no such profiles nor significant deviations.

Even in the outer part maximum temperatures of approximately 150°C were recorded (Fig. 1b) exceeding the maximum temperatures observed in most other experiments performed in underground or hard rock laboratories (Table 1).



Table 1: Experimental parameters of important projects for assessment of bentonite buffers in different underground or hard rock laboratories.

Experiment	Lab	Metal (heater)	Host rock	T (max)	Salinity (groundwater)	Scale
LOT	Äspö	copper	crystalline	ca. 140 °C	high (Na-Ca-Cl-SO ₄)	intermediate scal
ABM-I	Äspö	iron	crystalline	ca. 140 °C	high (Na-Ca-Cl-SO ₄)	intermediate scal
ABM-II	Äspö	iron	crystalline	ca. 140 °C	high (Na-Ca-Cl-SO ₄)	intermediate scal
ABM-V	Äspö	iron	crystalline	ca. 250 °C	high (Na-Ca-Cl-SO ₄)	intermediate scal
Prototype Repository	Äspö	copper	crystalline	ca. 85 °C	high (Na-Ca-Cl-SO ₄)	full scale
FEBEX-DP	Grimsel	iron	crystalline	ca. 100 °C	low (Na-Ca-HCO ₃ -F)	full scale
Heater B	Mont Terri	iron	clay	ca. 100 °C	Mont Terri pore water	intermediate scal

During the heating groundwater entered the blocks for water saturation by diffusion from the rock side to the heater. As expected from the results of former experiments, exchangeable cations were redistributed between different bentonite materials. However, in contrast to the former experiments, the average exchangeable Na⁺ occupation for ABM-I and II was in the same range as for the reference materials. The exchangeable Mg²⁺ occupation was reduced by half in the lower 15 blocks, whereas exchangeable Ca²⁺ occupation increased accordingly. The sum of the exchangeable cations was in the range of the total CEC (102%) in the reference materials and increased to 110% after retrieval. Similar to ABM-II [2], horizontal variation of the EC_{population} in single blocks was also observed in ABM-V. The total CEC was reduced by 3% on average, however, in two blocks (Ibeco, Kunigel) the CEC increased significantly towards the outer part (Fig. 1c) whereas in two other blocks (FEBEX, GMZ) the CEC decreased significantly towards the outer part (Fig. 1d). It should be noted that the GMZ block was disintegrated when received and could not be clearly cut in the described units.

References:

[1] SKB 2018. ABM45 experiment at Äspö Hard Rock Laboratory. Installation report ABM45. SKB P-18-20. ISSN 1651-4416 <https://www.skb.se/publikation/2491709/P-18-20.pdf>

[2] Dohrmann, R., Kaufhold, S. 2017. Characterization of the second package of the alter-native buffer material experiment (ABM) – II Exchangeable cation population rearrangement. Clays and Clay Minerals, 65, 104–121.



Dissolution Mechanism of Kaolinite in Alkaline Media: DFT Study

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Over the past few years alkaline-activated materials or geopolymers have attracted increasing attention as a promising sustainable alternative to Portland cement-based binders [1, 2]. Clay minerals, in particular kaolinite and its thermally induced metastable phase, metakaolin, are the most common and affordable source of raw materials for the geopolymerization reaction [3]. The understanding of the mechanism of kaolinite dissolution becomes critically important for the synthesis of geopolymers, predicting their long-term mechanical properties and chemical resistance. Progress in understanding the dissolution mechanism of aluminosilicate minerals was made in theoretical papers [4-6] performing an energy assessment of the breaking of Al–O and Si–O bonds in the ab initio and AM1 semiempirical approximations. At the same time, the models used in these works are limited by typical frame elements, for example, five-membered aluminosilicate framework rings [4, 5], or hydrated Al–O–Si clusters [6]. This significantly reduces the ability to correctly evaluate the parameters of kaolinite dissolution, since it does not take into account the crystalline features of its atomic structure. This work presents a density functional theory (DFT) study of the dissolution of kaolinite in an alkaline environment outside the framework of typical aluminosilicate cluster models. The desilication and dealumination processes have been studied, and the energy assessment of the selectivity of dissolution of Al–O and Si–O bonds taking into account the crystalline atomic structure of kaolinite has been given.

Acknowledgments:

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References:

- [1] Amran Y.H.M., Alyousef R., Alabduljabbar H., El-Zeadani M. (2020) Clean production and properties of geopolymer concrete; A review. *Journal of Cleaner Production*, 251, 119679.
- [2] Zhang P., Wang K., Li Q., Wang J., Ling Y. (2020) Fabrication and engineering properties of concretes based on geopolymers/alkali-activated binders - A review. *Journal of Cleaner Production*, 258, 120896.
- [3] Liew Y.-M., Heah C.-Y., Mohd Mustafa A.B., Kamarudin H. (2016) Structure and properties of clay-based geopolymer cements: A review. *Progress in Materials Science*, 83, 595-629.
- [4] Xu H., Van Deventer J.S.J., Roszak S., Leszczynski J. (2004) Ab Initio Study of Dissolution Reactions of Five-Membered Aluminosilicate Framework Rings. *International Journal of Quantum Chemistry*, 96 (4), 365-373.
- [5] Yunsheng Z., Wei S. (2007) Semi-empirical AM1 calculations on 6-membered alumino-silicate rings model: Implications for dissolution process of metakaoline in alkaline solutions. *Journal of Materials Science*, 42 (9), 3015-3023.
- [6] Morrow C.P., Nangia S., Garrison B.J. (2009) Ab initio investigation of dissolution mechanisms in aluminosilicate minerals. *Journal of Physical Chemistry A*, 113 (7), 1343-1352.

Development of Yet Another Classical Forcefield for Molecular Simulations of (Clay-)minerals

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Molecular simulation techniques (electronic or classical DFT, *ab initio*, classical Monte Carlo and molecular dynamics simulations) have emerged as useful tools in order to obtain detailed insights into the structure, thermodynamics and dynamics of hydrated clay minerals and other geochemical systems [1]. These computational techniques are particularly powerful when they complement the experimental techniques (spectroscopic, calorimetric, scattering or diffraction techniques), hence combined experimental and *in silico* (i.e. computer simulations) investigations are steadily becoming more and more popular in the clay science community. Nevertheless, both *ab initio* and classical simulation approaches rely on the ability to accurately describe the bonds and angles in atomic structures (i.e. the mineral lattices) typically obtained from the X-ray diffraction or other experimental methods. In this research a new mechanistic forcefield (suitable for the classical molecular dynamics and Monte-Carlo simulations) is being developed. The motivation for developing a new forcefield aimed at molecular modelling of (clay-)minerals is to improve the agreement between simulated and experimental structural data (unit cell dimensions and atomic positions), compared to the existing models/forcefields, such as Clayff and the Interface [1, 2], as revealed by the Bond Valence Sum (BVS) analysis (Fig. 1) and a direct comparison to ideal unit cells of minerals.

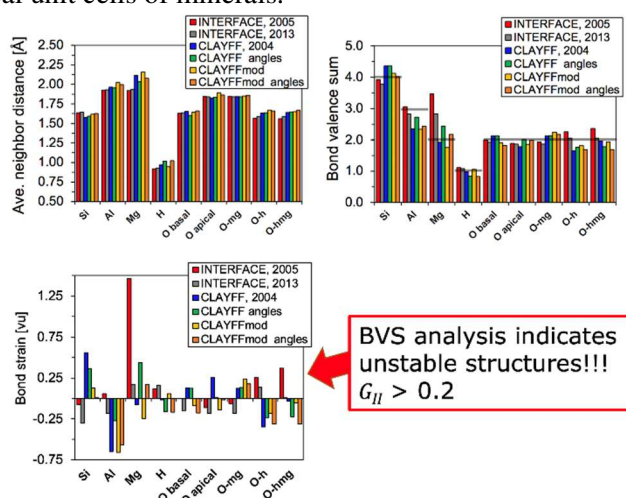


Figure 1. Figure illustrating the agreement between theory and experience, given the experimental error.

The forcefield optimization targeting both the Lennard-Jones *sigma* and *epsilon* values (i.e. the VdW related parameters) as well as partial charges was performed using an in-house code utilizing the *atom* MATLAB Toolbox [3] as a wrapper for the MD package Gromacs.

Acknowledgments:

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References :

- [1] Cygan, R.T., Liang, J.J., & Kalinichev, A.G. (2004). *Journal of Physical Chemistry B*. 108(4), 1255–1266.
- [2] Heinz, H., Koerner, H., Anderson, K.L., Vaia, R.A., & Farmer, B.L. (2005). *Chemistry of Materials*. 17(23).
- [3] Holmboe, M. 2019. *Clays and Clay Minerals*, 67(5), 419–426.



MgAl Hydrotalcite-derived Mixed Oxides for CO₂ Adsorption

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Layered Double Hydroxides (LDHs) and LDH-derived materials are potentially good adsorbents for CO₂. Moreover, they are relatively cheap, they are easy to synthesize, they present high sorption capacity, and surface basicity. They have been intensively studied with regard to the capture of CO₂ at high temperature, presenting variable sorption capacities for MgAl LDHs with the same composition, but being prepared under different synthesis conditions.

The sol-gel synthesis method is an attractive one-step procedure to synthesize LDHs under mild conditions, with low energy consumption and short synthesis time. The present study is based on the synthesis of hydrotalcites (HTs) by sol-gel process for the adsorption of CO₂. The structural and physico-chemical properties of the as-synthesized and calcined HTs have been deeply characterized. Moreover, the effect of the surface basicity and the CO₂ sorption capacity have been investigated.

Adsorption calorimetry was applied for determining the concentration (from the adsorption volumetric isotherms), strength and strength distribution (using the differential heat of adsorption as a function of coverage) of the basic sites involved in the adsorption of CO₂. The hydrotalcite-derived mixed oxides surface basicity was probed by the adsorption calorimetry of SO₂. Two populations of the basic sites were identified, at low energy (heat of adsorption below 60 kJ/mol) and at high energy (heat of adsorption higher than 150 kJ/mol).

The sol-gel method led to the formation of hydrotalcites with similar (sometimes higher) performances than the conventional LDHs prepared by time- and energy-consuming methods (like coprecipitation). The calcined hydrotalcites exhibit CO₂ adsorption capacities of around 0.5 mmol/g, a value similar to those reported in the literature for sample generally synthesized by coprecipitation (Fig. 1).

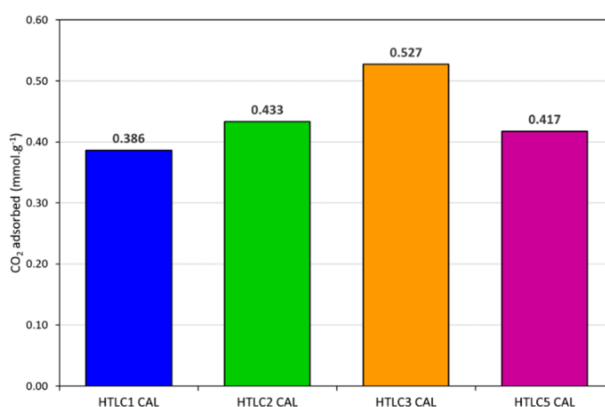


Figure 1. Quantity of CO₂ adsorbed by the calcined hydrotalcite samples.

A linear correlation between the surface basicity (concentration of low and high energy sites) and the adsorption capacity was found.

The possibility to tune the Mg/Al molar ratio is a promising feature to obtain a wide range of LDHs (with various surface basicity) with a higher efficiency in the adsorption of CO₂.

Acknowledgments:

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Insight Into the Phosphate Uptake Properties of Layered Double Hydroxides

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Phosphorus in the form of phosphate is a nutrient essential for life and a pollutant, which lead to poor water quality due to algae bloom. Moreover, phosphate rock is a critical resource and on the list of critical raw materials of the European Union. This creates a strong demand for the recovery of phosphate from e.g., wastewater. Layered double hydroxides (LDH) are considered promising filter materials due to their high affinity for phosphate. This research was aimed at gaining detailed insight into the phosphate uptake properties and pathways for a series of different LDH under conditions mimicking those found in wastewater using a combination of analytical chemistry and advanced characterization techniques (solid state NMR, PXRD, and electron microscopy). The phosphate adsorption studies were performed both in simple phosphate solutions and wastewater. The LDH tested included MgAl[1], ZnAl[2], MgFe[3], and CaAl-LDH[4] as well as the effect of the particle size, M(II):M(III) ratio, and intercalated anion. This allowed for a detailed comparison of the different LDH, especially with regard to their stability as well as phosphate uptake pathway and capacity. The discussion revolves around approaches used to reliably assess the phosphates adsorption properties and LDH stability as well as future directions in the formulation of LDH-based sorbents.

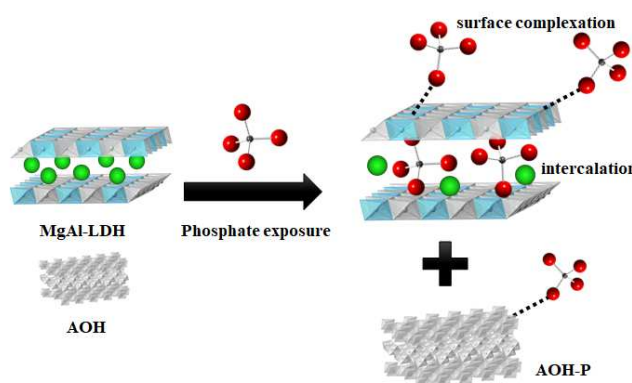


Figure 1. Different phosphate adsorption mechanism by LDH, which were identified and quantified.

Acknowledgments:

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References :

- [1] L. Lundehøj et al. J. Phys. Chem. C 123(39) (2019) 24039-24050.
- [2] L. Lundehøj, et al. Water Res. 153 (2019) 208-216.
- [3] T.-H. Kim, et al., Appl. Clay Sci. (2020) accepted.
- [4] B. Bekele, et. al. Appl. Clay Sci. 176 (2019) 49-57.

Computational Study of Diuron-smectite Interactions

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Beidellite (Bd) and Montmorillonite (Mt) have been proposed as adsorbents of the herbicide diuron (D), which shows a high toxic potential [1]. Despite the fact that smectites have a very limited adsorption capacity for hydrophobic organic pollutant [2], such as D, it is possible to modify the clay surface by organic surfactants, e.g., tetramethylphosphonium (TMP), in order to obtain a higher adsorption. The aim of this study is a characterization of the stability and interactions that occur in the interlayer space of the unmodified and modified Bd/Mt clays intercalated with the herbicide D.

The calculations have been performed by the Vienna Ab Initio Simulation Package (VASP) program using the Density Functional Theory (DFT) method in a solid state with the PBE functional [3] and the DFT-D3 scheme for dispersion corrections [4] in order to study the interactions and stability of the diuron-smectite complexes. The suggested models are: i) for unmodified clays, where D intercalated in Bd/Mt (D-Bd and D-Mt); and ii) for modified clays, where D and TMP cation intercalated in the smectites (DTMP-Bd and DTMP-Mt).

The results have shown that D has a flat arrangement in the interlayer space of both Bd and Mt clays (Fig. 1). The interactions formed between the D and clay surface are weak hydrogen bonds. The calculations showed a higher stability in the modified diuron-smectite complexes, DTMP-Bd (-280.9 kJ/mol) and DTMP-Mt (-199.8 kJ/mol), in comparison with D-Bd (-118.7 kJ/mol) and D-Mt (-107.7 kJ/mol) indicating that beidellite forms more stable intercalates than montmorillonite in both unmodified and modified structures.

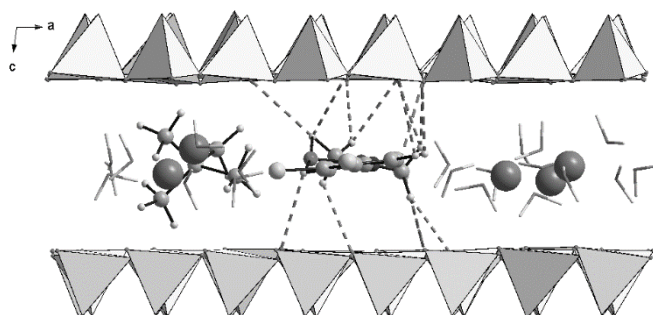


Figure 1. The hydrogen bonds (C-H...Ob) among the D and Bd (dashed lines) in the DTMP-Bd model.

Acknowledgments:

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References :

- [1] Mendoza-Huizar, L. H. (2015). Chemical Reactivity of Isoproturon, Diuron, Linuron, and Chlorotoluron Herbicides in Aqueous Phase: A Theoretical Quantum Study Employing Global and Local Reactivity Descriptors. *Journal of Chemistry*, 2015, 1–9.
- [2] De Paiva, L. B., Morales, A. R., & Valenzuela Díaz, F. R. (2008). Organoclays: Properties, preparation and applications. *Applied Clay Science*, 42(1-2), 8–24.
- [3] Perdew, J. P., Ernzerhof, M., & Burke, K. (1996). Rationale for mixing exact exchange with density functional approximations. *The Journal of Chemical Physics*, 105(22), 9982–9985.
- [4] Grimme, S., Antony, J., Ehrlich, S., & Krieg, H. (2010). A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu. *The Journal of Chemical Physics*, 132(15), 154104.

Evolution of Germanium-based Imogolite Nanotubes During Dehydroxylation

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Metal oxide aluminosilicate and aluminogermanate nanotubes, called imogolite nanotubes (INT), are fascinating nanotubes, easily synthesized with well-controlled diameter and with different morphologies and organization [1, 2]. These nanotubes undergo major structural changes at high temperatures, including the transformation from one-dimensional (1-D) nanochannels into a structure which is supposed to be lamellar [3, 4] but which is not studied in detail in the research literature.

This paper presents complete analysis of the structural transformation of single or double-walled aluminogermanate nanotubes up to 900°C. An original approach is applied combining in-situ X-ray absorption spectroscopy measurements (LUCIA & DiffAbs beamlines), which allows to investigate the evolution of both Al and Ge atoms coordination during the transformation process (Fig. 1A). The quantitative analysis of XANES spectra reveals that the dehydroxylation of nanotubes does not lead to a lamellar phase but rather to metastable intermediate states that the authors have named “meta-imogolite” by analogy with the thermal transformation of kaolinite to meta-kaolinite (Fig. 1B). Between 600 and 800°C progressive atomic reorganization of this phase was observed followed by the transition to a mullite-type structure above 900°C. The understanding of the structural modifications of these nanomaterials at high temperatures represents a benchmark for further studies concerning the properties of these transformed INT-based compounds, for instance with respect to the topical issue of geopolymers.

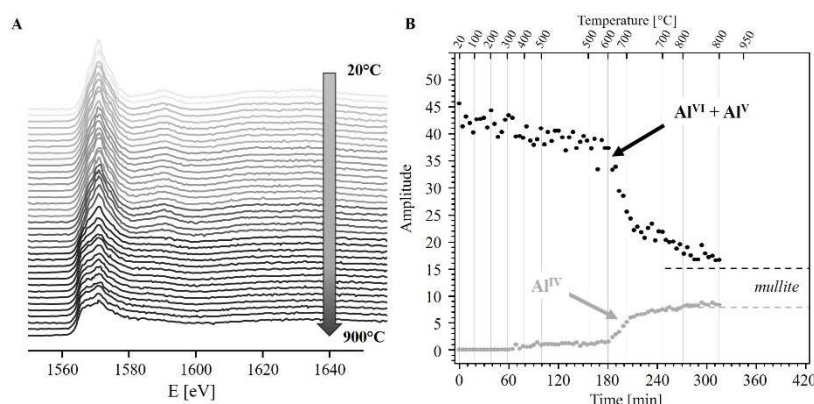


Figure 1. (A) Evolution with temperature of Al K-edge XANES spectra for a powder of double-walled aluminogermanate imogolite nanotubes; (B) Amplitude of the fitting Gaussians related to the coordination of Al, derived from the deconvolution of the spectra as a function of temperature (upper axis) and time (lower axis).

References :

- [1] Paineau E. & Launois P. (2019) In. *Nanomaterials from clay minerals*. Amsterdam, Netherlands: Elsevier, pp. 257-284.
- [2] Monet G., Amara M.S., Rouzière S., Paineau E., Chai Z., Elliott J.D., Poli E., Liu L.M., Teobaldi, G. & Launois P. (2018) Structural resolution of inorganic nanotubes with complex stoichiometry. *Nat. Commun.*, 9, 2033.
- [3] MacKenzie K.J.D., Bowden M.E., Brown I.W.M. & Meinhold R.H. (1989) Structure and thermal transformations of imogolite studied by ²⁹Si and ²⁷Al high resolution solid-state nuclear magnetic resonance. *Clays Clay Miner.*, 37, 317-324.
- [4] Zanzottera C., Vicente A., Armandi M., Fernandez C., Garrone E. & Bonelli B. (2012) Thermal collapse of single-walled aluminosilicate nanotubes: Transformation mechanisms and morphology of the resulting lamellar phases. *J. Phys. Chem. C*, 116, 23577-23584.



Relationships Between Structural and FTIR Characteristics of Kaolinites: New Insights

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A representative collection of kaolinites with different origin, particle size and degree of disorder was studied by powder X-ray diffraction (XRD) and Fourier-transform infrared (FTIR) spectroscopy in order to establish relationships between the structural and spectroscopic features and thus resolve the ambiguities in the interpretation of the OH stretching region of the FTIR spectra of kaolinites. Modelling of the experimental XRD patterns based on the C-vacant orthogonal layer unit cell having a mirror plane showed each sample to be a mixture of nearly defect-free high-ordered (HOK) and low-ordered (LOK) kaolinite phases, with HOK varying from 86 to 4%. The wavenumbers, heights, areas and full widths at half-maximum (FWHM) were determined for the OH-stretching bands at ~ 3697 (ν_1), ~ 3670 (ν_2), ~ 3652 (ν_3) and 3620 cm^{-1} (ν_4) by decomposition and fitting of the FTIR spectra.

The $\text{FWHM}(\nu_1)/\text{FWHM}(\nu_4)$ (Fig. 1) and $\text{FWHM}(\nu_3)/\text{FWHM}(\nu_2)$ values were found to be linearly related to the HOK contents, which may be associated with the in-phase and out-of-phase character of the corresponding pairs of vibrations, respectively. The integrated intensities of the OH-stretching bands are sensitive to the HOK phase contents in such a way that, e.g., for samples with $\text{HOK} \geq 50\%$, a decrease in the HOK is accompanied, depending on the sample particle size, either by an almost linear decrease or increase in the $A(\nu_1)/A(\nu_4)$ ratios. The intensity distribution of the ν_2 and ν_3 bands is controlled by the triclinic structure symmetry in the defect-free kaolinite and the orthogonal layer symmetry in low-ordered structures. Therefore, the kaolinite FTIR spectrum is the result of the statistically weighted sum of the contributions from the coexisting high- and low-ordered structures. This reflects the competition between the unit-cell triclinic symmetry and the mirror symmetry of the layer, respectively. It also corresponds to the observed evolution of the corresponding band intensities.

The ν_1 and ν_2 band positions for the low-ordered samples are within the wavenumber range for the high-ordered samples. In contrast, the ν_3 and ν_4 band positions for the low-ordered samples are shifted towards the higher wavenumbers with respect to those high-ordered samples, which indicate that at least some of the low-ordered kaolinites should contain dickite-like structural fragments distributed among the kaolinite layers.

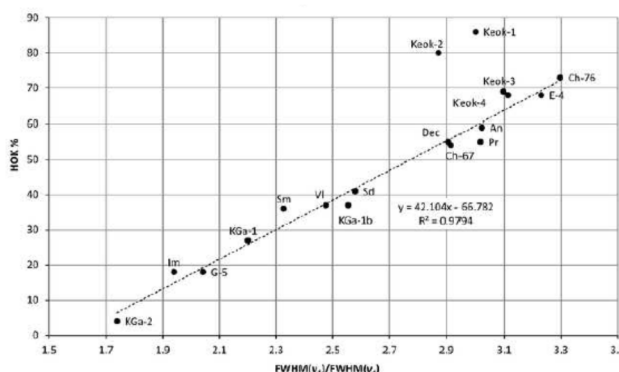


Figure 1. The HOK contents in the kaolinite samples plotted vs. the ratios of full widths at half-maximum for the ν_1 and ν_4 bands, $\text{FWHM}(\nu_1)/\text{FWHM}(\nu_4)$.

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SESSION 4:
Clay mineral synthesis



Influence of the Precursor and the Temperature of Synthesis on the Structure of Saponite

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Porous silicates are widely used in heterogeneous catalysis [1]. Important characteristics for this application are the type, quantity and distribution of reactive sites, specific surface area and porosity, as well as the ability to regenerate the catalyst. Zeolites, one of the best solid catalysts, with a pore size <0.8 nm, are not suitable for adsorption of large molecules. On the other hand, clay minerals, such as saponite, with an expandable interlayer space (> 1 nm) make it possible to have a surface accessible to the adsorption of complex molecules and enzymes.

The synthesis of saponite is relatively simple. However, knowledge of the reactions of hydrolysis and condensation and crystal growth is still limited. Thus, precise control of the synthesis conditions in order to obtain a material with a well-defined structure remains a challenge. Different experimental protocols concerning the preparation of precursor are reported in the literature [2]. In this work, the influence of the temperature of synthesis and the precursor on the structure of the product are studied.

The results show that the temperature of the pre-treatment of precursor has an impact on the configuration of aluminum in the structure of the synthesized saponite. The synthesis carried out using a precursor calcined at 450°C produced a saponite with about 90% aluminum in tetrahedral configuration. A precursor dried at 200°C led to the material consisting of a heterogeneous mixture of different clay minerals with 80% tetrahedral aluminium. A precursor without prior heat treatment yielded a material with 60% aluminium in tetrahedral configuration. The synthesis temperature did not have a significant impact on the characteristics of the final product.

Calcination is known to promote the tetrahedral configuration of aluminum [3]. This configuration in the precursor is then somehow preserved during the synthesis and impacts the structure of the final material. In summary, the use of precursor calcined at 450°C, and a synthesis carried out at 90°C allows to obtain saponite with most of aluminum in the tetrahedral configuration. The increase of the synthesis temperature did not have a significant influence on the final structure of saponite.

Acknowledgments:

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References:

- [1] Clark J.H., Rhodes C.N. (2000) *Clean Synthesis Using Porous Inorganic Solid Catalysts and Supported Reagents*. Cambridge, UK: Royal Society of Chemistry.
- [2] Jaber M., Komarneni S., Zhou C.-H. (2013) Synthesis of Clay Minerals, in: F. Bergaya, G. Lagaly (Eds.), *Handb. Clay Sci. Fundam.*. Elsevier, 223–241.
- [3] Nampi P.P. *et al* (2010) Aluminosilicates with varying alumina-silica ratios: Synthesis via a hybrid sol-gel route and structural characterisation. *Dalt. Trans.*, 39, 5101–5107.

Optimization of Iron-rich Clay Mineral Synthesis via Design of Experiments and Response Surface Methodology

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The formation of clay minerals in Si-Fe-O-H system can be found in different geological and engineered settings. Apart from nontronite (di-octahedral smectite), the quantities of other iron-rich clay minerals are not sufficient to obtain their formation and dissolution constants experimentally. This in turn limits the robustness of geochemical models, which include these minerals. In order to obtain sufficient quantities of these minerals for experiments, their synthesis can be foreseen.

A Design Of Experiments (DOE) and Response Surface Methodology (RSM) were used in order to find optimum synthesis conditions for these clay minerals. The main objective is to obtain the maximum of information from a minimum of experiments (DOE), and RSM enables to explore relationships between the studied functions and the operating factors. Three parameters were considered: temperature T, synthesis time t and the molar ratio OH/Fe. The studied functions are the ratios of peak area of (001) reflection for 1:1 and 2:1 type clay structure.

The experimental and RSM results were used for investigating the optimal balance between synthesis parameters favouring formation of 2:1 or 1:1 type clay mineral structure. The Fig. 1A shows the conditions of temperature and synthesis time favouring the formation of 2:1 type clay mineral, corresponding to a R(A)>30 (high OH/Fe ratio and temperature, short time). The Fig. 1B shows that the formation of 1:1 type clay structure is favoured at low OH/Fe ratio and the synthesis can be achieved at low temperature and short time.

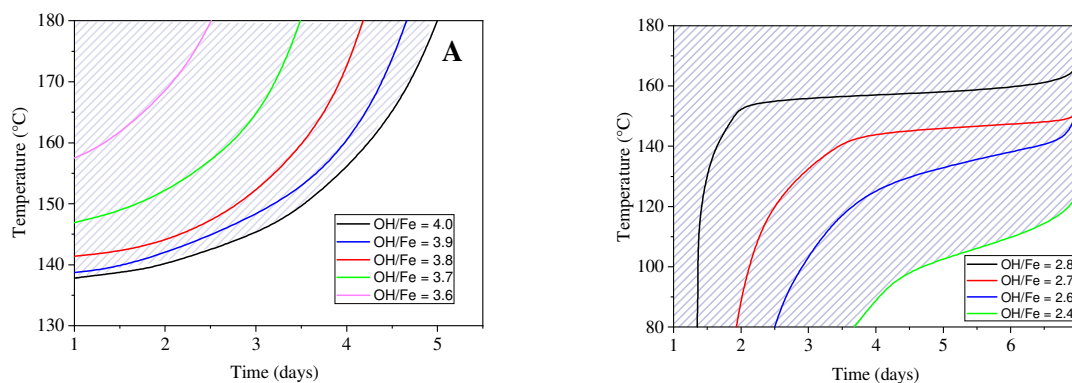


Figure 1. Conditions of temperature and synthesis time favouring: A) the formation of 2:1 phase; and B) 1:1 type clay mineral.

Acknowledgments:

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References :

Boumaiza H. et al. (2020) Iron rich clay mineral synthesis using design of experiments approach. *Applied Clay Science*, 199, 105876.

Influence of the Synthesis Parameters on the Formation and Characteristics of Organic-inorganic Hybrids Having a Talc-like Structure

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Organic-inorganic hybrids having a talc-like structure (TLH) are versatile and attractive materials. It is possible to synthesize them by a sol-gel process, at room temperature and within short crystallization times. In these structures, the organic chains are covalently linked to the silicon atoms of the tetrahedral sheets and pending in the interlayer space and at the surface. The silicon source is an organotrialkoxysilane ($\text{RSi}(\text{OR}')_3$), where R stands for an organic chain and R' for an ethoxy or methoxy group. The goal of this study was to decipher the influence of several parameters (such as pH, water, duration of synthesis, solvent type) on the formation of TLH and especially on the condensation degree of the silicon species. Beside the X-Ray diffraction, chemical analysis and thermogravimetric analysis, ^{29}Si solid-state nuclear magnetic resonance has been performed to characterize different samples. For TLH, T^1 , T^2 and T^3 sites are expected, T^3 sites corresponding to $\text{RSi}(\text{OM})_3$ groups, where silica is covalently bonded to three M (Si or Mg) and represents the highest degree of condensation. T^1 and T^2 sites are related to the presence of defects in the structure and/or border sites. This study has shown that the addition of water to the synthesis medium leads to organic-inorganic hybrids with a silicon species having a low condensation degree (T^3 sites ratio below 20%), while a high condensation degree (around 60%) could be obtained for syntheses carried out in the absence of water. Moreover, in the presence of water, the addition of a base, such as sodium hydroxide, seems to further decrease the condensation degree. The stirring duration also plays a role; syntheses carried out during 5 days show a higher amount of T^3 sites compared to those performed during 24 hours. Apparently, the solvent choice does not influence the condensation of the formed TLH. These results open the possibility to synthesize hybrids with a tunable condensation degree only by changing the amount of water in the synthesis medium.

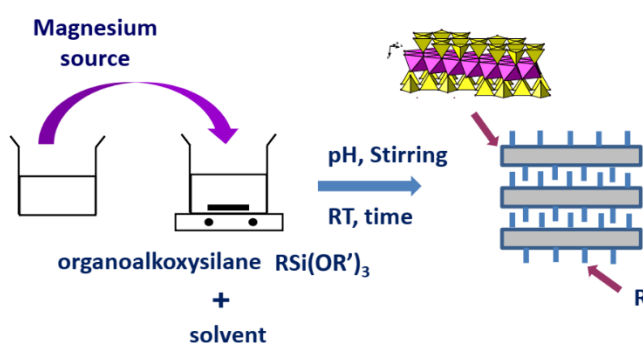


Figure 1: Preparation and structure of an organic-inorganic hybrid having a talc-like structure.

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XRD, TGA, and NMR measurements have been performed on the technical platforms of IS2M. The authors are very grateful to L. Michelin, H. Nouali, and S. Rigolet for their contributions.



Hybrid Inorganic-organic Lamellar Materials Containing Fe(III): Effect of Fe(III)/Mg(II) Ratio on the Condensation State

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The accumulation of organic pollutants inert to the regular wastewater treatment is a major treat to the environment and it has human health consequences [1, 2]. Advanced oxidation processes (AOPs) are capable of degrading these so-called persistent organic pollutants (POPs), and Electro-Fenton (EF) process stands out among AOPs due to its relatively low cost and great efficiency (in-situ generation of H₂O₂). However, iron salts are added to each load of wastewater and posteriorly released into water bodies along with treated effluents [2]. In this context, the incorporation of iron in the structure of layered silicates is a promising approach to developing a stable supported heterogeneous catalyst for EF systems [3, 4]. Thus, the goal of this study is to investigate the influence of Fe(III) on the condensation of these hybrid inorganic-organic talc-like structures in order to optimize its synthesis.

The experimental procedure has been based on a previous study of Miron et al [4] and involves hydrolysis and posterior condensation of an organo-modified alkoxide (3-aminopropyl)triethoxysilane (APTES) in the presence of Fe(III) and/or Mg(II) salts in absolute ethanol at room temperature. The Fe(III)/Mg(II) molar ratio varied from 0 to 6.67. The powder materials were investigated by Fourier transformed infrared (FTIR) spectroscopy, X-ray diffraction (XRD) and X-ray fluorescence (XRF) in order to evaluate structure and elemental composition of the resulting materials.

The FTIR spectra suggests formation of a silicate framework containing Mg(II) and Fe(III). Besides, vibrational bands attributed to N-H and C-H bonds are also observed and confirm presence of amino chains bonded to such framework. The XRD pattern indicates existence of a layered structure and the reflections are consistent to those observed for talc-like materials. The reflection of (060, 330) planes are used to determine occupancy of octahedral sheet that rearranges from tri-octahedral to di-octahedral upon an increase of Fe/Mg molar ratio indicating incorporation of Fe(III) in the structure. However, the results of elemental analysis by the XRF show that molar ratios of Si/Fe and Si/Mg differ from theoretical values revealing that such increase of Fe(III) favours only partial condensation of the structure and possibly other amorphous phases containing iron. Besides, the XRF results show that incorporation of structural Fe(III) is limited to a Si/Fe molar ratio of 0.45-0.51 even upon an increase of Fe/Mg molar ratio. Thus further optimization studies are necessary in order to maximize content of Fe(III) without compromising condensation of the talc-like structure and, as a consequence, yield and stability of this hybrid lamellar material.

Acknowledgments:

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References :

- [1] United Nations Environment Programme (UNEP) (revised in 2017) Stockholm Convention on POPs - Text and Annexes, *Secretariat of the Stockholm Convention (SSC)*, Geneva, Switzerland.
- [2] Brillas E., Sirés I. & Oturan M. A. (2009) Electro-Fenton Process and Related Electrochemical Technologies Based on Fenton's Reaction Chemistry. *Chemical Reviews*, 109, 6570–6631.
- [3] Hartmann M., Kullmann S. & Keller H. (2010) Wastewater treatment with heterogeneous Fenton-type catalysts based on porous materials. *Journal of Materials Chemistry*, 20, 9002-9017.
- [4] Miron S. M., Brendlé J., Josien L., Fourcade F., Rojas F., Amrane A. & Limousy L. (2019) Development of a new cathode for the electro-Fenton process combining carbon felt and iron-containing organic-inorganic hybrids. *Comptes Rendus Chimie*, 22, 238–249.



SESSION 5:
Clay composite based materials



Research on the Use of Lake Clay in Medicine and Aesthetic Cosmetology

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Lake clay contains typical clay crystalline phases – illite, kaolinite, and rock forming minerals – quartz, dolomite, calcite, plagioclase, albite, and enstatite. The granulometric content of lake clay is mostly characterised by silt (2 – 63µm) and clay (<2µm) fractions. Specific surface area varies from 9.45 to 20.68 m²/g. Adsorption capacity of lake clay varies from 25.8 to 45.8 mg/g [1].

Lake clay meets the requirements of the Cabinet Regulation No 354 “Procedure for Meeting the Significant Requirements for Cosmetics” (Latvia) and the Standard EN ISO 17516:2014 Cosmetics - Microbiology - Microbiological limits. No presence of *Candida albicans*, *Pseudomonas aeruginosa*, *Staphylococcus aureus*, *Escherichia coli*, *Salmonella* was found in any of the samples, the total amount of aerobic mesophilic microorganisms is $\leq 1 \times 10^3$ CFU per g.

In comparison with other commercial clays used in cosmetics [2], it was found that lake clay contains lower amounts of elements, which are traditionally considered as toxic. As, Ni, Cu, Zn, Sr, Pb, Ba concentrations are significantly lower.

The odour of unmodified clay samples was determined – typical for clays odour, colour – blue-gray, green-gray, moisture – 30.9 - 49.2%, consistency – plastic, soft, smooth.

Considering its chemical and biological parameters, granulometric content, specific surface area and adsorption capacity, lake clay is suitable for the cosmetical and medical treatment. In long-term tests lake clay applications showed a statistically significant ($p < 0.001$) improvement of skin elasticity and hydration with no significant changes in the skin pH level. Even though statistically insignificant, transepidermal water loss tended to decrease [3]. In 99% of cases, there were no allergic reactions, complications, and the overall health was not affected. Furthermore, in some cases it was noted that store-bought clay provoked allergic reactions but this lake clay did not. In 97% of cases the effect was positive yet in 3% of cases there was no effect. Volunteers stated that after using clay facial masks their skin became smoother and pores, redness, pigmentation, the amount of comedones and pimples reduced. After clay applications on the body skin became firmer, cellulite decreased and stretch marks became less visible. Volunteers noted that clay helped with swelling and itch associated with mosquito bites, promoted eczema healing. Respondents also used clay applications for skeletal, muscular, and connective tissue diseases, traumas. Based on the Brief Pain Inventory, the pain intensity of volunteers reduced. Volunteers also noted that clay reduces the edema, cramps, tingling and rigidity.

References :

- [1] Tretjakova R., Noviks G. & Mežinskis G. (2019) Investigation of structure and composition of Latgale lakes clay for their practical use. *Proceedings of the 12th International Scientific and Practical Conference. Environment. Technology. Resources*. I, 298-303.
- [2] Mattioli M., [Giardini L.](#), Roselli C. & Desideri D. (2016) Mineralogical characterization of commercial clays used in cosmetics and possible risk for health. *Applied Clay Science*. [119 \(2\)](#), 449-454.
- [3] Misiņa S. M., Tretjakova R., Kodors S. & Zavorins A. (2020) Lake Zeiļu Clay Application Induced Changes in Human Skin Hydration, Elasticity, Transepidermal Water Loss and PH in Healthy Individuals. *Cosmetics* 7(3), 51: 1-10.



Humic Substance - Clay Mineral Composites as Novel and Eco-friendly Sorbents for Environmental Remediation

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Humic substances are high-molecular-weight polycationites which are formed from long-term physical, microbial and chemical transformations of organic matter. Nowadays, humic substances are produced at an industrial scale, and they can also be obtained from waste materials, such as compost. As polyfunctional materials, humic substances strongly interact with organic and inorganic substances. Therefore, the biocompatibility of clay minerals and the high sorption properties of humic substances makes their combination a successful approach for developing composites that can be used for environmental remediation [1]. In this study, clay minerals were modified with humic substances to create innovative and environmentally friendly sorbents for removing emerging pollutants from the leachates in closed dumps and landfills. Thus, modified clay composites might be considered for landfill closure projects as valuable constituents in the production of covering material in a mix with reworked fine fraction of waste and natural soil [2-3]. First results have shown that fine fraction of reject material that may be up to 50-60% of inert waste weight have good properties in order to serve as methane degradation layer if used in combination with organic matter. It means that covering materials for landfill cell closures might be approached just nearby from the lost from life cycle material – landfill waste itself. Moreover, mineralogical studies indicate on presence of clay particles in fine fraction for elaborating sorption properties.

Acknowledgments:

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References :

- [1] Burlakovs, J., Pilecka, J., Grinfelde, I., Ozola-Davidane, R., 2020. Clay minerals and humic substances as landfill closure covering material constituents: first studies. *Research for Rural Development* 35, 219–226, <https://doi.org/10.22616/rdd.26.2020.032>.
- [2] Burlakovs, J., Kaczala, F., Vincevica-Gaile, Z., Rudovica, V., Orupõld, K., Stapkevica, M., Bhatnagar, A., Kriipsalu, M., Hogland, M., Klavins, M., Hogland, W. 2016. Mobility of metals and valorization of sorted fine fraction of waste after landfill excavation. *Waste Biomass Valori.* 7, 593–602. <https://doi.org/10.1007/s12649-016-9478-4>.
- [3] Burlakovs, J., Kriipsalu, M., Klavins, M., Bhatnagar, A., Vincevica-Gaile, Z., Stenis, J., Jani, Y., Mykhaylenko, V., Denafas, G., Turkadze, T., Hogland, M., Rudovica, V., Kaczala, F., Rosendal, R.M., Hogland, W., 2017. Paradigms on landfill mining: From dump site scavenging to ecosystem services revitalization. *Resour. Conserv. Recycl.* 123, 73–84. <https://doi.org/10.1016/j.resconrec.2016.07.007>.



Novel pH-sensitive Composites Containing Clay Minerals and Anthocyanins to Monitor Meat Freshness

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In the European Union, a significant amount of food is wasted due to the lack of customers' understanding of the difference between 'best before' and 'use by' dates on food labels. In total, 4,7 million tonnes of food are wasted in the EU households every year, equivalent to 92 kilos per person per year. This study aims to solve this problem by developing an innovative clay mineral-anthocyanin composite materials that can be used as intelligent sensors for detecting spoiled food. Due to the characteristic properties of anthocyanin, composite materials change colour from red to blue depending on the pH change of food and packaging environment caused by the bacterial contamination. It indicates the food quality in a very simple way and provides consumers with real-time information about food quality during its storage and transportation, thus reducing an avoidable food waste. The experimental results in controlled relevant environment conditions showed that sensor colour changes, when a food product is organoleptically unusable for its consumption and before bacterial contamination exceeds the threshold values set by the Commission Regulation No 2073/2005. The experimental results also showed that mineral-anthocyanin composites are the most effective for different raw and processed meat products, such as beef, pork, and chicken. The further experiments will focus on adapting the intelligent sensor technology that could be applicable not only for meat products but also for egg and fish products. Another challenge is to establish cooperation with the Latvian meat production companies in order to continue experiments in the conditions of real environment.

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Functional Surfaces of Polymer Nanocomposites Modified with Organoclay and Methylene Blue

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In this work synthetic saponite (Sap) was modified with hexadecyltrimethylammonium (HDTMA) cations leading to a highly hydrophobic material. Subsequently, the organoclay was functionalized with variable amounts of methylene blue (MB). The suspensions of Sap/HDTMA/MB were filtered through Teflon membranes to prepared thin films. The synthesis of nanocomposites with polycaprolactone (PCL) with the functionalized organoclays was performed via melt diffusion at the interface of the film and the polymer. Pristine silicate and modified materials, as well as the final nanocomposites with the modified surface, were characterized by a combination of analytical techniques including UV-Vis absorption and fluorescence spectroscopy.

The fluorescence spectra (Fig. 1) of PCL nanocomposites shows the trend reflecting MB concentration. At lower concentrations the fluorescence intensity increased with the dye concentration achieving the maximum for MB4. The presence of H-aggregates led to the quenching of fluorescence and to the shift of maximal emissions to partially higher wavelengths. Fluorescence quenched completely for the samples with the highest MB concentrations (MB9 and MB10) [1].

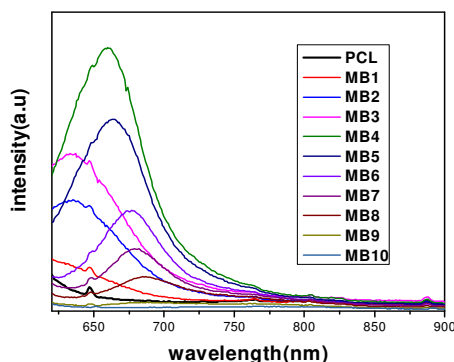


Figure. 1. Fluorescence spectra of MB1-MB10 polymer composites.

Some of the prepared specimens exhibited high photoactivity. The optical properties and photoactivity of the dye reflected the concentration of the dye in the materials. The samples with a higher concentration of methylene blue exhibited higher tendency to form H-aggregates which led to the quenching of luminescence. In the samples with lower concentrations of methylene blue the formation of monomers is more likely to occur.

Acknowledgment :

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References :

[1] Donauerová, A., et al., *Photophysical and antibacterial properties of complex systems based on smectite, a cationic surfactant and methylene blue*. J. Photochem Photobiol. B, 2015. 151: p. 135-141.



Characterization of Hybrid Luminescent Materials Based on Smectites, Rhodamine 6G and Cationic Surfactants

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The main motivation of the present work was to design hybrid materials based on clay minerals exhibiting luminescent properties, which would be suitable as potential precursors for preparation of fillers in composites with industrial polymers. The materials were prepared from montmorillonite (Mt) and saponite (Sap), modified with cations of organic surfactants (tetraoctylammonium TOA and tetraoctylphosphonium TOP) in various amounts (20, 50, 70, 100 %) relative to the CEC value of smectites and with a laser dye, Rhodamine 6G (R6G).

The optical properties of the prepared pigment powders were characterized by spectroscopy methods in the visible range (diffuse reflectance, emission, and excitation spectra). The hybrid systems based on Sap exhibited luminescence even without modification with surfactants on contrary to the samples prepared from Mt. The modification by the surfactants played a key role and evoked an increase in the integrated fluorescence intensities compared to pristine Mt and Sap. Increase was attributed to a reduction in the amount of H-aggregates in favour of luminescent species. However, such trend was detected only for certain dye concentrations applied ($<0.005 \text{ mmol}\cdot\text{g}^{-1}$). Luminescence generally decreased with increasing the dye concentration, due to the formation of non-luminescent types of molecular aggregates. The effect of surfactant amount was not so significant compared to the influence of dye concentration, although certain decline in the fluorescence intensities was observed for Mt and Sap fully saturated with organic cations. Wide bands of very complex character were exhibited in the fluorescence spectra of studied pigments, thus indicating the presence of various luminescent species. Chemometric method accompanied by statistical analysis of fluorescence spectra were very useful tools that helped to identify individual spectral components and to evaluate the influence of individual factors on formation of luminescent species. In addition to monomers of the maximal emission at about 570 nm, J-dimers and aggregates were identified with emission at higher wavelengths (600-700 nm). By a suitable choice of parameters (dye concentration, surfactant amount and smectite type) it was therefore possible to prepare luminescent materials that absorbed and emitted light at variable wavelengths.

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POSTER SESSION



Subsurface Drainage Effect on Clay-sized Mineral Content and Mineralogy in Two Agricultural Soils

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By affecting the redox environment of soils, water promotes mineral weathering, and changes the oxidation state of Fe in clay minerals. Water fluxes are also a major pathway for particle and element transportation both within and out of soil. Thus, changes in water fluxes can alter the evolutionary pathway of soils.

Over the last half century in Latvia, large areas of agricultural lands have been equipped with subsurface tile drains. This reduces the residence time of water in soil and changes its redox status by improving aeration. By diverting water from surface runoff into the soil, the amount of infiltrating water also increases.

The goal of this study is to quantify the effect of 40 years of artificial subsurface soil drainage on the clay content and properties in two agricultural soils in Latvia. At each site, we described and sampled soil profiles at various distances perpendicular from a drain.

The effect of the altered water fluxes was mostly mechanical and it did not cause any changes in the clay mineralogy. The results showed a 30% decrease in total clay content in areas closest to the drain. Interestingly, this decrease in clay content did not correlate with changes in Fe concentration in the < 2 mm soil fraction, suggesting that the coarser particles in this soil might be a major source of Fe. Further research on Fe oxidation states is planned.

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Yield of Grass Mixtures Depending on the Physical Clay content in *Luvisol* Soil

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Grasslands are not only an excellent source of fodder; they also serve as effective reducers of greenhouse gas emissions [1]. The choice of grass species appropriate to the soil conditions plays an important role in increasing grass yield and productive longevity [2]. Latvia has a long experience of growing grasses, however, research on their growing technologies is still relevant, especially over the recent decades, when the climate has changed significantly and the technologies used in agriculture have largely developed.

Taking into account that there is a great diversity of soils in Latvia [3], one of the most important factors influencing the yield of arable crops is soil texture. It is determined depending on the content of physical clay particles in the soil, taking into account the content of physical sand. In Latvia, soil texture groups are divided based on the soil classification system developed by Katcinskis [4], and consequently the grass mixtures included in the study were sown in well-cultivated light till loam with 21.5% and sandy loam with 16.7 % proportion of physical clay (<0.01 mm) *Luvisol* soil.

The experimental site was set up at the Priekuli Research Centre of the Institute of Agricultural Resources and Economics, in the crop rotation of agrotechnical research. The aim of the study was to find out the effect of soil granulometric composition on the green biomass yield of perennial grass mixture (red clover/timothy) by cultivating it with the conventional methods.

The obtained data show that the mixtures of red clover cultivar 'Raunis' and timothy cultivar 'Jumis' sown in light till loam soil are potentially more productive than in loamy soils, providing in average 12 t ha⁻¹ dry matter.

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References :

- [1] Abberton M., Conant, R. & Batello C. (2009) *Grassland carbon sequestration: management, policy and economics*. Proceedings of the Workshop on the role of grassland carbon sequestration in the mitigation of climate change. Rome.
- [2] Capstaff N.M. & Miller A.J. (2018) Improving the yield and Nutritional Quality of Forage Crops. *Front. Plant Sci.*, **9**, 1-18.
- [3] Kasparinskis R., Nikodemus O. (2017) International WRB Soil Classification Field Workshop in Latvia and Estonia. Guidebook. July 22-27, 2017.
- [4] Kārklīš A. Organiskās augsnes SEG emisiju kontekstā (2016) Līdzsvarota lauksaimniecība. Zinātniski praktiskās konferences raksti. Jelgava, 2017. 40-44.



Do Soluble Organic Acids Bind to Basal Mica Surfaces?

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Soluble organic acids are constantly supplied to soils as a result of the oxidative decomposition of organic matter by the plant roots and microorganisms. These carboxylic group-bearing organic molecules can interact with soil clay minerals and affect the formation and stability of organomineral aggregates. While it has been suggested that –COOH laden organics can strongly bind to broken clay edges, less is known about how such soluble acids interact with negatively charged basal clay surfaces.

This work presents a Surface Forces Apparatus (SFA) study of interactions between two mica surfaces in dicarboxylic acid molecules with 2 to 7 carbon atoms. SFA allows measuring nanoscale surface forces acting between macroscopic surfaces as a function of surface separation. Since, unlike as in atomic force microscopy, the absolute surface separation in the SFA is known, it is possible simultaneously probe the adsorption of dicarboxylic acids onto mica.

The results show that significant amounts of dicarboxylic acids can adsorb on mica surfaces, but only in the presence of Ca²⁺ ions. Ca²⁺ acts as cationic bridges between the negatively charged mica surface and deprotonated –COO[–] functionalities. In addition, the multilayer binding of larger dicarboxylic acids (C5-C7) *via* an assembly of hydrophobic chains is resolved. Na⁺ does not promote any substantial dicarboxylic acid adsorption and induce strong repulsion between mica surfaces. In summary, although these face-specific SFA measurements show that dicarboxylic acids adsorb onto mica basal surfaces only by weak forces including electrostatic, hydrophobic, and likely hydrogen bonding, they demonstrate that even such weak outer-sphere adsorption can affect adhesion between clay surfaces and play a role in the organomineral aggregate formation.

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Alkaline Activation of Illite Clay

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Alkaline treatment of clay minerals has been widely studied topic over the past decades due to their potential of forming geopolymers (an alternative to the Portland cement with lower environmental impact and higher durability) and zeolites (microporous materials used as sorbents and catalysts). Most of the research in this area is focused on 1:1 clay minerals, such as kaolinite. While studies suggest that illite does have capacity to react and form alkali aluminosilicates, the required conditions for this process are still not clear. Alkaline treatment with Ca, Na and K hydroxides and following curing at the low temperatures for extended period of time is a common method for producing geopolymers from kaolinite. Due to the structural differences producing geopolymers and zeolite from illite requires more intense treatment process, such as using high concentration hydroxides and curing at elevated temperatures [1]. Combination of methods, such as alkaline-hydrothermal, can be more effective approach for obtaining zeolites [2].

This study investigates the structural changes of illite and possibility of obtaining geopolymer and zeolite from illite clay by alkaline and alkaline-hydrothermal activation.

The raw material used in this study was fractioned illite clay from Kuprava pit (Latvia). Chemical treatment was done on illite calcined at 500-600°C using NaOH solutions with concentration of 1M, 2M and 3M, followed by the curing process at 20-150°C, alkaline-hydrothermal method at 180°C for 24-72 h was also tried. The specimens of the obtained material were analysed with XRD, DTA, FTIR and SEM.

References:

- [1] Khalifa Ahmed Z, et. al. (2020) Advances in Alkali-activation of Clay Minerals. *Cement and Concrete Research*, 132.
- [2] Buut B., Cyclone D. & Wipes N. (2006) Modification of a montmorillonite–illite clay using alkaline hydrothermal treatment and its application for the removal of aqueous Cs⁺ ions. *Journal of Colloid and Interface Science*, 295, 303-309.

Synthesis, Characterization, and Magnetic Properties of MAI₄(OH)₁₂SO₄·3H₂O with M = Co²⁺, Ni²⁺ and Cu²⁺ : Novel Class of 1D Spin Chains

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Layered double hydroxides (LDH) are finding their way into widespread applications as catalyst and energy materials, due to their versatile chemistry. But they also exhibit various magnetic properties one of these being low-dimensional spin systems (1D and 2D), which are of great interest due to their pronounced quantum behaviour. 1D spin chains may potentially exist in the so-called MAI₄-LDH with the general formula [M²⁺Al₄(OH)₁₂A_{2/x}^{x-}·3H₂O] based on their crystal structure (Fig. 1a) [1, 2]. The MAI₄-LDH are obtained by insertion of divalent cations into half of the vacant sites in aluminium hydroxide, Al(OH)₃, and several different M²⁺ ions can be incorporated, albeit synthesis of pure MAI₄-LDH is challenging [1, 2]. After the extensive synthesis optimization, we have successfully obtained isostructural MAI₄-LDH with M²⁺ = Co²⁺ (d⁷, S=3/2), Ni²⁺ (d⁸, S=1), and Cu²⁺ (d⁹, S=1/2), and A_{2/x}^{x-} = SO₄²⁻. The product purities were assessed in detail by multiple techniques: PXRD, ICP-OES, TGA, STEM, and ²⁷Al MAS NMR. Moreover, the isostructural MAI₄-LDH allow for studies on how the choice of magnetic ion (electron spin, S) affects the magnetic properties. Thus, the hyperfine shifted δ_{iso}(²⁷Al) of the MAI₄-LDH shows the local magnetic order and give hints to the low-temperature magnetic order. This is due to the δ(²⁷Al)-ranges, which are 5 to -130 ppm for Co²⁺ (S=3/2), -240 to -580 ppm for Ni²⁺ (S=1), and -70 to -300 ppm for Cu²⁺ (S=1/2), i.e., Co²⁺ has the largest number of unpaired electrons but the lowest hyperfine shift in δ(²⁷Al), hinting towards a local antiferromagnetic coupling. In contrast, the Ni²⁺ and Cu²⁺ exhibit stronger magnetic interactions despite fewer unpaired electrons, hinting towards local ferromagnetic couplings. These observations are confirmed by studying C_p and χ from the room temperature down to a few Kelvin.

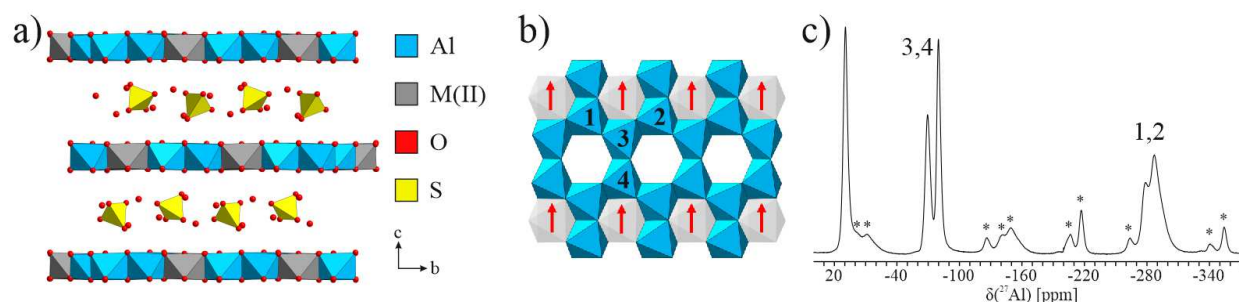


Figure 1: a) Crystal structure of MAI₄-LDH, b) 1D-spin chains, c) ²⁷Al MAS NMR of CuAl₄-LDH, spinning sidebands marked with *.

[1] E. Sokolova *et al* (2005). *Can. Mineral.* **43**, 1511-1519.

[2] N. D. Jensen *et al* (2019). *Inorg. Chem.* **58**, 6114-6122.



Composites of Clay Minerals and Natural Pigments: Their Synthesis, Characterization and Potential in Biocosmetics

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Anthocyanins are water-soluble natural pigments that colour the flowers, fruits, leaves and seeds of vascular plants. Anthocyanins are mainly responsible for the pink, red, blue, and purple colours, which change under different pH due to a shift in their molecular structure from a quinoidal base to a flavylium cation. Another significant property of anthocyanins is antioxidant activity, which plays a vital role in the protection against many health conditions, such as cardiovascular diseases, cancer, diabetes and other degenerative disorders. However, anthocyanins have a significant limitation – they are unstable under several conditions, such as pH and temperature changes and light irradiation [1, 2]. Clay minerals can be used to stabilize anthocyanins and prevent them from degradation, thus expanding the range of applications in industries, such as biocosmetics, food, and biomedicine [3, 4].

The research focuses on the application of anthocyanin-based composites in biocosmetics. They are used in a hair dye both serving as a nontoxic alternative to the synthetic hair dyes and being beneficial to the hair structure [5, 6]. It is aimed at intercalating anthocyanins into montmorillonite in order to enhance their stabilization and evaluate the physicochemical properties for the biocosmetic application. In this research, montmorillonite modified with anthocyanins extracted from black chokeberries (*Aronia melanocarpa* L.) and grape (*Vitis vinifera*) press residues were chosen. The sorption of anthocyanins was studied depending on the concentration of sorbate and sorbent, pH of the environment, contact time and temperature. The properties of the obtained composite materials were characterized using methods of Fourier transformation infrared spectroscopy (FTIR) and thermogravimetric analysis (TGA). Further dyeing experiments were carried out with the most promising composite material by using different approaches. The characterization methods confirmed the successful sorption of black chokeberry and grape anthocyanins in the clay mineral structure. The highest sorption capacity was achieved using black chokeberry anthocyanins at pH range from 1 to 4, sorbent mass 0.05 g and temperature 2°C. It was found that intense blue- and pink-coloured dyes with high colour strength on hair was achieved with anthocyanin extract, which was stable after several times of hair washing.

This is a growing research area with a particular interest in the analysis of plant-based health-related compounds. Further studies and use of the existing knowledge base on the montmorillonite-anthocyanin composites will open up new possibilities for application of the natural resources available in Latvia in the fields of new technologies.

References:

- [1] Ananga, A. Georgiev, V & Tsoleva, V. (2014) Recent Advances and Uses of Grape Flavonoids as Nutraceuticals. *Nutrients*. 391–415.
- [2] Glover, B.J. & Martin, C. (2012) Anthocyanins. *Current Biology*. 22(5), 147-150.
- [3] Ovando, A. et al., (2009) Chemical studies of anthocyanins: A review. *Food chemistry*, 113(4), pp.859–871.
- [4] Ribeiro, H.L., de Oliveira, A.V., de Brito, E.S., Ribeiro, P.R.V., Souza Filho, M.M. & Azeredo, H.M.C. (2018) Stabilizing effect of montmorillonite on acerola juice anthocyanins. *Food Chemistry*, 245, 966-973.
- [5] Rose P., Benohoud M., Blackburn R. S., Cantrill V., Rayner C. M. & Tidder A. (2018) Application of anthocyanins from blackcurrant (*Ribes nigrum* L.) fruit waste as renewable hair dyes. *Journal of Agricultural and Food Chemistry*, 66 (26), 6790–6798.
- [6] Silva, P., Ferreira, S. & Nunes, F.M. (2017) Elderberry (*Sambucus nigra* L.) by-products a source of anthocyanins and antioxidant polyphenols. *Industrial Crops and Products*. 95, 227-234.



Removal of Co (II) from Aqueous Solution Using Organically Functionalized Silica Gel

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In this study, the removal of Co (II) from aqueous solution[1] was investigated using silica gel which is functionalized with different organic acids: SA (Sulfamic acid), NTMP (Nitrilotrimethylphosphonic acid), HEDTA (N-[2-(bis(carboxymethyl)amino)ethyl]-N-(2-hydroxyethyl)-Glycine), and EDTMPA (Ethylenediaminetetra (Methylene phosphonic acid)). Silica gel[2] was functionalized with organic acids without template and its adsorption capacities were compared. The maximum Co (II) uptake by EDTMPA modified silica gel was ($q_e = 4.98$ mg/g). The adsorption capacity of silica gel functionalized with EDTMPA in the presence of template (n-dodecylamine) was compared to sample without template. The template sample (MSAWTL) showed higher adsorption capacity ($q_e = 5.99$ mg/g). The functionalized adsorbents were characterized using FT-IR and SEM/EDS analysis. Batch mode was used for adsorption studies. The optimum condition for the removal of Co (II) was achieved at maximum concentration of 60ppm at pH 7 for 1-hour contact time.

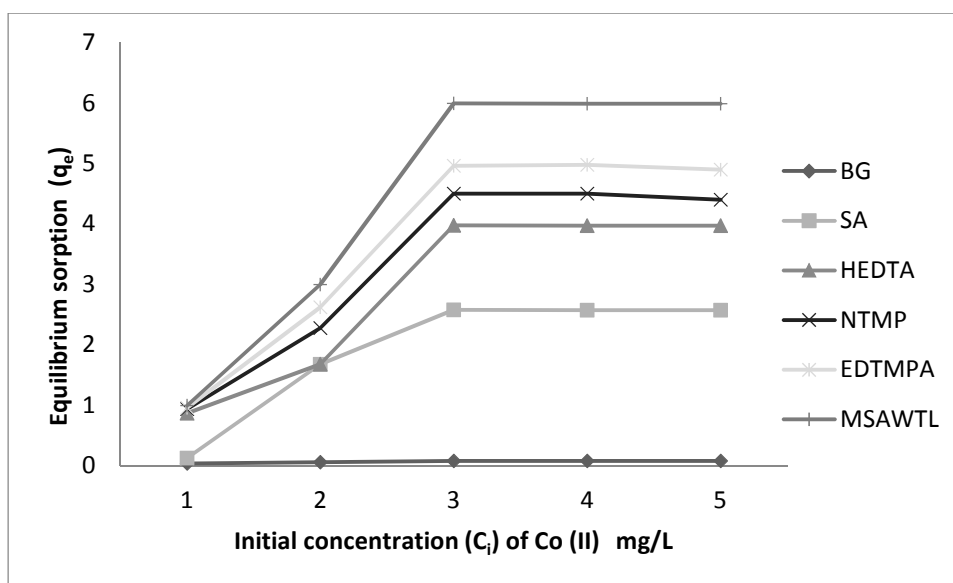


Figure 1. Adsorption Isotherm (BG : Blank gel is a non functionalized without template gel)

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References :

- [1] B. Samiey, C. Cheng, and J. Wu, "Organic-Inorganic Hybrid Polymers as Adsorbents for Removal of Heavy Metal Ions from Solutions: A Review," pp. 673–726, 2014, doi: 10.3390/ma7020673.
- [2] S. E. Pepper *et al.*, "Cobalt and nickel uptake by silica-based extractants," *Sep. Sci. Technol.*, vol. 53, no. 10, pp. 1552–1562, 2018, doi: 10.1080/01496395.2017.1405034.



Mineralogical Discrimination between Authentic and Recent Imitations of Pottery Manufacture in Zlakusa, Serbia

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The traditional coiling and hand-wheel manufacture of pottery with raw clay from the local source are characteristic for Zlakusa (western Serbia), which is on the UNESCO Representative List of the Intangible Cultural Heritage of Humanity. Mass production of utilitarian ceramics and pottery items occurred in the Neolithic, mid 7th millennium BC, in the area of current territory of Serbia. What makes it a unique phenomenon, in technological terms, is the fact that with the discovery of new techniques and production processes, the old ways, already adopted and mastered continued to live and actively coexist until today. This also brings a rise in imitations of pottery manufacture.

The village of Zlakusa lacks proper materials, thus the raw clay originates from the nearby village of Dobrodo [1]. All the investigated pots were made from clay body prepared with raw clay mixed with crushed calcite in the ratio of 50:50 [2]. As previously reported [1], the raw clay consists mainly of smectite, kaolinite/halloysite and illite minerals with quartz, feldspars and smaller amounts of goethite present as non-clay minerals. A total of three vessels were analysed, broken down by type of workmanship: coiling technique (traditional handmade clay pot made by coiling on a hand-turned wheel) marked -1-; wheel throwing (on a wheel with an electric drive) marked as -4- and by moulding (application of a mould) marked as -5-.

Close examination of surface features and morphology was conducted to determine the characteristic attributes for a specific technique. Phase and mineral composition, texture, and structure of the samples were analysed by microscopy of cross-section preparations perpendicular to the vessel walls (Leitz polarization microscope). The numerical colour specification was calculated according to CIE (1931) based on diffuse reflectance spectra recorded on a CCS200 spectrophotometer (Thorlabs) in the 380 - 1000 nm range. A standard method was used to determine the water absorption of the investigated shreds of pottery (SRPS ISO 10545-3) reduced to the same dimensions.

Based on the obtained results of tested samples of clay pottery, there are a couple of conclusions. Observed difference in the surface colour, the appearance of bumps and bulges, horizontal lines or their absence, smooth surface and the presence of irregularities are the main indicators for assessing differences in the production of vessels. The maximum temperature, heating mode and oxidation atmosphere in the ovens were not the same for all samples. In that aspect sample - 1 -, which has been burned traditionally (wood-fired oven), stands out. A microscopic examination of the thin sections revealed a uniform mineral composition and porosity. For sample -5- a specific fluid-structure is consistent with the way it was introduced by the application of a mould. The measurements of moisture absorption showed that in this respect there was no significant difference between the samples, which would indicate the manufacturing procedure. Sample -1- has slightly higher water absorption than the rest of the samples.

Differences in terms of manufacture processes and their characteristics are evident and should be emphasized for better understanding and awareness of the cultural heritage that is traditional hand clay pottery making in Zlakusa, Serbia.

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References :

- [1] Milošević M., Dabić P., Kovač S., Kaluderović L. & Logar M. (2019) Mineralogical study of clays from Dobrodo, Serbia, for use in ceramics, *Clay Minerals*, 1-9. doi:10.1180/clm.2019.49
- [2] Milošević M., Logar M. & Djordjević B. (2020) Mineralogical analysis of a clay body from Zlakusa, Serbia, used in the manufacture of traditional pottery. *Clay Minerals*, 55, 142–149



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