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COUPLING NON-LINEAR OPTICAL SPECTROSCOPY AND SURFACE CHEMISTRY FOR NEW INSIGHTS IN ATMOSPHERIC CHEMISTRY AND AEROSOLS

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For decades, the observation of atmospheric processes in general and ice nucleation in particular has covered the scales from macroscopic to microscopic levels. The available experimental investigations delivered a wide variety of results in cloud microphysics, particularly concerning the ice nucleation ability of atmospheric aerosol particles [1]. The surface of an ice-nucleating particles (INPs) and their specific properties play a major role in its ice nucleation ability. While a broad range of scales is covered, the role is not as well explored in terms of water/INP-surface molecular-level interactions. For example, it was found very recently that surface-charge induced templating hampers ice nucleation [2]. Aging of an INP in a cloud may change its surface properties and hence its ice nucleation efficiency. To improve the molecular-level understanding of heterogeneous ice nucleation, we combine chemical and optical surface techniques to probe the change in surface properties of an INP and the corresponding water structuring on it, respectively. The contribution will address the different scenarios after aging of an INP in a cloud and the impact on its ice nucleation ability.

[1] Hoose C., Mohler O. (2012). Heterogeneous ice nucleation on atmospheric aerosols: a review of results from laboratory experiments. Atmospheric Chemistry and Physics, 12(20) 9817-9854.
[2] Abdelmonem A., et al. (2017). Surface charge-induced orientation of interfacial water suppresses heterogeneous ice nucleation on α-alumina (0001). Angewandte Chemie (submitted).

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SYNTHESIS OF MAGNETIC PARTICLES WITH ND-PR BY LEACHING AND SEPARATE PURIFICATION FROM MONAZITE

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RE-Fe-B magnets (where RE is a rare earth element, Nd and Pr) are playing an essential role in various applications such as hybrid electric vehicles, hard disk drives, motors, generators, magnetic sensors. Nd and Pr based magnets are nearly identical over their intrinsic properties. Moreover the markets are growing rapidly as their magnetic properties and cost-effectiveness are improved. Many kinds of methods have been tried to fabricate RE-Fe-B magnets. For example, powder metallurgy, rapid quenching, bulk alloys by casting and melt-spinning. These methods require high purity of rare earth element as raw material, high manufacturing costs and energy consumption. In this work, we present reduction-diffusion (R-D) process for the synthesis of magnetic particles using leached product with Nd and Pr from monazite. $NdCl_3$•$6H_2O$, $PrCl_3$•xH_2O in liquid and (Nd-Pr) oxalate powders from monazite were used respectively. The precursors from separate purification liquid with $NdCl_3$•$6H_2O$, $PrCl_3$•xH_2O could be obtained by spray drying with various sizes from 2 to 10 μm by controlling concentrations of the solutions. The average size of 2 μm of precursors was selected for further steps. After heat treatment of both precursors mentioned above in air, Nd and Fe oxides were formed, followed by reduction processes in hydrogen atmosphere. Then, R-D was performed with Ca as reducing agent and diffusion between Nd and Fe occurred during Ca reduction. In order to remove CaO and residual Ca, the particles after R-D were washed with de-ionized water and ball milling was done in ethanol. Finally, high purity of $Nd_2Fe_{14}B$ magnetic particles were obtained after washing and their magnetic properties were examined by vibrating sample magnetometer (VSM).

[1] Pal A., Gabay A., Hadjipanayis G.C. (2012). Mechanochemical synthesis of NdFeB alloy with high coercivity. Journal of Alloys and Compounds, 31-33.
[2] Lin J.H, Liu S.F., Cheng Q.M., Qian X.L., Yang L.Q., Su M.Z. (1997). Preparation of Nd-Fe-B based magnetic materials by soft chemistry and reduction-diffusion process. Journal of Alloys and Compounds, 237-241.
[3] Kumari A., Panda R., Jha M.K., Lee J.Y., Rajesh Kumar J., Kumar V. (2015). Thermal treatment for the separation of phosphate and recovery of rare earth metals (REMs) from Korean monazite. Journal of Industrial and Engineering Chemistry, 696-703
[4] Chen C., Kim D., Choi C. (2014). Influence of Ca amount on the synthesis of $Nd_2Fe_{14}B$ particles in reduction-diffusion process. Journal of Magnetism and Magnetic Materials, 180-183.
[5] Zhu Y., Volkov V. (2001). Magnetic structure and magnetic imaging of $RE_2FE_{14}B$(RE=Nd, Pr) permanent magnets. Experimental Methods in the Physical Sciences, 227-269.

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FAST LITHIUM ION CONDUCTION OF $LI_{7-3X}FE_{X}LA_{3}ZR_{2}O_{12}$ WITH GARNET STRUCTURE

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The rise of new technologies leads to an increased demand for safe high-performance energy storage devices. The application of solid electrolytes is one approach to realize such novel battery concepts. Li-stuffed oxide garnets such as $Li_7La_3Zr_2O_{12}$ (LLZO) are among the most promising materials to be used as solid state Li^+ electrolytes. Besides its high lithium ion conductivity, LLZO also shows electrochemical inertness over a wide potential window. Another advantage of LLZO is its stability against lithium metal. Thus, LLZO is particularly suited to be used as solid lithium electrolyte [1,2].

Pure LLZO shows a tetragonal crystal structure with space group $I4_1/acd$ (no. 142). Around 650 °C, the material undergoes a phase transition to the cubic garnet-type modification with space group $Ia\bar{3}\bar{3}d$ (no. 230) [3]. Compared to conventional garnets with general formula $A_3B_2C_3O_{12}$, Li^+ does not only occupy the tetrahedrally coordinated C-site (24*d*), but also additional sites, resulting in a three-dimensional network of partially occupied lithium sites which forms a diffusion pathway [2,4].

For application as solid-state electrolyte, the cubic modification is preferred, as it shows a higher lithium ion conductivity compared to the tetragonal modification. A stabilization of the cubic garnet-type modification at room temperature can be achieved by the introduction of supervalent cations. These supervalent cations cause the formation of lithium vacancies, which lead to a disorder in the lithium ion distribution; resulting in a higher symmetry. It was shown that the substitution $3\ Li^+ \rightarrow Ga^{3+} + 2\ \square_{Li}$ leads to the formation of another structural modification, showing the acentric cubic space group $I\bar{4}\bar{4}3d$ (no. 220) [5]. The reduction in symmetry, compared to the common garnet structure, is caused by the site preference of Ga^{3+}. This garnet-similar LLZO modification shows superior properties compared to the garnet-type modification with space group $Ia\bar{3}\bar{3}d$ [5,6].

A recent study showed that the introduction of Fe^{3+} as substituent also causes the formation of the acentric garnet-similar $I\bar{4}\bar{4}3d$ modification [7]. The crystal structure of Fe^{3+}-substituted LLZO has been characterized by powder and single crystal X-ray diffraction as well as by powder neutron diffraction. In addition, ^{57}Fe Mößbauer spectroscopy has been applied to study the distribution of Fe^{3+} over different crystallographic sites. Electrochemical impedance spectroscopy of Fe^{3+}-substituted LLZO showed a lithium ion conductivity of up to 1.38×10^{-3} S cm^{-1} at room temperature, which among the highest values ever reported for lithium-stuffed oxide garnets.

[1] Murugan R., Thangadurai V., Weppner W. (2007). Fast lithium ion conduction in garnet-type $Li_7La_3Zr_2O_{12}$. *Angew Chem Int Edit*, 46, 7778-7781.

[2] Thangadurai V., Pinzaru D., Narayanan S., Baral A.K. (2015). Fast Solid-State Li Ion Conducting Garnet-Type Structure Metal Oxides for Energy Storage. *J. Phys. Chem. Lett.* 6, 292−299.

[3] Matsui M., Takahashi K., Sakamoto K., Hirano A., Takeda Y., Yamamoto O., Imanishi N. (2014). Phase stability of a garnet-type lithium ion conductor $Li_7La_3Zr_2O_{12}$. *Dalton T*, 43, 1019-1024.

[4] Awaka J., Takashima A., Kataoka K., Kijima N., Idemoto Y., Akimoto J. (2011). Crystal Structure of Fast Lithium-ion-conducting Cubic $Li_7La_3Zr_2O_{12}$. *Chem Lett*, 40, 60-62.

[5] Wagner R., Redhammer G.J., Rettenwander D., Senyshyn A., Schmid W., Wilkening M., Amthauer G. (2016). Crystal Structure of Garnet-Related Li-Ion Conductor $Li_{7-3x}Ga_xLa_3Zr_2O_{12}$: Fast Li-Ion Conduction Caused by a Different Cubic Modification? Chem Mater, 28, 1861-1871.

[6] Rettenwander D., Redhammer G., Preishuber-Pflügl F., Cheng L., Miara L., Wagner R., Welzl A., Suard E., Doeff M.M., Wilkening M., Fleig J., Amthauer G. (2016). Structural and Electrochemical Consequences of Al and Ga Cosubstitution in $Li_7La_3Zr_2O_{12}$ Solid Electrolytes. Chem Mater, 28, 2384-2392.

[7] Wagner R., Redhammer G.J., Rettenwander D., Tippelt G., Welzl A., Taibl S., Fleig J., Franz A., Lottermoser W., Amthauer G. (2016). Fast Li-Ion-Conducting Garnet-Related $Li_{7-3x}Fe_xLa_3Zr_2O_{12}$ with Uncommon $I\bar{4}3d$ Structure. Chem Mater, 28, 5943-5951.

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MAGNETITE SYNTHETIZED UNDER ANOXIC CONDITIONS: IMPLICATION IN ARSENIC REMOVAL FROM WATER

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Removal of heavy metal contamination from natural waters is of considerable concern due to the harmful effects of these pollutants on the environment/health. Arsenic is classified as one of the most toxic and carcinogenic chemical elements even at low concentration. Adsorption by means of synthetic magnetite is a reliable alternative to remove this pollutant from water, because the chemical stability and non-toxicity of this iron oxide as well as the flexibility and low cost of the process. The aim of the present contribution deals with the characterization of the performance of using magnetite as an As-sorbent from aqueous solutions. The synthesis of a suite of Fe_3O_4 samples were successfully carried out by chemical precipitation at 80 °C from a Fe(II) sulphate heptahydrated solution, adding, at different flow rates, variable volumes of an oxygen-free solution containing KOH and KNO_3. Several magnetite samples were analysed through X-ray powder diffraction and tested for their adsorption capacity toward arsenic (V) removal from model aqueous solutions at known initial arsenate concentrations. The adsorption efficiency was calculated from Freundlich adsorption isotherm. XRD results indicated that nanoparticle diameter was controlled by hydroxide concentration and, therefore, by final pH. A reliable correlation has been found between crystal sizes, synthesis conditions and adsorption isotherms.

[1] C. Su (2017). Environmental implications and applications of engineered nanoscale magnetite and its hybrid nanocomposites: A review of recent literature, *J. Hazard. Mat.*, 322, 48–84.

[2] C.-H. Liu, Y.-H. Chuang, T.-Y. Chen, Y. Tian, H. Li, M.-K. Wang, W. Zhang (2015). Mechanism of Arsenic Adsorption on Magnetite Nanoparticles from Water: Thermodynamic and Spectroscopic Studies, *Environ. Sci. Technol.*, 49, 7726−7734.

[3] S.R. Chowdhury, E.K. Yanful (2011). Arsenic removal from aqueous solutions by adsorption on magnetite nanoparticles, Water Environ. J., 25, 429–437.

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TAILS OF ZHEZKAZGAN COPPER SANDSTONE DEPOSIT IS THE SOURCE FOR REPLENISHMENT OF THE RAW MATERIAL BASE

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Zhezkazgan deposit of copper sandstones is located in Central Kazakhstan, 25 km northeastwest of Zhezkazgan city and has been known since ancient times. A huge contribution to the study of Zhezkazgan made academician K.I. Satpayev. The deposit is unique and has no equal among the deposits of this type by the number of mineralized horizons and multi-component material composition of ores. Zhezkazgan is exploited for 100 years. During the whole period of operation from earth interiors was extracted more than 1 billion tonnes of commercial ore. Today's strategic project - a replenishment of the raw material base of Zhezkazgan region, rich deposits are practically worked out. Replenishment is possible due to the involvement in the production of off-balance copper sulphide ores, refractory oxide and mixed copper ores and copper-bearing of refuse ore of the mill tailings (Zhezkazgan enrichment factories 1 and 2). There are new effective reagents that enable to concentrate the thin minerals.

The study results of the tails showed that copper minerals mostly are found in dimensions of 0.01-0.05 mm, and rarely up to 0.07 mm and more. Chalcopyrite among copper minerals is the most widespread, bornite, chalcocite, covellite are in subordinate amounts. Copper minerals in the free form are rare. They are all in the grains of quartz or feldspar separately and in intergrowths together. They are located in the center of the grains, along the edges of and around the grains. This requires the technology extraction for thin copper minerals which are in the grains of quartz and feldspar.

Keywords: technogenic deposit, tails, copper minerals.

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KOKKIYA DEPOSIT IS THE NEW GOLD-METASOMATIC TYPE IN KAZAKHSTAN

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Kokkiya deposit is located at northern slopes of the Kyrgyz Mountain range, in the eponymous Kokkiya ore cluster of Karakystak ore region which belongs to the Republic of Kazakhstan.

The gold-quartz-propylitic formation is the main in the Kokkiya ore cluster. It is closely related to the Devonian volcanic edifice. Volcan-plutonic activity in the ore cluster area is controlled by faults of northwestern and northeastern directions. Along the northeastern zone fixed shear zone with quartz-sericite metasomatites which include Kokkiya deposit. The distribution of gold mineralization in the field is extremely complex. The ore bodies within the externally monotonous zone of quartz-sericite metasomatic rocks are distinguished only by the analyzes data. There are 24 ore bodies at the deposit, which mainly occur in quartz-sericite metasomatites. The ore bodies are characterized by a lack of available geological boundaries, complex morphology caused by variability along strike (60-300 m) and thickness (up to 15-20 m). The ore body 1 among them is the richest and associated with sericite quartzites. Micro-veinlet silicification, carbonization and chloritization superimposed on the sericite quartzites. The main ore mineral is pyrite (up to 10-15 %), mainly pentagon dodecahedral shape, represented in the form of scattered disseminations in metasomatite and more coarse-grained in intergrowths and small aggregates are usually strongly corroded and contains rare minerals of tellurium and bismuth. Other minerals - chalcopyrite, galena, sphalerite, fahlerz, pyrrhotite, magnetite, hematite, covellite, cassiterite, molybdenite and minerals of tellurium and bismuth are rare.

Gold is found: 1) in grains of pentagon dodecahedral pyrite in micron size; 2) free gold in sericite and quartz (second decimal places of micron); 3) in the composition of the tellurides of gold and silver; 4) in the late of galena; 5) in the iron hydroxides. Tellurides and bismuth minerals are closely associated with pyrite. They are intergrowths with pyrite or enclosed therein and serve as a positive indicator of gold.

Keywords: gold, pyrite, metasomatites, quartz, sericite.

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FAST AND SCALABLE ROUTE FOR TETRAHEDRITE PELLET PRODUCTION FOR THERMOELECTRIC APPLICATIONS

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The interest in thermoelectric materials raised in the recent years due to the possibility to design thermoelectric generators (TEGs), reliable solid-state devices for waste heat recovery valuable in particular contexts where the employment of other technologies results inconvenient. Nowadays, the challenge in the thermoelectric field seems to be the identification of efficient thermoelectric materials which should be also inexpensive, easy to synthesize, and comprised of earth-abundant elements.

On this basis, tetrahedrite mineral family ($Cu_{12-x}Tr_xSb_4S_{13}$ where, for instance, Tr could be Mn, Fe, Co, Ni, or Zn), one of the most widespread sulfosalts on Earth's crust, seems to meet the right features for an attractive sustainable p-Type Pb-free thermoelectric material showing relatively high conversion efficiency [1,2]. The sulphide precursor powders were ball milled and then one-step simultaneous synthesis and sintering process was performed by open die pressing (ODP) [3]. By this simple, fast, and easy scalable route, thermoelectric pellets with a whole process lasting less than 6 hours. Both Zn and Ni cations were added as partial substituents of Cu in $Cu_{12}Sb_4S_{13}$ permitting to considerably improve the thermoelectric performances of the undoped material prepared by ODP. The influence of precursor ratio on the tetrahedrite phase, secondary phase content and stoichiometry were investigated by X-ray diffraction, scanning electron microscopy and energy dispersive X-ray spectroscopy. The density and mechanical stability of samples were evaluated as a function of the chemical composition and processing parameters. A complete thermoelectric characterization was carried out for samples with different Zn and Ni substitution up to 400 °C.

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[1] Lu X., Morelli D.T., Physical Chemistry Chemical Physics 15 (2013) 5762.
[2] Lu X., Morelli D.T., Xia Y., Ozolins V., Chemistry of Materials 27 (2015) 408.
[3] Ceresara S., Fanciulli C., Passaretti F., Vasilevskiy D., Journal of Electronic Materials 42 (2013) 1529.

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NEUTRON AND SYNCHROTRON CHARACTERIZATION OF BRØNSTED ACID SITES IN ZEOLITE L

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Acidic zeolites are widely used in the chemical and petroleum industries due to their catalytic activity, their remarkable reaction selectivity, and their excellent chemical and thermal stability [1]. The efficiency in catalyzing these reactions stems from their high acidity, which is mainly due to the presence of Brønsted sites. The aim of this work is to determine the number and location of Brønsted sites in zeolite L, a large pore material whose acidity influences the photo-physical behaviour of encapsulated dyes and can affect the properties of photonic antenna systems based on dye–zeolite host–guest materials [2].To achieve this goal a sample of a synthetic zeolite L (LTL) with a SiO_2/Al_2O_3 ratio (SAR) equal to 6.1 (500KOA, Tosoh Corporation; Na2O ~ 0.25 wt.%, K_2O content ~ 16.8 wt.%, BET 290 m2/g.) was exchanged in a 1M solution of ND_4Cl on D_2O for 192 h at 40 °C (ND4-LTL), washed with D_2O and dried overnight at 96 ºC, finally calcined at 550 ºC for 2 hours under a stream of air to obtain the acidic form (D-LTL). Powder patterns of LTL and D-LTL were collected at both the D2B (ILL, Grenoble), and ID22 Beam Lines, (ESRF, Grenoble) by combining neutron and synchrotron diffraction sources. Rietveld structure refinements revealed the presence of two Brønsted acid sites. The first was on framework oxygen O5, not far from the center of the 8-ring of the cancrinite cage. The other Brønsted site was on the framework oxygen O1, heading towards the center of the 12 MR channel. On the whole 7.6 hydroxyl groups were recognized, in very good agreement with which would be expected on the basis of the aluminum content.

The information gathered in this study are fundamental to elucidate the accessibility of Brønsted acidic sites to host molecules within the zeolite channels as well as to provide a complete understanding of the host-guest interactions which are crucial in catalytic reactions in zeolites, catalyzed by acid sites, where location and occupancy of Brønsted sites play a fundamental role.

[1] Corma A., (1995). Inorganic solid acids and their use in acid-catalyzed hydrocarbon reactions. Chemical. Rewiews, 559-614.
[2] Albuquerque R.Q., Calzaferri G. (2007). Proton activity inside the channels of zeolite L. Chemistry-A European. Journal, 8939-8952.

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ZEOLITE FROM CLAY MINERALS: A SINGULAR REVIEW OF SYNTHESIS METHODS THROUGH LABORATORY TRIALS AT A LOW INCUBATION TEMPERATURE

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Clays are phyllosilicate minerals with a crystalline structure characterized by simple tetrahedral and octahedral sheets firmly connected with two-, three- or four-sheet structural layers. The total negative charge of fundamental structural layers is balanced by cations trapped into the interlayer space. Zeolites are tectosilicates characterised by a three-dimensional network of tetrahedral units that form a system of interconnected pores. The aluminium ion produces a net negative charge, which is balanced by the presence of an extra cation in the framework. Although the crystalline structure of clays and zeolites is different, both classes of minerals are characterized by similarities such as the high cation exchange capacity (CEC) or cation selectivity.

Many literature data showed that zeolites can be synthesised using several clay minerals as raw materials [e.g 1-3]. This paper provides a singular review of methods for zeolite synthesis from clay minerals through laboratory trials at a low incubation temperature (40 °C). Ca- montmorillonite, Na-montmorillonite, illite and chlorite from Source Clay Repository of Clay Minerals Society were used as raw materials. These samples were acid- treated, calcined and NaOH pre-fused, in separate experiments. Zeolite synthesis was performed by means of: i) a conventional alkaline hydrothermal method and ii) a pre-fusion hydrothermal method. Both were also carried out with the addition of $Al(OH)_3$ to the hydrothermal solution.

The results confirm that a greater Si and Al availability, as a consequence of dissolution of silicate and aluminosilicate formed during the NaOH pre-fusion treatment, controls geopolymer formation as well as the crystallization of zeolite nuclei- directly involved in the geopolymer activation during the hydrothermal incubation. This effect is stronger using acid-treated samples because of the chemical raw material changes determined by HCl treatment. However, the data indicated that the crucial parameter for the zeolite synthesis is represented by aluminium addition since it has the most detectable effect on SiO_2/Al_2O_3 ratio of synthetic products.

[1] Belviso C., Giannossa L.G., Huertas F.J., Lettino A., Mangone A., Fiore S. (2015). Synthesis of zeolites at low temperatures in fly ash-kaolinite mixtures. Micropor. Mesopor. Mat. 212, 35-47.
[2] Belviso C., Cavalcante F., Lettino A., Fiore S. (2013). A and X type zeolite synthesized from kaolinite at low temperature. Appl. Clay Sci. 80, 162-168.
[3] Musyoka N.M., Missengue R., Kusisakana M., Petrik L.F. (2014). Conversion of South African clays into high quality zeolites. Appl. Clay Sci. 97-98,182-186.

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WHEN MATERIAL SCIENCE MEETS PLANETARY SCIENCE: THE DISCOVERY OF NATURAL QUASICRYSTALS

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Quasicrystals are solids whose diffraction patterns are composed of Bragg peaks, like periodic crystals, but with symmetries forbidden to crystals. Over the last thirty years, more than one hundred examples have been identified, but, until now, all have been produced in the laboratory under controlled conditions ranging from rapid to moderately slow. Nevertheless, one could not be sure of their long-term stability because they could not be kept in equilibrium at low temperatures or annealed over eons. An interesting test would have been to see if Nature beat us to the punch. If quasicrystals are on the same footing as crystals, then it would be conceivable that quasicrystals formed under natural conditions and simply have not been noticed until now. The search to answer this question, culminated with the discovery in 2009 of the first natural icosahedral quasicrystal [1,2] and in 2015 of the second quasicrystal with decagonal symmetry [3,4]. The search took more than a dozen years and has opened a new frontier in mineralogy that could lead to new discoveries in geoscience, astronomy, condensed matter physics, and materials engineering [5].

For the first time, minerals have been discovered that violate the symmetry restrictions of conventional crystallography. That nature could accomplish this without human intervention was unexpected, requiring the existence of petrological processes never considered previously. The fact that the quasicrystals were found in a meteorite formed in the earliest moments of the solar system means these processes have been active for over 4.5 billion years and influenced the mineral composition of the first objects to condense around the Sun [6-8]. Finding quasicrystals formed in these extreme environments informs the longstanding debate about the stability and robustness of quasicrystals among condensed matter physicists. Recent shock experiments [9], with starting materials similar to the exotic intermetallic alloys in the meteorite hosting the quasicrystals, lend support to the hypothesis that the extraterrestrial quasicrystals formed as a result of hypervelocity impacts among objects in the early Solar system. Finally, the discovery inspired further searches for quasicrystals and other new forms of matter not seen in the laboratory previously which may provide valuable new materials for physics and engineering. This culminated in the recent discovery of an icosahedral phase with a composition not predicted before in laboratory experiments [10].

[1] Bindi L., Steinhardt P.J., Yao N., Lu P. (2009). Natural quasicrystals. Science, 324, 1306-1309.
[2] Bindi L., Steinhardt P.J., Yao N., Lu P. (2011). Icosahedrite, $Al_{63}Cu_{24}Fe_{13}$, the first natural quasicrystal. American Mineralogist, 96, 928-931.
[3] Bindi L., Yao N., Lin C., Hollister L.S., Andronicos C.L., Distler V.V., Eddy M.P., Kostin A., Kryachko V., MacPherson G.J., Steinhardt W.M., Yudovskaya M., Steinhardt P.J. (2015). Natural quasicrystal with decagonal symmetry. Scientific Reports, 5, 9111; DOI:10.1038/srep09111.
[4] Bindi L., Yao N., Lin C., Hollister L.S., Andronicos C.L., Distler V.V., Eddy M.P., Kostin A., Kryachko V., MacPherson G.J., Steinhardt W.M., Yudovskaya M., Steinhardt P.J. (2015). Decagonite, $Al_{71}Ni_{24}Fe_5$, a quasicrystal with decagonal symmetry from the Khatyrka CV3 carbonaceous chondrite. American Mineralogist, 100, 2340-2343.
[5] Bindi L., Steinhardt P.J. (2015). Natural quasicrystals: A new frontier in mineralogy and its impact on our understanding of matter and the origin of the solar system. In "*Highlights in Mineralogical Crystallography*" (Armbruster T. & Danisi R.M., Eds.), De Gruyter, Berlin, Germany, pp. 109-125. (ISBN 978-3-11-041710-4).
[6] Bindi L., Eiler J.M, Guan Y., Hollister L.S., MacPherson G.J., Steinhardt P.J., Yao N. (2012). Evidence for the extra-terrestrial origin of a natural quasicrystal. PNAS, 109, 1396-1401.
[7] Hollister L.S., Bindi L., Yao N., Poirier G.R., Andronicos C.L., MacPherson G., Lin C., Distler V.V., Eddy M.P., Kostin A., Kryachko V., Steinhardt W.M., Yudovskaya M., Eiler J.M., Guan Y., Clarke J.J., Steinhardt P.J. (2014). Impact-induced shock and the formation of natural quasicrystals in the early Solar system. Nature Communications, 5, 4040, DOI: 10.1038/ncomms5040.
[8] MacPherson G.J., Andronicos C., Bindi L., Distler V.V., Eddy M., Eiler J., Guan Y., Hollister L.S., Kostin A., Kryachko V., Steinhardt W., Yudovskaya M., Steinhardt P.J. (2013). Khatyrka, a new CV3 find from the Koryak Mountains, Eastern Russia. Meteoritics and Planetary Sciences, 48, 1499-1514.
[9] Asimow P.D., Lin C., Bindi L., Ma C., Tschauner O., Hollister L.S., Steinhardt P.J. (2016). Shock synthesis of quasicrystals with implications for their origin in asteroid collisions. PNAS, 113, 7077-7081.
[10] Bindi L., Lin C., Ma C., Steinhardt P.J. (2016). Collisions in outer space produced an icosahedral phase in the Khatyrka meteorite never observed previously in the laboratory. Scientific Reports, 6, 38117.

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REMEDIATION OF SOILS CONTAMINATED BY COPPER MINING WASTE IN CHILE

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This research was born due to the need of a mining company to perform the remediation of soils belonging to arsenic deposits stabilized in one of its mines.

The methodology for the initial assessment of the bottom and slopes in a given waste storage cell (waste places) was applied according to USEPA recommendations [1], resulting in the 20 quadrants sampled, 6 of them were above the Values Remediation Objectives (VOR), these being 200 ppm for the case of As and 3500 ppm for the case of Pb. [2].

In these quadrants, an extraction of the soil was carried out until obtaining the Values Remediation Objectives of the As and the Pb in the bottom and the slopes.

The volumes of extracted soils were treated as contaminated and were final disposal to safety landfill complying with the current legislation in Chile [3,4,5], being retired a total of 1163 m3 with contents in As (up to 7000 ppm) and in Pb (up to 6000 ppm).

In conclusion, it can be established that the proposed standards for the remediation process of the studied cell were reached according to the methodology implemented of remediation.

In addition, according to the remediation measures taken, the currently soil in the cell studied doesn´t have any risk to human health according to the scenario of future use of the site (industrial with restricted access).

[1] Soil Screening Guidance; Technical Background”. Doc: USEPA, Publication 9355.1-17A, May 1996.
[2] Calculo de valores de remediación y Estudio de Factibilidad Técnico – Económico de Tecnologías de Remediación de Suelos en Arica, (CONAMA, Fundación Chile, 2010).
[3] Manual de Gestión de Riesgos Asociados a Sitios Contaminados CONAMA, MINSAL, SAG (Fundación Chile, 2003).
[4] Política nacional para la gestión de sitios contaminados (CONAMA 2009).
[5] Marco Regulatorio para la Remediación Ambiental en Chile (CONAMA, Arcadis US, 2006).

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CERAMIC BEHAVIOR OF COMMON, BAUXITIC AND PLASTIC CLAYS AND KAOLINS OF VI, VII AND XIII REGIONS OF CHILE

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In Chile, according to the National Geology and Mining Service, there are approximately 188 deposits of clays, of which 27 deposits (bauxite clays, common clays and kaolins) are found in the Metropolitan Region (XIII Region of Chile). In Region Libertador General Bernardo O'Higgins (VI Region) are located 25 clay deposits, kaolin, plastic clay and common clay [1], and in the Maule Region (VII Region) are located 16 deposits of clay (kaolin, common clay and plastic clay).

The large amount of rocks and industrial minerals that are exploited in Chile generates a great disinterest for the extraction and use of the abundant and varied deposits of clays located throughout the country. These have a very low exploitation compared to their volume of reserves because they are only used in ceramic and industrial applications for the domestic market [2].

The objective of the work is the study of the mineralogical, physical-chemical and ceramic behavior of clays in the Commune of Pirque (XIII Region), Commune of Malloa (VI Region) and in the Province of Cauquenes (VII Region).

Samples were taken from the outcrops studied taking into account the criteria and methodology established by Sanfeliu (1991) [3]. The chemical analysis was performed using X-ray Fluorescence (FRX) and loss of calcination (LOI). The mineralogical analysis was performed by X-ray diffraction (XRD). The diffractograms have been interpreted with the help of the computer application EVA of the firm Socabim and tabs JCPDS, until identifying the minerals present in each one of the samples. Plasticity (Pfeferkorn method), drying behavior (barelatography), water absorption (%), linear shrinkage (%)were determined from clayey ceramics [4,5].

Based on the results obtained it is concluded that the studied clays of the XIII Region can be used like structural ceramics, gres and semigres taking into account their chemical-mineralogical and technological properties. The outcrops studied in VI Region indicate the possibility of using the samples for ceramic tiles, and the VII Region samples can be used like a ceramic pavement and coating, as well as structural ceramics and semi-refractory bricks.

[1] Gajardo A. (2000). Rocas y minerales industriales de Chile. Servicio Nacional de geología y minería, Boletín, Nº 58, 181 p. Santiago.
[2] Pardo F. (2011). Mineralogía y comportamiento cerámico de arcillas en las Regiones IV, VI y VII de Chile. Tesis Doctoral. U. Jaume I.
[3] Sanfeliu T. (1991). Mineralogía de las arcillas terciarias cerámicas de Castellón, Col.lecció Universitaria, Diputación de Castellón.
[4] Jordán M.M., Boix A., Sanfeliu T., de la Fuente C. (1999). Firing transformations of cretaceous clays used in the manufacturing of ceramic tiles. Applied Clay Science, 14, 225–234.
[5] Meseguer S., Pardo F., Jordan M.M., Sanfeliu T., González I. (2011). Ceramic behaviour of five Chilean clays which can be used in the manufacture of ceramic tile bodies. Applied Clay Science, 47, 372-377.

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SILICA CHARACTERIZATION AND BENEFICIATION DESTINED FOR SILICON SOLAR GRADE PRODUCTION

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We study the Algerian silica from Tirek and AinBarda deposits as potential raw material intended to photovoltaic cells production.

The samples are examined with optical microscopy, cathodoluminescence, X-Ray fluorescence (XRF) and Raman spectroscopy. The microscopic investigations show the presence of solid inclusions such as rutile, zircon, micas, amphiboles, tourmaline and Fe-oxides in quartz. The XRF results show 96-97 wt.% SiO_2 and display the following average values of the main oxides: 1.83wt.% Fe_2O_3, 0.2 wt.% MgO, 0.43wt.% TiO_2, 0.35wt.% CaO, 0.38wt.% Al_2O_3,0.05 wt.% K_2O,0.13wt.% ZrO_2. Raman spectroscopy revealed the presence of aqueous fluid inclusions with CO_2; the aqueous phase can also be a source of contamination of quartz with Ca, Mg, Cl and K.

We employ acid leaching process to remove the mineral impurities from the quartz. As chemical reagent we use H_2SO_4 to increase the porosity of the raw material, and HF to dissolve the metal oxides and silicate minerals. Finally, we use the gravimetric separation to remove the residual impurities from the surface of quartz grains.

The acid leaching treatment and the gravimetric separation increase the content of SiO_2 up to 99.68%. This value is optimal to use the quartz from Tirek and AinBarda deposits as raw material to produce high purity solar grade silicon.

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2D-3D LIBERATION COMPARISONS IN HCT TESTWORK AND IMPLICATIONS FOR QUANTIFYING THE EFFECT OF STEREOLOGICAL BIAS

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The Hannukainen Iron-Oxide-Copper-Gold (IOCG) deposit is located in northern Finland approximately 25 km northeast of Kolari. The deposit consists of the Hannukainen deposit and its northern extension, the Kuervitikko deposit. Geochemical assessment of high sulfur potentially acid-forming waste rock has included kinetic humidity cell tests (HCTs) lasting >200 weeks. In order to understand the relative importance of textural controls on acid generation, pre-leach HCT material was split into several size fractions and analysed by 2D (Zeiss Mineralogic) and 3D (High-resolution X-Ray computed tomography) methods.

Assay results show that sulfide concentrations increase slightly into the fine size fractions and that both automated mineralogy and micro-CT detect that trend but with slight differences in quantification. In the finest size fractions the correlation between 2D and 3D grade estimations are close but as the size fractions go coarser there is a slight grade overestimation in 2D based work. Comparisons of area grade liberation between automated mineralogy and micro-CT show a similar trend with a close correlation in the finest size fraction but an over-estimation of liberation by 2D automated mineralogy in the coarser size fractions. The results have implications for quantifying the effect of stereological bias in 2D grade and liberation calculations.

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PHYSICAL PROPERTIES OF CUPROSTIBITE, A NATURAL INTERMETALLIC COMPOUND

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Cuprostibite [1] is a relatively rare mineral with chemical composition $Cu_2Sb(Tl)$. The natural aggregates show silver- gray to red-violet colour and metallic lustre. It crystalizes in the tetragonal space group *P*4/*nmm* (nr. 129) with lattice parameters a = 3.992-4.003 Å, c = 6.091-6.1058 Å and two formula units per unit cell [2-5]. From the composition, the compound may be considered as a mixed-valence one. The relatively simple crystal structure combining the features of intermetallic and inorganic substances attracted the attention since several decades (e.g. [4,6]). Calculated electronic density of states reveals the metal-like behaviour of the stoichiometric compound.

We report on the characterization of the chemical composition and physical properties of natural cuprostibite obtained from the mineral collection of the UTFSM. The lattice parameters of the cuprostibite as the majority phase were refined from the X-ray powder diffraction data ($CuK\alpha_1$ radiation, λ = 1.54056 Å): a = 3.9962(6) Å, c = 6.097(1) Å. Metallographic analysis was carried out on embedded sample with subsequently quantitative chemical analysis via wavelength dispersive x-ray spectroscopy (WDXS). Electrical and thermal conductivity, as well as magnetic susceptibility measurements were performed on a bar-shaped specimen.

[1] Sørensen H., Semenov E.I., Bezsmertnaya M.S., Khalezova E.B. (1969). Cuprostibite, a new natural compound of copper and antimony. Zapiski Vserossijskogo Mineralog. Obshch., 98, 716-724.
[2] Elander M., Hägg G., Westgren A. (1935). The Crystal Structure of Cu_2Sb and Fe_2As. Ark. Kemi Mineral. Geol. 12B, 1, 1-6.
[3] John W. Anthony, Richard A. Bideaux, Kenneth W. Bladh, Monte C. Nichols, Eds., Handbook of Mineralogy, Mineralogical Society of America, Chantilly, VA 20151-1110, USA. http://www.handbookofmineralogy.org/.
[4] Nuss J. Jansen M. (2002). Zur Abgrenzung der PbFCl- und Cu_2Sb-Strukturfamilien: Neubestimmung und Verfeinerung der Kristallstrukturen von CuMgSb, Cu_2Sb und CuMgAs. Z. Anorg. Allg. Chem. 628, 1152-1157.
[5] Kift R. L., Prior T.J. (2010). Reductive synthesis of metal antimonides. J. Alloys Compd. 505, 428-433.
[6] Pearson, W.B. (1985). The Cu_2Sb and related structures. Z. Kristallogr., 171, 23-39.

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THE MINERAL TENNANTITE, A MATERIAL FOR THERMOELECTRIC APPLICATIONS

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The mineral tennantite with chemical formula $Cu_{10}(Zn,Fe)_2As_4S_{13}$ belongs to the tetrahedrite-group. Natural aggregate pieces shows gray-black colour and metallic lustre. It crystalizes cubic in the space group I-43m (nr. 217), with lattice parameters $a = 10.19$ Å and two formula units per unit cell [1].

Tetrahedrite self is an Antimony based mineral and, due to its natural abundance, has attracted special attention for thermoelectric applications [2]. Tennantite shows similar electronic conditions as tetrahedrite, as can be observed in the calculated electronic density of states. Consequently it has also been considered as potential thermoelectric material. In this sense, the thermoelectric properties of mineral samples of tetrahedrite-tennantite (minerals containing different Sb/As ratios) of different origin have been studied [3].

We present the chemical characterization of a tennantite mineral representative of Copiapo-Chile and its thermoelectric properties, based on measurements of electrical resistivity, thermal conductivity and Seebeck coefficient.

[1] www.mindat.org
[2] Chetty R., Bali A., Mallik R.C. (2015). Tetrahedrites as thermoelectric materials: an overview. J. Mater. Chem. C 3, 12364-12378.
[3] Levinsky P., Vaney J.-B., Candolfi C., Dauscher A., Lenoir B., Hejtmánek (2016). Electrical, Thermal, and Magnetic Characterization of Natural Tetrhedrites-Tennantites of Diferent Origen. J. Elec.Mat. 1351-1357.

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THE EFFECT OF ADDITIVES ON THE PLASTICITY OF SMECTITIC PASTES

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Clayey material is commonly used for cosmetic and pharmaceutical formulations as well as for application on aesthetic medicines. For these purposes, its plasticity promotes the ability of adhesion to skin and the malleability of the product. The plasticity is affected by several physicochemical properties of the materials such as mineralogical composition, aggregation of the particles, grain size distribution and type of exchangeable cations.

The aim of this study is to analyze the influence of the addition of glycerol, hidrogel, calcium and kaolin on the plasticity of a smectitic sample, and to check if some improvement on smectitic samples plasticity is achieved after mixture with different additives.

We studied several formulations of smetictic pastes, using bentonites from Avis and Montargil (South Portugal) and from Porto Santo (Madeira archipelago) and blended with variable but always minor quantities of kaolin from Vila Chã (North Portugal); glycerol, hidrogel, calcium were also blended in variable proportions.

Mineralogical characterization was performed by X-ray diffraction; grain size analysis was carried out by wet sieving (for fraction >63 µm) and for fraction <63 µm was used a X-ray grain size analyzer (Micromeritics® Sedigraph 5100). Liquid limit was determined using the fall cone test and the plasticity limit followed the procedure recommended by ASTM D4318 – 10. Exchangeable cations (Na^+, K^+, Mg^{2+} and Ca^{2+}) were assessed by atomic absorption spectrophotometry (AAS) following EPA 7000B. For calcium saturation, a solution of $CaCl_2$1M was prepared and a suspension of each sample with the solution was stirred during 24hr followed by the removal of the solution. The procedure was repeated four times and then sample was cleaned with distilled water.

The smectitic samples are composed mainly by phyllosilicates, calcite, feldspars and quartz, being rich in clay fraction (mainly smectite, with discrete illite and kaolinite). Formulation with kaolin has higher content in quartz and kaolinite than the remaining formulations. Regarding Atterberg limits, it is possible to classify the samples with glycerol as no plastics and the samples with hidrogel as highly plastics. The formulation combining saturation with calcium and hydrogel is the most plastic. Concerning exchangeable cations, in general, all formulations show an enrichment in Ca and Na when compared with the initial raw samples.

As main conclusions, the addition of hidrogel, glycerol, kaolin and calcium affected the plasticity of the initial samples. Hidrogel plus saturation with calcium can be considered as the most suitable combination if an improvement of the plasticity is requested.

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THE APPLICATION OF CLAY MINERALS ON REMOVING CS$^+$ AND SR^{2+} IONS FROM RADIOACTIVE CONTAMINATED WATER

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$^{137}Cs^+$ and $^{90}Sr^{2+}$ are the main secondary products of nuclear reaction which is troublesome for the treatment of nuclear waste owing to their radioactive half-life as long as 30 years. In comparison with the synthetic absorbents, natural minerals are abundant and low cost, which are suitable for treating massive radioactive wastewater. Zeolite is known as a good adsorbent to remove Cs^+ ions; however, it exhibits quite low uptake efficiency for Sr^{2+}. This work intends to explore promising natural absorbents that allow removing Sr^{2+} and Cs^+ simultaneously. Due to the great variety of natural minerals, the aim of this work is to find the key factors that determine the uptake capability of Sr^{2+} and Cs^+ ions in order to facilitate the selection of appropriate natural adsorbents for the decontamination treatment for radioactive wastewater. Two clay materials, i.e. kaolinite and bentonite that exhibited different structures and chemical compositions, were studied. To modify the structure and composition of clay minerals but also to enhance the adsorption efficiency, post-treatments, such as acid and basic washing processes were employed. The adsorption efficiency of the raw and modified clays in correlation with their elemental composition, the structural coordination and surface areas, were carefully examined. According to the experimental results, the ionic exchange capacity strongly depended on the coordination properties of Al^{3+} and Na^+ ions, which was effectively modified by the post-treatments and as a consequence enhanced the adsorption efficiency. The isotherm batch adsorption experiments showed that the uptake efficiency of Sr^{2+} of the modified kaolinite and bentonite effectively increased from 5.84 and 28.9 to 32.9 mg/g and 78.1 mg/g, respectively. Moreover, the modified bentonite also exhibited good removing capability for Cs^+ ions up to 169.49 mg/g, which was comparable to zeolite (172.4 mg/g).

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EFFECTS OF ADDITION OF SUBMICRON CU@AG PARTICLES AND SURFACE MODIFICATION ON ELECTRICAL CONDUCTIVITY OF CU@AG-BASED EPOXY ADHESIVES

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Fabrication and use of submicron Ag-coated Cu (Cu@Ag) particles as a sub-filler material for micron Cu@Ag flakes/epoxy conductive adhesives were examined. Submicron Cu@Ag particles were successfully prepared and surface-modified using oleic acid. Synthesized Cu particles exhibited a polygonal shape and a smooth surface and the Cu@Ag particles fabricated with an L-ascorbic acid reductant showed very rough surfaces. Adhesives were fabricated by mixing the 80 wt% Cu@Ag powder (a concentration of 40 wt% for the commercial micron-sized Cu@Ag flakes with/without surface modification and a concentration of 40 wt% for the submicron-sized Cu@Ag particles with surface modification) with a 20 wt% resin formulation (a mixture of an epoxy resin and a curing agent).

Diffuse reflectance infrared Fourier transform spectroscopy and thermogravimetric differential scanning calorimetry results indicated the formation of an organic layer by the chemical interaction between the Cu@Ag surface and oleic acid and the survival of the organic layer after treatment at 160 °C for 3 h in air. The enhanced antioxidant property by the organic layer is beneficial in suppressing increase of electrical resistivity in the resultant film after curing of the adhesive in air. Moreover, the organic layer on the particles provided superior dispersion behaviour by suppressing the aggregation between particles during mixing for the preparation of the adhesive. The superior dispersion permits each submicron particle to settle to the vacant spaces between micron particles separately, which mainly increases the number of contacts between the micron flakes and broadens the contact area. Hence, the increase in the number of contact points per unit area is clearly beneficial for enhancing the electrical conductivity of the cured film. Consequently, the surface modification of Cu@Ag fillers using oleic acid is effective for enhancing the electrical conductivity of adhesives.

Because the submicron Cu@Ag particles played a viscosity reducer in the adhesives when they were added in a small quantity, they were added into the adhesives with amount of 2-6 wt% before and after percolation threshold of micron Cu@Ag flakes. Through measuring electrical resistivities of the films after curing the adhesive co-containing micron-sized Cu@Ag flakes and submicron particles, the optimal contents of submicron Cu@Ag particles as well as micron Cu@Ag flakes were decided and the mechanism was discussed.

[1] Zhang R., Lin W., Lawrence K., Wong C.P. (2010). Highly reliable, low cost, isotropically conductive adhesives filled with Ag-coated Cu flakes for electronic packaging applications. Int. J. Adhes. Adhes., 30, 403.
[2] Lin Y.-S., Chiu S.-S. (2008). Electrical properties of copper-filled electrically conductive adhesives and pressure-dependent conduction behavior of copper particles. J. Adhes. Sci. Technol., 22, 1673.
[3] Xu X., Luo X., Zhuang H., Li W., Zhang B. (2003). Electroless silver coating on fine copper powder and its effects on oxidation resistance. Mater. Lett., 57, 3987.
[4] Hai H.T., Ahn J.G., Kim D.J., Lee J.R., Chung H.S., Kim C.O. (2006). Developing process for coating copper particles with silver by electroless plating method. Surf. Coat. Tech., 201, 3788.
[5] Choi E.B., Lee J.-H. (2015). Ethylene glycol-based Ag plating for the wet chemical fabrication of one micrometer Cu/Ag core/shell particles. J. Alloys Compd., 643, S231.
[6] Shin Y.M., Lee J.-H. (2015). Effects of process parameters on Cu powder synthesis yield and particle size in a wet-chemical process. Arch. Metall. Mater., 60, 1247.
[7] Kohinata S., Terao A., Shiraki Y., Inoue M, Uenishi K. (2013). Relationship between the conductivity of isotropic conductive adhesive (ICAs) and the lubricant coated on silver filler particles. J. Jap. Inst. Electron. Packag., 6, 104.
[8] Li C., Gong X., Tang L., Zhang K., Luo J., Ling L., Pu J., Li T., Li M., Yao Y. (2015). Electrical property enhancement of electrically conductive adhesives through Ag-coated Cu surface treatment by terephthalaldehyde and iodine. J. Mater. Chem. C, 3, 6178.
[9] Lu C.-A., Lin P., Lin H.-C., Wang S.-F. (2006). Effects of metallo-organic decomposition agents on thermal decomposition and electrical conductivity of low-temperature-curing silver paste. Jpn. J. Appl. Phys., 45, 6987.
[10] Choi E.B., Lee J.-H. (2017). Enhancement in electrical conductivity of pastes containing submicron Ag-coated Cu filler with palmitic acid surface modification. Appl. Surf. Sci., In press.

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ALENDRONATE DOPED DIATOMS AS SCAFFOLDS FOR BONE REGENERATIVE ENGINEERING

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Sodium Alendronate is a second generation bisphosphonate with therapeutic applications in osteoporosis, Paget's disease, and the prevention of skeletal-related events in cancer [1]. The double phosphonate moiety makes sodium alendronate suitable for Ca^{2+} chemisorption, hydroxyapatite formation via crystallization, osteoblasts enhancement and osteoclasts inhibition [2].Moreover, surface immobilized bisphosphonates can be used to improve biomaterials fixation in bone [3].

Diatom are unicellular eukaryotic microalgae microalgae that can be regarded as living factories producing nanostructured and mesoporous biosilica shells (frustules) having a highly ordered hierarchical architecture. These unique, morphological, chemical and mechanical properties make diatoms' biosilica a very attractive nanomaterial for a wide variety of applications.

In our previous work [4], we demonstrated that diatoms microalgae can uptake various organic molecules from the culture medium during the growth cycle: into the diatom cell, the Silica Deposition Vesicles (SDV) can recognize molecules with a specific biochemical *consensus* (the terminal amino-propyl moiety, in our case) and incorporate into the silicon network during the biosalicification process.

We present here a method to easily embed sodium alendronate into naturally nanostructured biosilica shells extracted from Thalassiosira weissflogii with the aim to produce a biomaterial attractive for implants and fillers applications in medical devices. The resulting alendronate-doped biosilica was fully characterized by FTIR, SEM-EDX and TGA analyses confirming the incorporation of the drug into the silica structure together with the exposure of the bisphosphonate moieties onto the silica surface.

[1] Russell R.G.G. (2011). Bisphosphonates: The first 40 years, Bone, 49, 2-19
[2] Schilling A.F., Filke S., Brink S., Korbmacher H., Amling M., M. Rueger J.M. (2006). Osteoclasts and Biomaterials. Eur. J. Trauma, 107-113.
[3] Tengvall P., Skoglund B., Askendal A., Aspenberg P. (2004). Surface immobilized bisphosphonate improves stainless-steel screw fixation in rats. Biomaterials, 25, 2133-8.
[4] Cicco S.R., Vona D., De Giglio E., Cometa S., Mattioli-Belmonte M., Palumbo F., Ragni R., Farinola G.M. (2015). Chemically Modified Diatoms Biosilica for Bone Cell Growth with Combined Drug-Delivery and Antioxidant Properties. Chempluschem, 80(7), 1104-1112.

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VISCOSITY BEHAVIOUR OF PORTUGESE CLAY SUSPENSIONS

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Clays and clayey materials are used for a large range of applications, so it is very important to know their rheological, mineralogical and textural characteristics. Moreover, viscosity is an important parameter due to the widely use of clays in the ceramic industry, for example on ceramic tiles, in the chemical and pharmaceutical industries, among other applications.

The aim of this study is to assess the influence of some parameters such as texture, mineralogical composition and liquid limits on viscosity of selected Portuguese clay suspensions for application in pelotherapy.

We studied 10 samples from different geological settings, 5 clay sediments from Palaeogene to Pleistocene formations (C1, TAV, MAR, RED and BV), 2 from Upper Cretaceous (B1 and B2), 1 bentonitic alteration product (PS) and 2 alteration products of eruptive rocks (LAG and CB), from mainland as well as from the Azores and Madeira archipelagos.

The mineralogical characterization was performed by X-ray diffraction, the grain size analysis was carried out by wet sieving (for fraction >63 microns) and for fraction <63 microns was used X-ray grain size analyzer (Micromeritics® Sedigraph 5100). The liquid limit was determined using the fall cone test and the plasticity limit followed the procedure recommended by ASTM D4318 – 10. The viscosity was determined using Brookfield DV-III Ultra Programmable apparatus. Results were submitted to statistical analysis, namely principal components analysis.

According to the triangular diagram of Folk soil classification, samples are silty clay (RED, B1, B2, MAR), silty clay loam (BV, TAV) and silt loam (C1, PS, CB, LAG). Concerning fine fraction, samples B1, B2, TAV, and MAR are samples richer in clay fraction.

The samples are constituted mainly of phyllosilicates, feldspars and quartz. The samples from Azores have sulphates and alunite.

It was identified three main clay minerals: smectite, illite and kaolinite. There are 3 groups of samples: smectitic (PS and BV), kaolinitic (C1, RED, MAR, LAG and CB) and kaolinite+illite rich (B1, B2, TAV).

Regarding Atterberg limits it is possible to classify the samples as high plastics, being PS and BV samples the more plastic. The behaviour of all samples is explained by their high content in phyllosilicates and their different composition in terms of clay minerals.

As might be expected samples BV and PS are those with a higher cation exchange capacity due to their high contents of smectite.

In preliminary studies on the viscosity it was found that the samples PS and BV have a high viscosity, this behaviour is mainly related with its mineralogical composition and its grain size.

The principal components analysis allowed us to establish a relationship between the mineralogical composition, texture, viscosity and liquidity limits. It was verified that the viscosity can be directly related to the liquidity limits, the content of certain minerals mainly phyllosilicates, in particular, smectite, and texture. There are minerals which reduce the viscosity of the samples such as quartz.

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MINING WASTES RECYCLING IN CLINKER AND GEOPOLYMERS

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This contribution reports the use of mining wastes obtained upon processing metallic materials ore primary ore; i) red mud (R) from alumina production from bauxite and lead-zinc mining by-products. Two distinct valorisation ways were explored, namely production of sulfoaluminous clinker, and geopolymers.

These clinkers were produced by using the lead-zinc mining wastes. Corresponding cements were then used to formulate mortars and their compressive strength was found similar or better than the one of corresponding mortars prepared by using cement produced from pure chemicals.

After 28 days curing, the best mechanical resistance (24.34 MPa under compression) was obtained for the clinker calcined at 1350ºC and showing a suitable particle size distribution.

Also, new red mud based geopolymer formulations were explored thought sodium silicate/NaOH activation. Tests on the influence of composition and the alkaline character of this mining waste were assessed following several techniques.

The influence of red mud addition on mechanical properties was also studied. It revealed that at lower ratio of red mud/metakaolin (not exceeding 10%) and with extending curing time for geopolymers, the mechanical toughness increased considerably from day 1 to 28 reaching practically 11 MPa.

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COLLOIDAL MAGNETIC HETEROSTRUCTURED NANOCRYSTALS WITH ASYMMETRIC TOPOLOGIES: SYNTHESIS, GROWTH MECHANISMS AND PROPERTIES

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Colloidal inorganic nanocrystals, free-standing crystalline nanostructures generated and processed in solution phase, represent an important class of advanced nanoscale materials owing to the flexibility with which their physical–chemical properties can be controlled through synthetic tailoring of their compositional, structural and geometric features and the versatility with which they can be integrated in technological fields as diverse as opto-electronics, energy storage/ conversion/production, catalysis and biomedicine [1]. In recent years, building upon mechanistic knowledge acquired on the thermodynamic and kinetic processes that underlie nanocrystal evolution in liquid media, synthetic nanochemistry research has made impressive advances, opening new possibilities for the design, creation and mastering of increasingly complex "colloidal molecules", in which nanocrystal modules of different materials are clustered together via solid-state bonding interfaces into free-standing, easily processable multifunctional nanocomposite systems [2-5].

In this talk, I will provide a glimpse into this fast-growing research field by illustrating progress achieved by our research group in the wet-chemical development and characterization of last-generation breeds of all-inorganic heterostructured nanocrystals (HNCs) in asymmetric non-onionlike geometries, inorganic analogues of poly-functional organic molecules, in which distinct nanoscale crystalline modules are interconnected in hetero-dimer, hetero-oligomer and anisotropic multidomain architectures via epitaxial heterointerfaces of limited extension. The focus will be on modular HNCs entailing at least one magnetic material component combined with semiconductors and/or metals, which hold potential for generating enhanced or unconventional magnetic properties, while offering diversified or even new chemical-physical properties and functional capabilities [5]. The available toolkit of synthetic strategies, all based on the manipulation of seeded-growth techniques, will be described and critically interpreted within the framework of the currently understood mechanisms of colloidal heteroepitaxy.

[1] Cozzoli P.D., Pellegrino T., Manna L. (2006). Synthesis, Properties and Perspectives of Hybrid Nanocrystal Structures. Chem. Soc. Rev., 35 (11) 1198-1208.
[2] Casavola M., Buonsanti R., Caputo G., Cozzoli P.D. (2008). Colloidal Strategies for Preparing Oxide-based Hybrid Nanocrystals. Eur. . Inorg. Chem., (6), 837-854.
[3] Carbone L., Cozzoli P.D. (2010). Colloidal Heterostructured Nanocrystals: Synthesis and Growth Mechanisms. Nano Today, 5 (5) 449-493.
[4] Baghdanzadeh M., Carbone L., Cozzoli P.D., Kappe C.O. (2011). Microwave-Assisted Synthesis of Colloidal Inorganic Nanocrystals. Angew. Chem. Int. Ed., 50 (48) 11312-11359.
[5] Scarfiello R., Nobile C., Cozzoli P.D. (2016). Colloidal Magnetic Heterostructured Nanocrystals with Asymmetric Topologies: Seeded-Growth Synthetic Routes and Formation Mechanisms. Front. Mater., 3, 56.

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COLLOIDAL MULTIFUNCTIONAL HETEROSTRUCTURED NANOCRYSTALS: SYNTHESIS, GROWTH MECHANISMS AND PROPERTIES

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Since the discovery of the size-dependent behavior of nanoscale matter, colloidal inorganic nanocrystals (NCs), solution free-standing crystalline particles made of a few hundred up to several thousand atoms, have developed more rapidly than other classes of nanomaterials owing to the high degree of control with which their properties can be tailored through geometric and compositional engineering in the synthesis stage, and to the versatility with which they can be processed and implemented into a number of technologically valuable applications [1,2]. Two major reasons account for the exclusivity of NCs: the significant fraction of atoms residing at the surface and the restriction of charge carrier motion to a small space volume. By virtue of these contributions, NCs exhibit unique chemical–physical responses that, for a given material composition, systematically correlate with size and shape, a feature prohibited to their bulk counterparts. As of today, NCs with controlled sizes and shapes not only represent model systems for the study of new phenomena in nanostructured solids, but also serve as building blocks for the bottom-up development of artificial functional materials, key active elements in miniaturized devices, and novel platforms on which innovative concepts in magneto-optoelectronics, biomedicine, and catalysis are being founded [1,2].

More recently, in response to the growing demand for "smarter" multifunctional colloidal objects with enhanced and/or diversified capabilities, nanochemistry research has devoted efforts toward the realization of brand-new hybrid nanocrystals (HNCs) with a spatially controlled distribution of their chemical composition and crystal structure [2,6]. These can comprise all-inorganic multicomponent nanoheterostructures arranged in elaborate concentric/eccentric onion-like or oligomer-type architectures, in which domains of different materials are interconnected together via direct epitaxial interfaces. Their structural complexity makes HNCs "smart" encounter platforms, where various nonhomologous properties can coexist and exchange-couple, leading to increased functionality, modified or amplified chemical–physical responses, or even emergence of entirely new properties. The development of HNCs thus embodies a generic paradigm to multi-component nanoscale entities, for which an increasingly higher level of structural-architectural sophistication opens access to enhanced and/or diversified functionalities by combining control over the geometry and composition of the constituent domains with the engineering of their relative spatial arrangement [2,6].

The synthesis of HNCs, the understanding of property-structure-functionality relations in such hybrid nanomaterials, and their exploitation in practical applications are all hot fields of research in their infancy, which are continually attracting increasingly high attention. In this talk I will highlight progress made by our research group in the synthesis and advanced structural characterization of a rich selection of elaborate HNCs based on diverse associations of semiconductor, plasmonic and magnetic materials. The mechanisms through which HNCs may be accessed in nonequivalent topological configurations with distinctive chemical-physical properties will be discussed. The technological potential offered by such multifunctional HNCs will be shortly highlighted.

[1] Talapin D.V., Lee S., Kovalenko M.V., Shevchenko E.V. (2010). Prospects of Colloidal Nanocrystals for Electronic and Optoelectronic Applications. Chem. Rev., 110 (1) 389-458.

[2] Cozzoli P.D., Pellegrino T., Manna L. (2006). Synthesis, Properties and Perspectives of Hybrid Nanocrystal Structures. Chem. Soc. Rev., 35 (11) 1198-1208.

[3] Casavola M., Buonsanti R., Caputo G., Cozzoli P.D. (2008). Colloidal Strategies for Preparing Oxide-based Hybrid Nanocrystals. Eur. . Inorg. Chem., (6), 837-854.

[4] Carbone L., Cozzoli P.D. (2010). Colloidal Heterostructured Nanocrystals: Synthesis and Growth Mechanisms. Nano Today, 5 (5) 449-493.

[5] Baghdanzadeh M., Carbone L., Cozzoli P.D., Kappe C.O. (2011). Microwave-Assisted Synthesis of Colloidal Inorganic Nanocrystals. Angew. Chem. Int. Ed., 50 (48) 11312-11359.

[6] Scarfiello R., Nobile C., Cozzoli P.D. (2016). Colloidal Magnetic Heterostructured Nanocrystals with Asymmetric Topologies: Seeded-Growth Synthetic Routes and Formation Mechanisms. Front. Mater., 3, 56.

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VOLUME REDUCTION OF RADIOACTIVE WASTES AND RADIONUCLIDE RECYCLING BY MICROORGANISMS

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The present study proposes to systematic studying the interaction mechanisms between typical actinides (uranium/ plutonium/ americium) and microorganisms for volume reduction and nuclides recover. The damage in living microorganisms and the structure changes in dead microorganisms by gamma irradiation has also been reasearched. The completed results are as following: (1) The microorganisms show excellent biosorption capacity for uranium which efficiency was 97%. The optimized biosorption pH of uranium were 5 and 3 respectively as to living and died microorganisms, and the maximal adsorption quantities were 325.50 mg/g (DW) and 45.44 mg/g(DW) respectively. The optimized biosorption pH was 5 for 239Pu and 1 for 241Am. After repeated biosorption, the radioactivity of 238U in the wastewater could be reduced from 100 mg/L to 0.027 mg/L at the sixth time, while 241Am in the wastewater could be reduced from 129000 Bq/L to 2 Bq/L at the third time and that of 239Pu from 7350000 Bq/L to 1500 Bq/L at the sixth time. (2) The uranium adsorbed on the surface of microorganisms was still hexavalent. It is assumed that the biosorption mechanism of uranium is mainly through chelating ligand and ion exchange. After ashing treatment, the rate of reduced capacity was more than 4500 and the uranium in the ash content was shown in the form of phosphate crystals. The quality percentage of uranium was greater than 50%. The new phase of UO_2HPO_4•$4H_2O$ (HUP) was found on the surface of microorganisms under acid condition. In the case of Ce and Eu, the needle crystal containing Ce and P was found on the surface of microorganisms while Eu was only adsorbed in amorphous form. (3) More than 60% of the absorbed actinides were through chelating ligand in extracellular. The biosorption capacities of uranium, plutonium and americium by biomacromolecule, phospholipid and protein were better than glucan. The carboxyl and ester groups on the surface of microorganisms had the greatest effect on the biosorption of actinides. (4) There was no obvious difference in the structure of microorganisms and biomacromolecule of cell wall-membrane under 5 to 30 kGy dose of irradiation, but the removal rate of uranium was decreased to 1/2 at 600Gy dose of irradiation. (5) After a repeated adsorption by Saccharomyces cerevisiae (twice), the total alpha radioactivity could be reduced 2 orders of magnitude and more than 90% of the uranium could be removed from the real radioactive liquid waste, while the total beta and gamma radioactivity could only be reduced less than 20%. The presented results indicate that the extraction and separation of actinides from the real radioactive wastewater is possible by microorganisms. (6) The interaction between Acidithiobacillus ferrooxidans (A.f) and typical actinides indicated that the secondary mineral jarosite had enhanced adsorption and calcination reduction effect on actinides. These findings give new insights on application of microorganism in radioactive waste treatments.

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THE INCORPORATION OF THE CRITICAL METAL COBALT INTO SYNTHETIC IRON OXYHYDROXIDE SYSTEMS – IMPLICATIONS FOR NATURAL LATERITE DEPOSITS

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The most common iron oxyhydroxide is goethite with its ideal formula α-FeOOH. It is a commonly encountered weathering product and present in (almost all) soils, ore deposits (e.g. nickelferous ores, laterite deposits), and continental and marine sediments, such as deep-sea ferromanganese nodules [1,2]. Due to its small particle size and the resulting high specific surface area (8 to 200 m^2g^{-1}), goethite has a high potential to readily incorporate other minor elements and rarely occurs with its ideal formula in naturally occurring deposits [3]. Foreign cations can either be adsorbed on the surface of goethite crystallites or substitute for Fe. A range of valencies are possible, e.g. divalent (Ni, Zn, Cd), trivalent (Al, V, Cr, Mn, Co) or tetravalent (Si, Ge and Pb) [1]. An understanding of elements present in the mineral, their incorporation into the structure, whether they are structurally or surface adsorbed, are vitalfor optimising extraction processes for the mineral processing industry.

However, many of these non-iron-elements are present in low concentrations (<2 mol%) in the structure of natural goethite and it is often challenging to determine their presence [4]. To investigate the substitution or sorption mechanisms of non-iron-elements, using controlled laboratory studies of synthetic goethite materials is one approach. Over the last few decades, many laboratory studies of incorporation processes into synthetic FeOOH systems have been reported, with certain cations studies more extensively than others. For instance, Al-goethites are the most frequently analysed samples in the literature, but in contrast, little is known about the incorporation process of the critical metal cobalt into goethite and the properties of cobalt containing goethites.

For over 2000 years, cobalt has been used, for instance for colouring glass and ceramics in Persia or Egypt. Up until the beginning of the 20th century, its main use was as a pigment. Since then, with a deeper understanding of its properties, the typical uses of cobalt have changed. Cobalt has important physical and chemical properties, which makes it an irreplaceable and strategic element in a diverse range of applications and for many different value chains. It is used in super alloys, which maintain their strength at high temperatures, it is usedin working environments which are aggressive (e.g. hot and acidic), in the hard metal industry as a component in highly effective cutting tools andas well as in the magnet industry. Nevertheless, the globally leading and to date irreplaceable use of cobalt is as a cathode material in lithium rechargeable batteries [5].

This research is focused on cobalt doped iron oxyhydroxide systems, such as goethite and ferrihydrite, to investigate the effects of time, concentrations of cobaltdopant levels, pH and temperature on the phases formed. The synthesis of a set of cobalt doped iron oxyhydroxide samples and preliminary results from characterisation techniques, such as Powder X-ray Diffraction (XRD), Infrared Spectroscopy (IR spectroscopy) and Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) will be presented.

[1] Manceau A., Schlegel M., MussoM., Sole V., Gauthier C., Petit P., Trolard F. (2000). Crystal chemistry of trace elements in natural and synthetic goethite.GeochimicaetCosmochimicaActa, 3643-3661.
[2] Guimaraes I.R., Giroto A., Oliveira L.C., Guerreiro M.C., Lima D.Q., Fabrisj.D. (2009). Synthesis and thermal treatment of Cu-doped goethite: oxidation of quinolone through heterogeneous Fenton process. Applied Catalysis B: Environmental, 581-586.
[3] Cornell R.M., Schwertmann U. (2003). The iron oxides: structure, properties, reactions, occurrences and uses, 703.
[4] Gasser U.G., Jeanroy E., Mustin C., Barres O., Nüesch R., Berthelin J., Herbillon A.J. (1996). Properties of synthetic goethites with Co for Fe substitution.Clay Minerals, 465-476.
[5] Cobalt Development Institute (2006). Available at: http://www.thecdi.com/.

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PASSIVE MINERAL CARBONATION OF ULTRAMAFIC MINING WASTES: A WAY FOR WASTES VALORIZATION

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Several processes have been developed to reduce the greenhouse gas emissions responsible for the global warming. Mineral carbonation where CO_2 reacts with a divalent cation to form a carbonate mineral that is stable over geological periods is one of them. The serpentinized ophiolite of Thetford Mines area (Québec, Canada) has been exploited for chrysotile ($(Mg)_3Si_2O_5(OH)_4$) for more than one century. The Black Lake mining waste heap contains more than 130 Mt of serpentinized ultramafic rocks that have been deposited by conveyors and reworked in a flat surface. Mineral carbonation occurs naturally in these ultramafic mining wastes forming cemented crusts at surface composed of hydrated magnesium carbonate minerals. Moreover, warm air vent capable of melting snow have been located at the upper surface of the waste piles. CO_2 concentration as low as 10 ppm was measured using a Li-Cor in the air vent. The CO_2 depleted warm air vent indicates that atmospheric CO_2 is captured by exothermic mineral carbonation reactions within the chrysotile milling waste pile. Mg-rich process tailings and waste rocks from mining operations are a promising material for passive mineral carbonation because in addition to containing high content of Mg these wastes are already of reduced particle size.

A large number of laboratory experiments on both mine waste rocks and different types of mine tailings from Ni-Cu, chrysotile, and diamond deposits were conducted to identify critical processes that control reaction rates in order to optimize carbon sequestration and recovery of the geothermal energy associated with the reaction. Real time monitoring of CO_2 uptake at atmospheric conditions was performed using the Laval eudiometers which allows calculation of the rate of the mineral carbonation reaction. Tests were conducted by varying the concentration of CO_2 in the gas phase, the tailing and waste rocks water contents and the material porosity by addition of inert coarser material to determine the optimal carbonation conditions.

Results obtained using the Laval eudiometers have shown that the gas diffuses through all the material and that the carbonation reaction is not only found on the surface layer in contact with the gas but throughout the volume. For optimal carbonation reaction, the materials must have a sufficient water content acting as solvent for dissolution of Mg ions necessary for the formation of the carbonate minerals. However, the water content must not be too high to allow the gas to circulate in the unsaturated porosity. An optimal water content of between 20 and 60% was obtained according to the type of tailing tested. CO_2 in mining waste pore space dissolves in the interstitial water to precipitate hydrated magnesium carbonates. A linear relationship was obtained between the CO_2 concentration in the gas mixture and the CO_2 absorption rate of the mine tailings. Increase of tailings porosity by addition of inert aluminum oxide also helps promoting the carbonation reaction probably by facilitating CO_2 diffusion in increased pore space. Laboratory experiments have shown that brucite ($Mg(OH)_2$), followed by chrysotile, are the most reactive minerals for carbonation of Mg-rich mine waste and their proportions in mine waste are critical to assess the carbon capture potential. Selecting mine waste rich in brucite, or chrysotile, enhances mineral carbonation reactions. These data show that it is possible to significantly promote the natural mineral carbonation reaction of various ultramafic mine tailings by adequate porosity, water content, and increased CO_2 concentration in air. The combination of carbon sequestration with the recuperation of heat generated by the exothermic carbonation reaction is an opportunity to improve the environmental footprint of the mining industry.

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MINERALOGICAL STUDY OF THE POZZOLANIC PROPERTIES OF CALCINED CLAYS

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Portland cement-based materials, like concrete, are nowadays the most important construction material. The expansion of the cement industry might be a cause for concern, since the production process is very energy-intensive and because of the large amounts of carbon dioxide that are emitted, it's extremely large-scale production implies that it is responsible for 5 – 8% of the anthropogenic CO2 emissions. The addition of supplementary cementitious materials (SCMs) is considered to be one of the most effective ways of reducing the environmental impact of the cement industry. SCMs, also known as pozzolans, chemically react at ambient temperature with calcium hydroxide in the presence of water to form compounds that possess cementitious properties. Common used SCMs like blast furnace slag, fly ash and silica fume face complete utilization. One of the most promising alternative sources of SCMs are calcined clays. However, calcined clays are hardly used as SCM due to the complexity of clay minerals and the ignorance of the underlying reaction mechanism and reaction products. Hence this study investigates the potential use of calcined clays from a mineralogical point of view by linking the characteristics of the untreated clays to the pozzolanic activity of the calcined clays and to the reaction products of the cement-calcined clay reaction.

The key starting point of this study consists of a detailed chemical, mineralogical and physical characterization of both the raw and calcined material. To increase the reactivity of natural clays, the raw clay is calcined in a fixed-bed electrical furnace at temperatures ranging between 500 °C and 900 °C. The characterization of the raw and calcined clays includes the determination of the mineralogical (XRD) and chemical (ICP-OES) composition, physical characteristics like grain size (laser diffraction) and specific surface area (BET) and spectroscopic characteristics (FTIR & NMR). After heat treatment, their pozzolanic activity is evaluated with the Chapelle test and with thermal analysis (TGA) on mortars after 3, 7 and 28 days. The combined results of this study indicate the mineralogical composition of the starting material is one of the primary factors controlling the pozzolanic reactivity of the calcined clay. Especially two mineralogical features are critical namely:

1) The type of the dominant clay mineral, with its characteristic thermal behaviour, for pure clays the reactivity can be summarized as follows: Kaolinite >> Ca montmorillonite > Na montmorillonite > illite > hectorite.

2) The amount of the clay mineral and presence of impurities. The presence of non-clay minerals can have an effect on the pozzolanic reactivity. Inert materials like quartz, feldspar and muscovite have no direct influence on the reactivity, but feldspar and muscovite enhance the sintering phenomenon upon calcination resulting in a coarser grain size and consequently a decrease of the reactivity. Moreover, several reactivity tests on artificial mixtures with a variable impurity content demonstrated that the quantity of the inert material can be linearly correlated to the pozzolanic reactivity. Additionally the presence of up to 30% of calcite appears to increase the pozzolanic potential of the clay, especially at early ages of the hydration reaction.

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IN SITU GROWN FLOWER-LIKE NANOSTRUCUTRED CUO ON SCREEN PRINTED CARBON ELECTRODES FOR CATALYTIC NON-ENZYMATIC GLUCOSE SENSORS

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Reliable and fast determination of glucose is essential in many fields such as clinical diagnostics, biotechnology and food industry, therefore over the past few decades great attention has been paid to the development of glucose sensors [1]. In this context, electrochemical glucose sensors based on metal oxide materials (e.g., NiO, Co_3O_4, MnO_2, CuO) offer many advantages compared to enzyme-based glucose sensors. In recent years, in order to increase the sensitivity, 1-dimensional metal oxide materials, like nanowires or nanorods, with special physical and chemical properties, have been widely applied in chemosensors and biosensors [2,3]. Sensors improved with metallic nanoparticles habitually reveal improved electrochemical performance, due to very large surface–to-volume ratio and dimensions analogous to the extension of surface charge region, increasing the mass transport and catalysis. Among these catalysts, nanostructured CuO, a nontoxic, low cost p-type semiconductor with a narrow band gap of 1.2 eV, has gained much attention in the development of non-enzymatic glucose sensors because of its intrinsic electronic and catalytic properties such as high specific surface area, good electrochemical activity, and lower overpotential for electron transfer reaction.

Recently we have reported interesting results obtained with a three electrodes planar electrochemical sensor, based on CuO nanowires growth “in situ” on Cu working electrode, fabricated by a simple micromachining technique and employed for the non-enzymatic determination of glucose [4]. On these premises, this report presents a novel strategy for the fabrication of non-enzymatic glucose sensors, based on modified carbon working electrodes. A planar electrochemical sensor, based on flower-like CuO nanostructures growth “in situ” on commercial screen printed carbon working electrode, was fabricated by a facile and effective technique and employed for the non-enzymatic determination of glucose. The prepared CuO nanostructures were characterized by scanning electron microscopy (SEM) and X-ray diffraction (XRD). The carbon electrode modification with CuO was optimized investigating the effect of the number of deposition cycles of precursor and their concentration. Furthermore, the electrodes modified by in situ growth of CuO were compared with an electrode prepared by simple deposition of CuO powder previously synthesized with the same technique. The deposition method was optimized by analysing the electrochemical performance of different electrode towards the oxidation of glucose in alkaline media. It has been observed that more deposition cycles starting from lower concentrated solutions of precursors, allows obtaining more uniform and better structured films then higher performance, compared to the use of more concentrated solutions of the precursors. Furthermore, the in situ growth of CuO on carbon electrode achieves significantly better performance compared to an electrode prepared by direct deposition of CuO powder previously synthesized. The cyclic voltammetry (CV) and the chronoamperometric tests have demonstrated that the in situ growth of CuO on carbon electrode leads to excellent electrochemical performance toward glucose oxidation in alkaline media. The best sensor here developed showed a high sensitivity of 1460 $\mu A/mM\ cm^{-2}$ with a calculated low detection limit of 2.5 μM (S/N=3). In addition, tests carried out within six month showed an excellent long-term stability. The proposed sensors should have advantages such as low cost, simplicity, high stability, reproducibility and good selectivity for the detection of glucose in many application fields such as in clinical diagnostics and in biomass fermentation processes.

[1] Heller A., Feldman B.(2008). Chem. Rev., 108, 2482–2505.
[2] Chao Chen, Qingji Xie, Dawei Yang, Hualing Xiao, Yingchun Fu, Yueming Tan, Shouzhuo Yao (2013), RSC Advances, 2013, 3, 4473.
[3] Koschinsky T., Heinemann L. (2001). Diabetes Metab Res Rev; 17, 113.
[4] Espro C., Donato N., Galvagno S., Aloisio D., Leonardi S.G., Neri G. (2014). Chemical and Engineering Transactions 41, 415-420.

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NICKEL CATALYST: THE NEW FACE OF CATALYSIS IN GREEN CHEMISTRY

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The last few years have witnessed an ever growing scientific interest for new nanomaterials to be used for catalytic processes [1]. Noble metal nanoparticles have been widely employed in catalysis [2] and several studies have been devoted to the recyclability of noble metal catalysts [3]. However, the high cost of noble metals has limited their practical use. The conservation of the elemental resources of our planet is a global challenge, and the replacement of noble metals by abundantly available transition metals (base metals) is an appealing noble-metal conservation strategy. In this context, recently, due to their low cost, Ni catalysts have been employed in several organic reactions (mainly hydrogenations). The synthesis of aromatic amines through the hydrogenation of the corresponding nitroarenes is a basic chemical reaction. Such reduction is also frequently applied in industry, as anilines are important intermediates for the production of fine chemicals, pharmaceuticals, polymers, herbicides, and more.

Another key aspect in many industrial processes is the necessary use of organic solvents which increases the costs and causes environment pollutions. On the contrary, water is cheap, safe and widely available and may be used as an environmentally benign solvent.

With the aim to set up new environmentally friendly synthetic methods to be performed under mild and sustainable conditions with high efficiency, herein we report the synthesis and characterization of a polymer supported Ni(II) complex [in the following *Ni(II)-pol*], obtained by co-polymerization of $Ni(AAEMA)_2$ ($AAEMA^-$ = deprotonated form of 2-acetoacetoxyethyl methacrylate) with suitable co-monomer (*N,N*-dimethylacrylamide) and crosslinker (*N,N*-methylenebisacrylamide). *Ni(II)-pol* was subsequently thermally reduced under inert atmosphere to give polymer supported Ni(0) nanoparticles (*Ni-NPs-pol*). *Ni-NPs-pol* was employed as active and re-cyclable unsoluble catalyst for the reduction of different nitroarenes to give the corresponding anilines, under sustainable conditions*, i.e.* in the presence of $NaBH_4$ as reducing agent, using water as the solvent at 25 °C. The new catalyst was fully characterized by IR, elemental, SEM and TEM analyses before, during and after several catalytic runs.

[1] Polshettiwar V., Asefa T. (2013). Nanocatalysis: Synthesis and Applications, First Edition, John Wiley & Sons.
[2] Navalona S., Dhakshinamoorthy A., Alvaro M., Garcia H. (2016). Metal nanoparticles supported on two-dimensional graphenes as heterogeneous catalysts. Coord. Chem. Rev. 312, 99–148.
[3] Astruc D., Lu F., Aranzaes J.R. (2005). Nanoparticles as recyclable catalysts: The frontier between homogeneous and heterogeneous catalysis. Angew. Chem., Int. Ed., 44 (48), 7852-7872.

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NATURAL WATER PURIFICATION BY "GREEN RUSTS" RELATED MINERALS, FOUGERITE AND TREBEURDENITE, AS MONITORED BY MÖSSBAUER SPECTROSCOPY

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The discovery in 1996 of the "green rust" related minerals in the gleys of hydromorphic soils of aquifers opened a new field of potential applications since synthetic green rusts may reduce oxidized pollutants. Belonging to the double layered hydroxides family, they own unchallenged redox properties if both divalent and trivalent cations come from the same iron element, where Mössbauer spectroscopy allows us to determine very easily within the solid phase the molar ferric ratio $x = \{[Fe^{III}]/([Fe^{II}] + [Fe^{III}])\}$.

As an example, the disappearance of nitrates, which is concomitant to the appearance of Fe^{II} as due to the formation of Fe^{II-III} minerals under the water table in anoxic conditions by bacterial activity, is documented nowadays using Mössbauer spectra. Moreover, it has been checked in the laboratory that nitrates are reduced by "green rusts" following an*in situ* deprotonation process. This mode of oxidation makes think that some kind of a phase Fe^{II-III}oxyhydroxycarbonate with formula $Fe^{II}_{6(1-x)}Fe^{III}_{6x}O_{12}H_{2(7-3x)}CO_3 \bullet 3H_2O$ does exist instead of dissolving in solution for precipitating a usual ferric oxyhydroxide FeOOH as it does with oxygen explaining the corrosion of steels [1]. However, any average value of $x$ratio comes from mixing domains of three distinct minerals of the "*fougèrite* group" [2](IMA 2012-049), *fougèrite*,*trébeurdenite* and *mössbauerite*[3] for x values of 1/3, 2/3 and 1 that transform topotaxicaly during the redox reaction.

By comparing the E_h-pH diagrams between the *in situ* deprotonation mode and that of the reduction of nitrate or nitrite into nitrogen gas or ammonium, a synergy between bioreduction and abiotic mode does exist: the mixture of *fougèrite* and *trébeurdenite* making x around 0.5 plays the role of catalyst for obtaining nitrogen alone by avoiding ammonium. Moreover, the bacterial activity regenerates the catalyst. This result is most important since it explains why in nature the formation of ammonium is not detected; here, the reduction of nitrate to nitrite by bacteria is confirmed and the role of the minerals is essentially to avoid the formation of ammonium with a small density of bacteria, several orders of magnitude lower than usually necessary in traditional activated sludge treatment.

Therefore, the minerals found in gleysols of characteristic bluish-green shade that come from the bacterial reduction of natural ferric oxyhydroxides in anoxic conditions under the water table of aquifers can now be used for developing a tertiary treatment for waste water denitrification using reed bed filter plants (rhizospheres). The landscaping of "watered areas with reinforced iron purification" (WARIP) which is envisioned in Brittany for large scale treatment in the field will be discussed (BZH-Bretagne Zones Humides®). This development is intended to solve in the long term the devastating proliferation of algae at the mouth of coastal rivers and beaches due to intense agricultural activity. Monitoring the kinetics of the reactions can be performed using the backscattering Mössbauer spectrometer MIMOSII, initially designed for the analysis of the soil of planet Mars, from outside the chemical reactor.

[1] Génin J.-M.R., Ruby C., Upadhyay C. (2006). Structure and thermodynamics of ferrous, stoichiometric and ferric oxyhydroxycarbonate green rusts; redox flexibility and fougerite minerals, *Solid State Sciences*, 8, 1330-1343.

[2] Mills S.J., Christy A.G., Génin J.-M.R., Kameda T., Colombo F. (2012). Nomenclature of the hydrotalcite supergroup; natural layered double hydroxides, *Mineralogical Magazine*, 76(5), 1289-1336.

[3] Génin J.-M.R., Mills S.J., Christy A.G., Guérin O., Herbillon A., Kuzmann E., Ona-Nguema G., Ruby C., Upadhyay C. (2014). Mössbauerite, $Fe^{III}_6O_4(OH)_8[CO_3].3H_2O$, the fully oxidized "green rust" mineral from Mont Saint Michel Bay, France. *Mineralogical Magazine,* 78(2), 447-465.

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EFFECT OF ACID PRE-TREATMENT ONZEOLITE SYNTHESIS FROM FLY ASH: PRELIMINARY DATA

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Fly ash is a by-product of thermal power plants partly disposed of in landfills since it finds no other application. Fly ash is composed of mineral material –refractory to combustion–, residual components –responsible for the incomplete combustion of the initial coal–, particular minerals –quartz, mullite, subordinately hematite and magnetite–, unburned coal particles and a prevalent phase of amorphous aluminosilicate.

Zeolites are tectosilicates characterised by a three-dimensional network of tetrahedral units that form a system of interconnected pores. The substitution of silicon with aluminium produces a net negative charge which is balanced by the presence of an extra cation in the framework. Due to their structure and their excellent ion exchange and sorption properties, zeolites are useful in a number of applications.

Many literature data have documented fly ash convertion into zeolite [e.g. 1-3]. The purpose of this study is to investigate the effect of different parameters on properties of zeolite formed from fly ash. With this aim, crystallization time (from 1 to 72 h); alkaline ratio (0.75 and 1.25), type of water used (distilled water and seawater), and action of acid treatment were investigated. The experiments were performed at 40, 60, 90^{o}C. The synthetic products were characterized by X-ray diffraction (XRD), scanning microscope (SEM), X- ray fluorescence (XRF) Spectophotometer, Infrared (IR) spectroscopy, and Brunauer- Emmett-Teller (BET) method.

The results cofirm that the investigated parameters have significant effects on the structural properties of zeolite synthesised.

[1] Belviso C., Cavalcante F., Fiore S. (2010). Synthesis of zeolite from Italian coal fly ash: Differences in crystallization temperature using seawater instead of distilled water. Waste Management 30 (2010) 839-847.
[2] Belviso C., Cavalcante F., Lettino A,. Fiore S. (2009). Zeolite Synthesis from fused Coal Fly Ash at Low Temperature Using Seawater for Crystallization. Coal combustion and gasification products. ISSN 1946-0198.
[3] Panitchakarn P., Laosiripojana N., Viriya-umpikul N., Pavasant P. (2014). Synthesis of high-purity Na-A and Na-X zeolite from coal fly ash. Journal of the Air & Waste Management Association 64 (2014) 586-596.

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SYNTHESIS OF TRICALCIUM ALUMINATE FROM ALUMINIUM DROSS

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The calcium aluminates are described in the CaO-Al_2O_3 binary phase diagram [1]. Within this system, five binary compounds can be distinguished that generically go by the name of calcium aluminates: $CaAl_2O_4$ (CA), $CaAl_4O_7$ (CA_2), $Ca_{12}Al_{14}O_{33}$ ($C_{12}A_7$), Ca_3AlO_6 (C_3A) and $CaAl_{12}O_{19}$ (CA_6), where C=CaO and A=Al_2O_3. These compounds are mainly generated by the diffusion of Ca^{2+} in an aluminium network, induced by the sintering of mixtures of CaO and Al_2O_3 at temperatures of around 1300ºC [2]. This is described by the following equations:

$$A + C \rightarrow AC$$

$$AC + C \rightarrow C_{12}A_7$$

$$C_{12}A_7 + C \rightarrow C_3A$$

Calcium aluminates have applications in heat-resistant cement since they are stable at high temperatures, and in steelmaking, in which the provision of a synthetic, calcium aluminate-based dross favours the desulphuring of the steel and the production of steel free of inclusions (especially of Al_2O_3). The presence of a molten calcium aluminate dross on the steel (i.e., synthetic slags) also facilitates secondary metallurgical work via its positive influence on the fluidity of the steel, its protection against re-oxidation, and via the prevention of temperature loss [3]. Most of the calcium aluminate used in the steel sector is sintered from mixtures of bauxite and lime. The Al_2O_3-rich dross produced during the melting of aluminium can be used as an alternative to bauxite.

The present work examines the synthesis of tricalcium aluminate (for use as a synthetic slags) from the dross produced in the manufacture of metallic aluminium in Holding furnaces. Three types of input dross were used with Al_2O_3 contents ranging from 51 to 82 wt%. Calcium aluminates were formed via the mechanical activation (reactive milling) of different mixtures of dross and calcium carbonate, and sintering at 1200ºC. The variables affecting the process, especially the milling time and the Al_2O_3:CaO molar ratio, were studied. The final products were examined via DRX, SEM, TEM and Raman spectroscopy, and their chemical composition compared with those of commercial synthetic slags.

The best results were obtained for a reactive milling time of 5 h in a ball mill, for a ball/dross mass ratio of 6.5. For a molar relationship of 1:3 (CaO: Al_2O_3), sintered products with calcium aluminate contents of over 90% were obtained, in which tricalcium aluminate was the majority compound (87%), followed by $C_{12}A_7$ (<5%). The calcium aluminate content of the commercial synthetic slags studied was 70% lower.

[1] Nurse R.W., Welch J.H., Majumdar A.J. (1965). The CaO-Al_2O_3 System in a Moisture-free Atmosphere, Trans. Br. Ceram. Soc., 64, 409-418.

[2] Williamson J., Glasser F.J. (1962). Reactions in Heated Lime-Alumina Mixtures, J. Appl. Chem. 12, 535-538.

[3] McGannon H.E. (1998). The Making, Shaping and Treating of Steel (Steel Making and Refining), 11th Edition, American Society for Metals, United States Steel Corporation, Pittsburgh, Pennsylvania.

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PYROMETALLURGICAL RECOVERY OF TIN FROM TAILINGS OF PENOUTA Sn-Ta-Nb DEPOSIT

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The Penouta Sn-Ta-Nb deposit is located in the Central Iberian Zone (CIZ) towards the innermost part of the Iberian Variscan Belt in Galicia, northwestern Spain. Here, the Viana do Bolo Series (which consists mainly of highly metamorphic rocks) and the Ollo de Sapo Formation (best represented in this zone by an augen gneiss) crop out. The deposit is largely a sheet-like albitized and greissenized granitic cupola, elongated in the SW-NE direction, with a maximum length of about 1100 m, a maximum E-W width of 700 m, and a maximum depth of over 200 m. It is mainly composed of quartz, albite, muscovite and K-feldspar, with garnet and beryl as common accessory minerals. Banded pegmo-aplite dikes commonly occur in the apical zone of the granite. The cupola system culminates with the development of a stockwork of quartz veins up to 2 m thick which caused the strong greissenization of the hosting augen gneiss and the granitic cupola. The deposit was extensively mined during the 1970s to obtain cassiterite from the granitic cupola and the related hydrothermal quartz veins. Tantalum was obtained as byproduct. The open pit methods employed targeted the kaolinised leucogranite and those portions of the country rock that had become muscovitised and soft enough to be extracted using free dig methods. These materials were not milled, and only fragments up to 2 mm in size were treated in the gravity plant. Thus, large amounts of cassiterite and columbite group minerals were never liberated from the host rock. Unused host rock was progressively dumped in tailing ponds.

Strategic Minerals Spain S.L. is now constructing a specialised gravity plant designed to process these wastes. Pyrometallurgical reduction smelting [1] is a very effective way of obtaining Sn from gangue minerals, and some authors have examined the reduction of cassiterite by carbonaceous reductants [2,3]. SnO_2 is mainly reduced by the gaseous intermediates of CO and H_2, and the overall reduction rate of SnO_2 controlled by the gasification of carbon ($C + CO_2 \rightarrow CO$, Boudouard reaction) [4,5]. Some admixtures, e.g., K_2CO_3, SiO_2, Al_2O_3, CaO or metallic Sn, can accelerate the reduction of cassiterite by graphite. All of these admixtures reduce the activation energy required for the reduction reaction to occur - they have catalytic effects on the Boudouard reaction [6,7].The present work examines the carbothermic reduction of these mining residues for the production of Sn ingot (98.73 wt% Sn and 1.14 wt% Fe). Finally, this ingot was then subjected to electrorefining (1.2 A of density of electrical current; electrolyte flow rate: 5 l/h, and cathode-anode separation distance of 4 cm). Under such conditions, 90 wt% of the Sn in the ingot was recovered at a purity of 99.97%. A slag ($Ca_2(Nb,Ta)_2O_7$: 86.7%; $Ca(Nb,Ta)O_3$:6.6%; $(Fe,Mn)(Ta,Nb)_2O_6$:4.2% and SiO_2: 2.4%) is also produced during the pyrometallurgical recovery of the Sn, equivalent to 25% of the mass of the initial concentrate. Its content in Nb_2O_5 (21.4 wt%) and Ta_2O_5 (25.5 wt%), adding further value to the mine tailings.

[1] Peng Z., Mackey P.J. (2013). New development in pyrometallurgy, JOM 65, 1150- 1151.
[2] Pommier L.W. (1979). Effect of the coke in the volatilization of tin. JOM 31, 161- 162.
[3] Wright P.A. (1982). Extractive Metallurgy of Tin, 2nd Rev. ed. Elsevier Scientific Publishing Company Press, New York.
[4] Padilla R., Sohn, H.Y. (1979). The reduction of stannic oxide with carbon. Metall.Trans.B10, 109–115.
[5] Mitchell A.E., Parker R.H. (1988). The reduction of SnO_2 and Fe_2O_3 by solid carbon, Miner. Eng. 1, 53–66.
[6] Deventer J.S.J.V. (1988). The effect of admixtures on the reduction of cassiterite by graphite. Thermochim. Acta 124, 109–118.
[7] Komkov V.G., Gostishchev V.V., Ri E.K. (2009). Physicochemical aspects of carbothermic reduction of cassiterite in the ionic melt, Russ. J. Non-Ferrous Met. 50, 596–599.

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HIDDEN OCEANS: UNRAVELLING THE STRUCTURE OF HYDROUS DEFECTS IN THE EARTH'S DEEP INTERIOR

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High-pressure silicate minerals, like ringwoodite (γ-Mg_2SiO_4), which make up the main proportion of the earth's interior, can incorporate a significant amount of water in the form of hydroxyl defects [1,2]. Generally, they are charge balanced by the removal of low-valent cations such as Mg^{2+} $(V_{Mg}``+ 2H{**})$ [1-3]. The recent discovery of natural hydrous ringwoodite trapped as an inclusion in a diamond containing about 1 wt% H_2O is proving the presence of high water contents in the transition zone, which over the volume of the mantle equates to a potential mass of H_2O in the Earth's interior that exceeds that of the oceans [4,5].

By combining high resolution 1D and 2D ^1H solid-state NMR spectroscopy with DFT calculations, we show that for ringwoodite (γ-Mg_2SiO_4) additionally to low-valent Mg^{2+} defects also high-valent Si^{4+} vacancies are formed, even at a water content as low as 0.1 wt%. They are charge balanced by either four protons $(V_{Si}````+ 4H{****})$ or one Mg^{2+} and two protons $(Mg_{Si}``+ 2H{**})$. Surprisingly, also a significant proportion of coupled Mg and Si vacancies $(Mg_{Si}V_{Mg}````+ 4H{****})$ are present. Furthermore, all defect types feature a pronounced orientational disorder of the OH groups which results in a significant range of OH···O bond distributions. We are able to reproduce these in MD-DFT simulations enabling a quantification of the ratio of the four realized defect types from the ^1H MAS NMR spectrum.

As such, we are able to present unique insight into the defect chemistry of ringwoodite, which not only accounts for a large fraction of the Earth's entire water budget but will also control transport properties like viscosity [6] and thermal conductivity [7] in the mantle. The quantification of the various defects now provides the basis for detailed analysis of their influence on the chemical and physical properties of ringwoodite's spinel structure and as such on the macroscopic properties of the Earth's mantle.

[1] Keppler H., Smyth J. (2006). Water in Nominally Anhydrous Minerals. Reviews in Mineralogy and Geochemistry, 1- 478.
[2] Griffin J., Ashbrook S. (2013). Solid-State NMR of High-Pressure Silicates in the Earth's Mantle. Annual Reports on NMR Spectroscopy, 241-332.
[3] Griffin J., Berry A., Frost D., Wimperis S., Ashbrook S. (2013). Water in the Earth's mantle: a solid-state NMR study of hydrous wadsleyite. Chemical Science, 1523-1538.
[4] Pearson D., Brenker F., Nestola F., McNeill J., Nasdala L., Hutchinson M., Matveev S., Mather K., Silversmit G., Schmitz S., Vekemans B., Vincze L. (2014). Hydrous mantle transition zone indicated by ringwoodite included within diamond. Nature, 507, 221-224.
[5] Inoue T., Yurimoto H., Kudoh Y. (1995). Hydrous modified spinel $Mg_{1.75}SiH_{0.5}O_4$: A new water reservoir in the mantle transition zone. Geophysical Research Letters, 117-120.
[6] Hustoft J., Amulele G., Ando J., Otsuka K., Du Z., Jing Z., Karato S. (2013). Plastic deformation experiments to high strain on mantle transition zone minerals wadsleyite and ringwoodite in the rotational Drickamer apparatus. Earth and Planetary Science Letters, 7–15.
[7] Thomas S.-M., Bina C., Jacobsen S., Goncharov A. (2012). Radiative heat transfer in a hydrous mantle transition zone. Earth and Planetary Science Letters, 130–136.

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DETECTION OF MINERAL IMPURITIES IN DIATOMITE ORES

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Diatomite deposits with major amounts of mineral impurities present a problem in the production Diatomaceous Earth (DE). This industrial minerals product, which is characterised by its high porosity and chemical inertness, is produced from diatomite, a sedimentary rock formed by the accumulation of the skeletal remains of diatom algae. The sediments consist mainly of opaline (amorphous) silica, with a common occurrence organic matter and secondary minerals. In deposits of economic interest, mineral impurities that alter the chemical reactivity and the porosity of the DE products cause an increment in the mine waste and reduction in the product quality. As a consequence, there is a strong industrial interest in characterising and quantifying such impurities in order to set strategies for mining optimisation.

This work presents a case study where the combination of multiple analytical techniques was used to characterise a diatomite deposit with known presence of carbonates. First, thin section and environmental scanning electron microscope (ESEM) observations of rock samples were used to describe the texture and main composition of the diatomite ore. Then, by using diffuse reflectance mid-IR spectroscopy in rocks and powders with a hand-held analyser, the type of silica and carbonate were determined. The images from thin sections and ESEM revealed that the diatomite ore is mostly composed of diatom frustules intercalated with laminae of carbonates. Based on the IR data, the silica phase is characterised as only opaline, without evidence of re-crystallisation; the carbonate phase is composed of calcite and aragonite. Additional XRF data suggested that a small clay fraction is present and evaporite minerals are discarded.

These findings show that for optimising the production of DE, the deposit can be described in terms of two components: opal and calcite-aragonite. In the diffuse reflectance spectra, the silica and carbonate phases have clear distinctive features that would permit the integration of spectral data with the quality parameters of the ore in order of not only identify but also quantify the carbonate impurities. Moreover, the use of a hand-held analyser offers the opportunity of measuring more thus more representative samples with little effort. Such results could be used to support mine planning and processing activities aiming to reduce waste and increase the efficiency of the production.

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PREDICTION OF SOLUBLE ALUMINA IN THE KAOLIN CALCINATION REACTION FROM DIFFUSE REFLECTANCE INFRARED SPECTRA

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For industrial applications, highly refined kaolin is calcined at temperatures above 1000ºC, triggering chemical, morphological and mineralogical changes. The aim of the calcination process is to create a white, non-abrasive and chemically inert product. In order to control these properties, the Standard Operating Procedure (SOP) in the industry is the extraction of soluble aluminium. This parameter measures the reactivity of the calcined kaolin and estimates on its abrasiveness. However, this procedure has a long turn-around time that prohibits operational feedback. As a consequence, there is a strong industrial interest on the development of an on-line and automated measurement of soluble aluminium.

This study proposes a methodology based on diffuse reflectance infrared (IR) spectroscopy that serves as a proxy for the measurement of soluble aluminium. The technique was chosen based on its capabilities for implementation as an on-line and automated tool, and because it can detect the mineralogical changes associated to the crystallinity of the calcined kaolin, which are linked to the soluble aluminium content. For this, feed and products collected from a calcined kaolin processing plant were characterised using diffuse reflectance IR spectroscopy in the mid- and long-wave ranges (MWIR and LWIR, respectively) using a portable instrument. The spectral features that explain the transformation in the calcined kaolin reaction were identified, and the IR spectra were used as input for a Partial Least Squares (PLS)-based regression model for the prediction of soluble aluminium.

In the IR spectra, the amorphous and highly reactive phase was characterised by broad Al-OH, Si-O and Al-O absorption features. The transition towards a crystalline phase was evidenced in the spectra by changes in the shape and wavelength position of the absorption features. These variations describe the stability of the mineral structure, which is related to the reactivity of the material, and the formation of crystals that influence the abrasiveness. The input for the PLS model was restricted to the wavelength ranges where the relevant absorption features occur, thus avoiding the influence of environmental factors. The resulting model has a good performance for the prediction of the soluble aluminium values, showing that the IR spectra can be used as a proxy for the measurement of the SOP.

In a mineral processing environment, portable IR instruments can record spectra from the calcined kaolin production on-site and periodically. The short time required for the data collection and processing enables the generation of results in near real-time. These data can be integrated to the plant's monitoring system giving timely feedback to operators for adjusting the parameters for calcination. As a consequence, reduction of energy and costs can be expected, thus increasing the efficiency of the operations.

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WETTABILITY ALTERATION IN MODEL SYSTEMS MIMICKING LOW SALINITY WATER FLOODING

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The effects of low salinity water flooding, an enhanced oil recovery technique, are believed to be caused by improvement of the water wettability of sandstone reservoirs. Ion-mineral interactions in thin brine films are likely underlying this macroscopic wettability alteration. However, the exact mechanism, in particular the influence of brine composition, is still under debate. To address this, we studied the dependence of the contact angle on the cation composition in a system with muscovite as substrate, and decane with stearic acid as ambient. Experiments with binary mixtures of cations revealed that both Ca^{2+} and Mg^{2+} compete with Na^{+}, where the former two increase and the latter decreases the contact angle. Also K^{+} competes with Ca^{2+}. Mixtures of the four cations, with concentrations as in seawater, were explored in three dilution series, two of them with supplementations: i) with monovalent salts to maintain ionic strength and ii) with divalent cations to maintain their concentrations. Our results clearly indicate that the divalent cations determine the contact angle, except at very low salinity where also ionic strength has an influence. The implication of our findings is that divalent cation bridging, rather than charge screening (in the thin aqueous film adjacent to the drop) is responsible for wettability changes induced by diluting seawater. This picture was corroborated by experiments where drops of artificial seawater were diluted (and selectively supplemented) in situ.

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SIMULTANEOUS REMOVAL AND RECOVERY OF URANIUM FROM AQUEOUS SOLUTION USING ANATASE PHOTOELECTROCHEMICAL REDUCTION

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U(VI)-containing wastewater has potential radiation hazard to the environment, but contains valuable uranium resource. Based on the reduction of U(VI) and the difference in solubility between U(VI) and U(IV), here we construct a anatase-based photoelectrochemical cell to remove U(VI) and recover uranium from aqueous solution. By irradiating anatase photoanode at *E*=0.45 V *vs.*SCE, U(VI) can be simultaneously removed from aqueous solution and recovered as solid uranium compounds on a FTO glass cathode. Since ethanol can act as hole scavenger to protect the formed U(IV) and provide CO_2^{-}× as reductant, ethanol adding improved the U(VI) reduction efficiency of anatase-based photoelectrochemical cell.

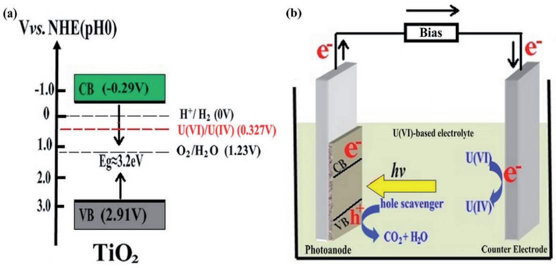

Fig. 1. (a) Relationship between the band structure of TiO_2 and redox potentials of water splitting and U(VI)/U(IV). (b) Schematic diagram of TiO_2-based photoelectrochemical cell for U(VI) photoelectrochemical reduction.

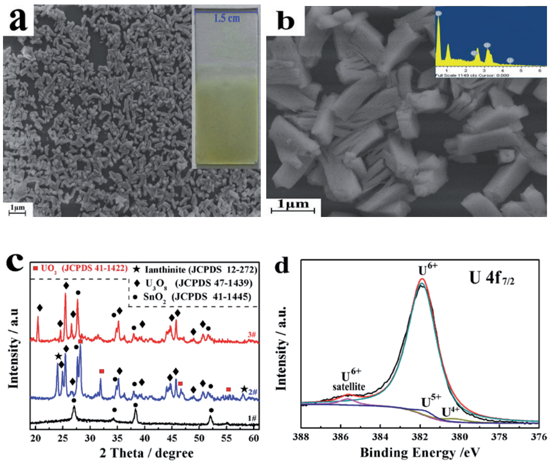

Fig. 2. (a) Photograph and SEM image of the uranium-based compounds film formed on FTO glass cathode, (b) high-magnification SEM image of the formed film (inset: EDX spectrum of the film), (c) XRD pattern of (1#) FTO glass and the formed film on FTO glass cathode (2#) before and (3#) after annealing in air at 300℃, (d) High-resolution U4$f_{7/2}$ spectrum.

[1] Wang G., Zhen J., Zhou L., Wu F., Deng N. (2015). Adsorption and photocatalytic reduction of U(VI) in aqueous TiO_2 suspensions enhanced with sodium formate. J. Radioanal. Nucl. Chem.304:579-585.
[2] Kim K., Lee S., Ryu J., Park H. (2015). Solar conversion of seawater uranium (VI) using TiO_2 electrodes. Appl. Catal. B 163:584-590.

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DEVONIAN DOLOMITE TYPES USED IN CULTURAL HERITAGE MONUMENTS OF LATVIA

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The present study deals with the re-investigation of dolomite in Latvia to evaluate the potential application of this rock for restoration as a replacing material of details in Cultural Heritage Monuments and in architecture as decorative material. It has been stated that Latvian dolomite resources meets the appropriate quality and reserves for production of required raw replacing materials.

Commercial dolomite beds in Latvia are distributed in the Frasnian Stage (Upper Devonian) bedrocks. Mineral deposits are in places, commercial dolomite beds of the Plavinas and Daugava formations are covered by the Quaternary deposits of small thickness. Various types of dolomites are in both formations. Study of raw stone materials in University of Latvia allows concluding that extracted Frasnian dolomites in geological section are highly variable by physical properties, mineralogical, and chemical composition.

Mineralogical and petrographical analyses (light microscopy, SEM, EDS) have helped to determine lithological types of rocks, and to specify important features and characteristics of dolomites. Small slabs of natural stone from renovated historical objects together with large samples of analogic material from outcrops and quarries were used to prepare thin sections or were involved in experimental study [1].

Petrographic investigations have confirmed that Upper Devonian carbonate rocks mainly are dolomites which have formed by the replacement of limestones in two stages of dolomitization process such as early (penecontemporaneous) and late (metasomatic), both leading to purely crystalline mosaic rock types. The results of detailed petrographic and mineralogical investigations show that some of stone materials have analogues in mineral deposits exploited today. According to structurally genetic classification system there are considerable differences among physical and mechanical properties of the marble-like and earthy-like lithological dolomite types [2].

A comparative investigation improves understanding of weathering processes of stone materials too [3]. Different changes caused by weathering, corrosion, and pollution of natural construction materials take place in stones used in ancient buildings of Medieval towns in Latvia or in modern architecture only some ten years ago.

Mineralogical and petrographic study of decay of different dolomite types leads to conclusion that correlation between rock's characteristics (mineral composition, texture, fabric, physical and mechanical properties) could be established, however results obtained up to date are insufficient to recommend this methodology for assessment, evaluation, and prediction of weatherability and durability of individual dolomite types.

[1] Lindina L., Krage L., Bidermanis L., Vitina I., Gaidukova I., Hodireva V., Kreilis J. (2011). Formation of calcium containing minerals in the low temperature dolomite ceramics. IOP Conference Series: Materials Science and Engineering, Volume 25, Issue 1: 9 p.

[2] Hodireva V., Sidraba I. (2010). Recognition and decay of Upper-Devonian dolomite lithological morphological types in Architectural Heritage. In: “Proceedings of the XIX CBGA Congress”, special volume 99, Thessaloniki: pp. 245-253.

[3] Hodireva V., Sidraba I., Purvins E. (2010). Lithological morphological types of Upper Devonian dolomite in Riga cultural heritage monuments. In: “Scientific Journal of Riga Technical University, Material Science and Applied Chemistry”, 22nd Vol., Riga: pp.105–113 (in Latvian).

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COMPUTER AIDED OPTIMIZATION OF DRAWING PROCESSFOR SHAPE MEMORY ALLOY MICRO-TUBE

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In this study, finite element analysis and optimization methodwere conducted onthe drawing process for shape memory alloy (NiTi alloy) tube with a diameter of 1.0 mm and, thickness of 0.1 mm.The initial outer diameter and thickness of thepreform tube were 10.0 mm, 0.5 mm, respectively and drawing speed was establishedconstantly at 3.8 mm/s. The drawntube will be used for stentsafter laser cutting and electrolytic polishing processes. Design variables of optimization procedure in our drawing process are the outer diameter, inner diameter of inlet tube, reduction ratiosin area and radius of each drawing pass. If the maximum plastic strain was more than 0.3 or the drawing force was more than 10 tons, then the penalty has been conceded to the variables. Untilthe outer diameter and inner diameter of theoutlet tube reached the target dimension, the calculation was conducted 50 times repeatedly, while changing the values of variables. MSC. Marc for drawing simulation and I-sight for the optimization of drawing process were used. From the drawing the 1st pass to the 7th pass, the soft mandrel drawing method was used and from the 8th drawing pass to the 20th pass, the fixed mandrel drawing method and sinking method wereutilizedto separate the mandrel from the tube and obtain the precise tubedimension.As a result of the optimization of thedrawing process, the target tube was obtained with the outer diameter 1.0 mm, thickness 0.09 mm at the 20th drawing pass. In the future, these results will be verified by drawing experiments.

[1] Yoshida K., Furuya H. (2004). Mandrel drawing and plug drawing of shape-memory-alloy fine tubes used in catheters and stents. Journal of Materials Processing Technology, 153-154, 145–150.
[2] Kuboki T., Nishida K., Sakaki T., Murata M. (2008). Effect of plug on levelling of residual stress in tube drawing. Journal of Materials Processing Technology, 204(1-3), 162–168.
[3] Palengat M., Chagnon G., Favier D., Louche H., Linardon C., Plaideau C. (2013). Cold drawing of 316L stainless steel thin-walled tubes: Experiments and finite element analysis. International Journal of Mechanical Sciences, 70, 69–78.
[4] Sang-Kon Lee, Myeong-SikJeong, Byung-Min Kim, Seong-Kon Lee, Seon-Bong Lee (2013). Die shape design of tube drawing process using FE analysis and optimization method, Int. J. Adv. Manuf. Technol., 66, 381–392.
[5] Béland J.-F., Fafard M., Rahem A., DAmours G., Côté T. (2011). Optimization on the cold drawing process of 6063 aluminium tubes, Applied Mathematical Modelling 35, 5302–5313.

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THE FUTURE OF SEM-BASED AUTOMATED MINERALOGY AND ARTIFICIAL INTELLIGENCE IN APPLIED MINERALOGY

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The ability to automatically collect data on mineral/phase identity, texture and their proportions in a sample (automated mineralogy, AM) is becoming essential in research and industry alike [1].

Scanning electron microscopy (SEM) based rapid X-ray acquisition and analysis methods used today are largely based on Reid's original work dating back to 1970 [1]. Since that time there has been tremendous development supported by improvements of the X-ray detectors, easily accessible computing power and advances in complex programing.

Current AM systems are capable of collecting millions of analytical points in resolution down to a couple of microns on a thin section or polished block in a short time and provide reliable mineral/phase identification and a full set of textural and other characteristics within hours or even minutes for the whole sample [2].

The general purpose of the automation is to collect statistically robust data from representative samples in a fast and repeatable manner. The automation can provide information which could not be obtained by any other means [1]. Automated mineralogy can now provide quantitative mineralogy data in a much more feasible and economic manner than human operators, thus making the previously impossible tasks possible.

The future of the technology can be seen in a potential for improved speed and even more precision and accuracy of the system on the hardware side. On the software side, the implementation of "Big Data" concepts, NoSQL databases, the use of massive parallelization of the tasks and higher incorporation of artificial intelligence in data collection and interpretation would be required. Better sample preparation, mounting and their automation [3,4] could be seen as an important part of the future developments to ensure good sample representativeness which is essential.

This is a very complex task and opens a lot of opportunities for research and development. The challenges also include standardisation of AM techniques and evaluation of variability in automated quantitative mineralogy for different instruments and methods [5,6] aiming for their full accreditation. Extending AM applications from the classical realm of process mineralogy towards everyday use in mineralogy, petrology and geoscience as well as environmental science and other areas is slowly becoming a reality. If the developments continue in the right direction, these systems will become the instruments of choice in the near future, for all geological departments and could even revolutionize the way electron microscopy is used in many areas of science.

[1] Gottlieb P. (2008). The Revolutionary Impact of Automated Mineralogy. XXIV International Mineral Processing Congress, At Beijing, China, Volume: Proceedings of XXIV IMPC.
[2] Sandmann D. (2015). Method Development in Automated Mineralogy. TU Bergakademie Freiberg, Dissertation, 176 pages.
[3] Grant D.C., Goudie D.J., Shaffer M., Sylvester P. (2016). A single-step trans-vertical epoxy preparation method for maximising throughput of iron-ore samples via SEM-MLA analysis. Applied Earth Science Vol. 125, Iss. 1.
[4] Kwitko-Ribeiro R. (2012). New sample preparation developments to minimize mineral segregation in process mineralogy, in Proceedings of the 10th International Congress for Applied Mineralogy (ICAM), (ed. M. A. T. M. Broekmans), 411– 417; Berlin: Springer-Verlag.
[5] Lastra R., Paktunc D. (2016). An estimation of the variability in automated quantitative mineralogy measurements through inter-laboratory testing, Minerals Engineering, Volume 95, September 2016, Pages 138-145, ISSN 0892-6875.
[6] Gu et al. (2014). The value of automated mineralogy. Miner. Eng., 58 (2014), pp. 100–103.

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USING AN AUTOMATED APPROACH IN BUILDING A DUST PARTICLE ATLAS FOR RESEARCH AND ENVIRONMENTAL MONITORING

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The transport of dust particles (both natural and artificial) is more important than previously thought. It possesses numerous potential risks for both human health and the environment. In the global perspective, the deposited dust is around 8 g/m^2/year for a worldwide average and about half that is preserved, buried into sediment or infiltrated into soils and rocks. It is represented by a mixture of organic and inorganic particles of a complex nature. All the dust particles tend to mix before deposition irrespective of their source and distance from origin.

At present, there is very little evidence about the individual sources and transport patterns of a large proportion of this material. We are facing the difficulty of evaluating very heterogenic material with particle sizes from 1 nm to 1 mm in terms of a better understanding of the sources and their effect on the environment.

In our research, we aimed to develop a simple sampling, sample preparation and automated analysis procedure to create a basic workflow for easy routine evaluation of deposited dust material primarily from the geological perspective. A monitoring method of “micromarkers” which can fingerprint a particular source/origin was used in conjunction with the modal and textural evaluation of the contained mineral matter.

Numerous preparation techniques were tested. The most appropriate for the majority of the materials proved to be the combination of polished sections/blocks doped with ultrafine (P80 = 75 µm) epoxide particles (for reducing the problem of agglomerate formation) and carbon tape imprints (where a small part of a sample is dispersed on a sticky carbon tape).

A newly developed “DOT mapping” [1] analysis mode designed in collaboration with TESCAN for the TESCAN Integrated Mineral Analyser (TIMA) [2] was tested to collect modal, textural and compositional data on large populations of deposited dust particles on carbon tape and in polished sections.

The DOT mapping analysis mode first uses a BSE image at a high resolution (0.3 µm in our case) to identify individual dust particles as well as preliminary phases. Then, a suitable spot inside each phase is chosen and each phase is covered by a lower resolution mesh of measurement points with the chosen point used as the origin of the mesh. A selected small number of X-ray counts is acquired at each measurement point (1500 in our case) to create a spectrum for analysis.

A combination of the high-resolution BSE image and the lower-resolution spectroscopic data is used to improve the phase segmentation when the spectroscopic data show that a preliminary phase comprises multiple mineral phases with different chemistry. This method provides an excellent compromise between high resolution x-ray mapping and the point spectrometry to speed up the analysis of both mounted particle sections and imprints without compromising spatial resolution.

One sample can produce up to 1 million representative analytical points in less than 1 hour and collect data to represent more than 50,000 dust particles of a ~10 µm size.

Future developments include the design of advanced “Adaptive” DOT map mapping techniques and the use of artificial intelligence and neural networks to cluster and interpret the collected data. Also the inclusion of data on the organic constituents in deposited dust is under development. As a part of the research a free online database of dust particles and micromarkers – a “DUST PARTICLE ATLAS” is being made available to the public and the research community.

[1] Motl D. (2015). Czech patent application, No. 2015-651, Unpublished (filing date Sep 22, 2015), (David Motl, applicant).
[2] Motl D., Filip V. (2013). Method and apparatus for material analysis by a focused electron beam using characteristic x-rays and back-scattered electrons. TESCAN, a.s., Brno, US Patent Application No: 2013/0054, 153. US 20130054153 A1, 20 pp.

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URANIUM BIOPRECIPITATION BY SHEWANELLA PUTREFACIENS UNDER AEROBIC CONDITIONS

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The removal behaviour of U(VI) by *Shewanella putrefaciens* (*S.* p*utrefaciens*) was investigated in this study. Our results demonstrated the formation of uranium phosphate biomineral, predominantly existed as chernikovite ($H_2(UO_2)_2(PO_4)_2 \cdot 8H_2O$), on the cell surface of *S.* p*utrefaciens.* The lamellar chernikovite was found at slightly acid pH, but not at pH > 7.0. Phosphate-containing groups played the key role in the formation of chernikovite based on the analysis of IR. After ashing and hydrothermal process, bacterially mediated chernikovite can be transformed into inorganic uranium phosphate and UO_2, respectively. The findings can provide a potential strategy for *in-situ* bioremediation of uranium in aerobic environment.

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STRUCTURE-BIO-ACTIVITIES OF SYNTHETIC SILICATE FIBERS RELATED TO DISSOLVED HIGH-VALENCE IONS AND OXIDE RADICALS

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The wide use of asbestos and its silicate substitutes has given rise to studies on their possible harmful effects on human health and environment. However, their toxic effects remain in unclear. The present study was aimed to disclose the coupled effects of dissolved high-valence ions and oxide radicals using the *in vitro* cytotoxicity and genotoxicity of chrysotile (CA), nano-SiO_2 (NS), ceramic fiber (CF), glass fiber (GF) and rock wool (RW) on Chinese hamster lung cells V79. Changed morphology of V79 cells clearly indicated cellular damage induced by exposure to theses dusts. The cell mortality was correlated well with chemical SiO_2 content of asbestos substitutes and the amount of dissolved Si. Alkali or alkaline earth metal elements relieved mortality of V79 cells, Al_2O_3 reinforced toxicity of materials. Asbestos substitutes generated lasting, increasing amount of a-cellular •OH of which formed at the fiber surface at sites with loose/unsaturated bonds, as well as by catalytic reaction through dissolved iron ions. Accumulated mechanical and radical stimulation induced the intracellular reactive oxygen species (ROS) elevation, morphology change and deviating trans-membrane ion flux. The cellular ROS appeared as NS > GF > CF ≈ CA > RW, consistent with cell mortality rather than with a-cellular •OH generation. However, both the cellular ROS and a-cellular ·OH were apt to attack to the cell membrane,even cell chromosomal and DNA. All dusts but CF induced significant increase of LDH and disturbance in ion influx and efflux balance of which revealed the membrane damage. In particular, the relative extracellular increase of Na^+ and Cl^- correlated inversely with LDH release, which may be attributable to Na^+ and Cl^- ionic pump malfunction. The asbestos substitutes (with concentration 50 to 200 μg/mL) all induced significant and dose-dependent increase of F_{MN}, TL, T% and OTM. The highest damage occurred in cells exposed to NS, other mineral dusts produced less damage. Chromosomal and DNA damage in V79 cells was not directly associated with the cellular ROS, while influenced by dissolved high-valence irons in co-culture medium. In conclusion, ions from short-time dissolution of dusts samples and the generation of extracellular •OH presented combined effects in the elevation of intracellular ROS, of which further synergistically induced the cytotoxicity and genotoxicity.

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THE HERBICIDE 4-CHLORO-2-METHYLPHENOXYACETIC ACID (MCPA) IS ENHANCING MOBILITY OF COPPER IN SOIL

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Crops designed and genetically modified to be tolerant to smart herbicides have led to a boost in agrochemicals application. Carboxylic acid herbicides such as 4-chloro-2-methylphenoxyacetic acid (MCPA; IUPAC name 4-chloro-*o*-tolyloxyacetic acid) are currently widely used to control the spread of annual and perennial broad-leaved weeds in crops. MCPA is worldwide the 2nd most widely applied herbicide after glyphosate because of both claimed for favorable toxicological properties such as very low toxicity to field workers handling the chemical, and for consumers ingesting residues of it through food. In MCPA, one methyl group of the phenoxy moeity is replaced by a chlorine atom, increasing its polarity and hence solubility in pure water. However, a fact yet neglected is that the residual carboxylate group of MCPA has strong chelating capacity with Cu and other trace metals to form bidentate chelate complexes. On the other hand, the application of Cu-containing fertilizers on soils which are deficit in available micronutrients, sewage sludge deposition, and in particular the massive application of Cu-bearing fungicides in the past (e.g., Bordeaux mixture known to control mildew in vineyards since 200 years), have steadily increased soil Cu content in soils. Therefore, the mobility of the Cu, if applied together or in sequence with the herbicide, could be enhanced in soil drastically. The herbicide may increase the concentration of Cu in soil porewater, and also competing with surface complexation. On the other hand, Cu-MCPA interactions may also facilitate immobilization via co-adsorption processes by ternary surface complex formation. This has been shown already for the case of glyphosate, but to our knowledge not yet for MCPA.

Pure MCPA is relatively weakly retarded by soil at ambient pH values, with typical $\log K_d$ values of -0.10 ± 0.56 L kg^{-1}. Biochar amendments were found to have little retarding effect on the behavior of MCPA in soil in terms of increasing sorption and decreasing leaching. Kersten et al. [1] have shown that anionic MCPA is physisorbed by outer-sphere complexation at its deprotonated, anionic carboxyl group to positively charged surface sites of ferric oxy-hydroxides, and even chemisorbed as neutral molecule forming inner-sphere surface complexes, but both effectively in the acidic pH range (pH <4) only. Although ferric oxy-hydroxides in soil are often coated with humic matter, this coating was not found to increase their sorption capacities for MCPA at ambient soil pH values significantly. MCPA is also barely adsorbed by soil organic matter because of the low $\mathrm{pH}_{\mathrm{pzc}}$ values of humic acids. Sorption of phenoxy acid herbicides to ferric oxy-hydroxides only was found to fully explain their K_d values after taking account of the strong pH dependence. Ferric oxy-hydroxides are in fact the most chemically reactive Fe compounds and contribute large proportions of the specific surface areas in soils, even though they are present at relatively low concentrations in bulk soil.

The present study concerns cooperative and competitive adsorption reactions among the Cu cation and the MCPA herbicide anion ligand in presence of the typical soil ferric oxy-hydroxide mineral goethite (α-FeOOH). The fit curves to the experimental batch equilibrium data are based on an adsorption model of the binary Cu-goethite and MCPA-goethite adsorption systems using a charge distribution multi-site surface complexation (CD-MUSIC) model. For both the binary adsorption systems Cu-goethite and MCPA-goethite, previously published CD-MUSIC model parameters were used [1,2]. An overall good match with experimental data on Cu adsorption in presence of MCPA was found when the Cu model is combined with the dissolved Cu-MCPA_2 complex formation constant, without invoking any ternary Cu-MCPA surface complex formation. This means that the Cu-MCPA2 complex is highly mobile at pH values below 6, but becomes highly insoluble (rather than adsorbed) and hence immobile at pH values above 6. Therefore, there is a mobility window in acidic soils (pH range 4-6), where pure Cu may become adsorbed, but not in presence of the herbicide. We used this mobility window for soil column tests at pH values of 5-6, where the high mobility of Cu in presence of the herbicide was visualized by radioisotope labeling with ^{64}Cu and positron emission tomography. Movies will be shown of the rapid Cu migration in the soil column as output of the sophisticated PET molecular imaging experiments.

[1] Kersten M., Tunega D., Georgieva I., Vlasova N., Branscheid R. (2014). Adsorption of the herbicide 4-chloro-2-methylphenoxyacetic acid (MCPA) by goethite. Environ. Sci. Technol. 48, 11803-11810.

[2] Weng L., Van Riemsdijk W.H., Hiemstra T. (2008). Cu^{2+} and Ca^{2+} adsorption to goethite in the presence of fulvic acids. Geochim. Cosmochim. Acta 72, 5857-5870.

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QUARTZ SANDSTONE TREATMENT FOR CARBOTHERMIC PROCESS

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The solar grade silicon as feedstock for photovoltaic cells production requires a high purity. Its cycle of production consists on silica carbothermic reduction and purification in order to obtained solar grade silicon [1]. However, often, preliminary silica enrichment is needed to remove impurities. This process will provide required silica quality up to 99% of SiO_2, which will be suitable for the solar grade silicon production [2].

The X-ray fluorescence, the scanning electron microscopy and Raman spectroscopy have been used to investigate the morphological and microstructural proprieties of El Taref silica (eastern Algeria). The most important impurities in the samples studied were iron oxide and titanium oxide. The After characterization, this raw material carried out the magnetic separation followed by acid leaching processes in order to remove the impurities concentration in the crystal lattice and on its surface.

After magnetic separation of the raw material with Fe_2O_3 and TiO_2 concentration up to 1.58% and 0.3%, respectively, a value less than 0.6% of Fe_2O_3 and less than 0.2% of TiO_2 have been reached. The magnetic separation was followed by acid leaching process to improve more the quality of treated silica.

After leaching process the content of SiO_2 achieves 99.22%. Gravimetric separation after leaching allowed us to obtain a residual iron concentration value of 96 ppm, which is in agreement with required content for silica as raw material for carbothermic process destined for photovoltaic field (< 100 ppm) [3].

[1] Braga A.F., Moreira S.P., Zampieri P.R., Bacchin J.M.G, Mei P.R. (2008). New processes for the production of solar-grade polycrystalline silicon, Solar Energy Materials & Solar Cells, 92, 418–424.
[2] Huang F., Chen R., Guoa J., Hong sheng Ding A., Yanqing Su A., Yang J., Fu H. (2014). J. Mater. Sci. Semicond. Process. 23, 14-19.
[3] Kheloufi A. (2009). Acid leaching technology for obtaining a high-purity silica for photovoltaic area, CET, DOI 10.3303/CET0917119, 197-202.
[4] Technical and Technological Report (2010). Zenith Mining and Construction Company, N°4, 126.

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EFFECTS OF HALLOYSITE NANOTUBE STRUCTURE ON PROPERTIES OF BIODEGRADABLE POLYMER NANOFIBERS

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Electrospinning technique enables to prepare nanofibers from synthetic as well as natural polymers important for many potential applications in the biomedical area [1]. In addition nanofibers have found utilization in filtration, desalination, protective clothing, and in sensors. In our earlier work we have found that by application tubular halloysite substantial improvement end use properties of biodegradable nanofibers have been achieved [2]. This research work focused on the effect of tubular halloysite (HNT) structure on properties of biocompatible nanofibers based on blend of hydrophobic, synthetic polycaprolactone and hydrophilic, natural gelatin (PCL/GEL) mixed at a 1:1 volume ratio. Nanofibers have been prepared on laboratory machine Nanospider™ based on needle-free, high voltage and free liquid surface electrospinning process [3]. As a solvent has been used environmentally acceptable acetic acid. To evaluate the effect of halloysite structure on properties of PCL/GEL nanofibers several types of tubular halloysite from different deposits have been used. The main attention was given to the examination of halloysite inner and outer diameter, aspect ratio and specific surface area on morphology and mechanical properties of PCL/Gel nanofibers. Geometry of halloysite nanotubes was measured by TEM microscopy. Specific surface area was determined from physical adsorption of nitrogen at the temperature of liquid nitrogen. The content of HNT in the nanofibers was varied from 0.5 up to 9.0 wt%. Chemical structure and thermal stability of the electrospun PCL/Gel/HNT mats were characterized by Fourier transform infrared spectroscopy (FTIR) and differential scanning calorimetry (DSC). Thermal stability of the nanofiber mats was investigated with thermal gravimetric analysis (TGA). The SEM analyses revealed that the volume and HNT type significantly influenced the morphology of the prepared mats. Fibre diameter as well as porosity and water uptake of nanofibers were gradually decreased in with increasing HNT concentration. The stress-strain analyses exposed that the incorporation of all types of HNTs significantly influenced the mechanical properties of the nanofibers. Young's modulus, elongation to failure and the tensile strength of the HNT/PCL/Gel nanofibers exhibited considerable improvements, in comparison to the pure PCL/Gel nanofibers. The highest improvements (100-300%) were observed when the content of HNT in nanofibers was 0.5 wt%. With increasing HNT content in nanofibers, the effect of HNT structure and specific surface area was much more evident.

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[1] Kai D., Liow S.S., Loh X.Y. (2014). Biodegradable polymers for electrospinning: Towards biomedical applications, Materials Science and Engineering, C 45, 659–670.
[2] Švachová V., Khunová V., Pavliňák D., Fohlerová Z., Vojtová L.. The effect of halloysite on structure and properties of polycaprolactone/gelatin nanofibers, Polymer Engineering & Science, in print.
[3] Jirsak O., Sanetrnik F., Lukas D., Kotek V., Martinova L., Chaloupek J. (2004). A method of nanofibers production from a polymer solution using electrostatic spinning and a device for carrying out the method, WO 2004CZ00056 20040908.

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FABRICATION OF ND-PR POWDERS BY CALCIOTHERMIC REDUCTION

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The rare earths in elemental form are required for a variety of scientific and technological purposes. They are not easily obtained in this form, due to the great chemical stability of the rare-earth compounds and the strong tendency of elemental metals to react with everything they come in to contact with. In recent years, a new generation of lanthanide-based intermetallic materials have emerged with excellent magnetic properties and also primary interest is focused on the light lanthanides, i.e. La, Ce, Pr, Nd, Sm and Y, even though the light lanthanides generally have smaller magnetic moments than the heavy lanthanides. Calciothermic reactions are metallothermic reduction reactions (more generally, thermic chemical reactions) which use calcium metal as the reducing agent at high temperature. Conventional metallothermic reduction is based on direct physical contact between feed (compound to be reduced) and reductant (metallic reducing agent). In this work, we present calciothermic reduction process for the synthesis of Nd-Pr powders using leached product from monazite. Two types of liquid after separate purification and oxalate solid particles were used respectivley [1]. Spray drying was employed for the preparation of precursors from $NdCl_3•6H_2O$, $PrCl_3•xH_2O$ and leaching solution from monazite. The precursors by spray drying could be obtained with various sizes from 2 to 10 μm by controlling concentrations of the solutions and process parameters. After heat treatment of precursors in air, Nd and Pr oxides were formed [2]. Nd-Pr oxalate complex was precipitated from leached product by adding oxalic acid. And it was simply oxidized by heat treatment. Both of oxide powders were mixed with Ca or CaH_2 as reducing agent and pressed into pellets. The pellet was then placed in a high density alumina crucible, which was placed in high temperature electrical furnace at 1000 ºC under argon atmosphere. In order to remove CaO and residual Ca, the particles were washed with water, ball milling in ethanol, rinsing with water and acetone and then dried in vacuum chamber. Finally, high purity of Nd-Pr powders was obtained.

[1] Suzuki R., Inoue S. (2003). Calciothermic reduction of Titanium oxide in molten salts. Metallurgical and Materials Transactions B, 34B, 277-285.

[2] Zheng H., Ito H., Okabe T. (2007). Production of Titanium powder by the calciothermic reduction of Titanium concentrates or ore using preform reduction process. Materials Transactions, 48, 8, 2244-2251.

[3] Kumar T., Kumar S., Rao M., Prakash T. (2013). Preparation of Niobium metal powder by two-stage Magnesium vapor reduction of Niobium pentoxide. Journal of Metallurgy, 2013, 1-6.

[4] Zhou Z., Hua Y., Xu C., Li J., Li Y., Gong K., Ru J., Xiong L. (2016). Preparation of ferrotitanium from illenite by electrolysis-assisted calciothermic reduction in $CaCl_2$-NaCl molten salt. The Journal of The Minerals, Metals & Materials Society, 68, 2, 532-539.

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THE ROLE OF AUTOMATED MINERALOGY IN THE IMPROVEMENT OF GOLD RECOVERY AT THE KITTILA MINE, FINLAND

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Automated mineralogy (AM) is increasingly becoming a widely used method in mineral processing. Both modal mineralogy and textural data (e.g. the degree of liberation of mineral grains within host particles) can help improve processing efficiency. Mining operations without access to either a central laboratory or on-site AM systems often use single sample analysis to generate this information. Mineral balancing, where the information is collected from feed, concentrate and tailings, is both more complex and useful, allowing calculation of recoveries of a given mineral with in specific liberation classes. Composite monthly samples or special plant surveys are often used for such studies.

In our paper, we introduce the integration of the TIMA (Tescan Integrated Mineral Analyzer) automated mineralogy solution for increasing the efficiency of mineral extraction. Routine daily composite samples from the Agnico Eagle Kittilägold mine in Finland were subjected to mineralogical analyses over several weeks. Modal mineralogy and textural data from all streams (over 600 samples) were collected to quantify the mineral texture of rocks, ores and plant products. All mineralogical, process control and metallurgical data were merged into a single large database form assbalancing and integrated examination. This novel approach enables the description of the key mechanisms driving recovery of gold and the selection of the most cost effective solution for flotation performance. Integration of both mineralogical and metallurgical knowledge points to the future exploitation of the hidden potential of automated mineralogy.

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FLY ASHES OF THE PECHORA BASIN, RUSSIA: WASTES AS RESOURCE

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Coal is one of major energy resources. The combustion of coal at power plants produces large quantities of fly ash and slag, occupying wide areas and causing damage to the environment. To reduce environmental risks we need strategy of waste recycling as resources of functional materials or minerals. The strategy is represented on the example of wastes of Pechora coal basin. Our researches used modern scientific instruments. The wastes were distinguished to ore and alumina silicate components.

The aim of work is a complex study of wastes of coal power plants as resources and their possible application in industry including extraction of valuable minerals and elements, zeolite synthesis (temperature, reaction time, alkali concentration) and researches of sorption-structural parameters of the synthesized zeolites and their cation-exchange properties for NH^{4+}, Ba^{2+}, Sr^{2+}, radionuclides (U, Ra, Th).

As a result of the hydrothermal reaction several types of zeolites were synthesized from the fly ash by adding NaOH (concentration from 1.5 to 4.5 mol/dm3) at 80-180°C: zeolite X, zeolite P and analcime. It was shown that the experimental conditions (temperature, reaction time and alkali concentration) had a significant influence on the type of zeolite and its content in the reaction products. The final product was powder: mix of zeolite and unreacted residue in various ratios with yield 70-80% to the weight of initial fly ash. The bulk density was 0.78-0.83 g/cm^3. The reaction temperature affected the type of synthesized zeolites: wide porous zeolites were formed at 90-100°C (zeolite X), increasing reaction temperature resulted in the formation of medium (zeolite P) and narrow porous (analcime) types. We showed that the type of zeolite and its content in the reaction products were significantly affected by the reaction time and the concentration of alkali. The series of experiments resulted in building schematic diagram of zeolites crystallization [1].

The sorption-structural characteristics of the synthesized products depend on the type and content of zeolite in the mixture. The specific surface area of the synthesized zeolites varies in a wide range from 28 to 269 m^2/g depending on the type of zeolite. The specific surface area of fly ash is 3-9 m^2/g.

Sorption capacity of Ba^{2+} has high values from 113 to 157 mg/g (1.65–2.29 mg·equiv/g). Capacities of Sr^{2+} and NH^{4+} equal 86 mg/g and 32 mg/g (1.94 и 1.78 mg·equiv/g), respectively.

Sorption degree of radium is up to 98%, thorium – 89%, uranium – 81%. Desorption of radionuclides is 5-10%. We showed that the combination of a high sorption activity with the ability of retaining of radionuclides (low desorption) was an important feature of sorbent due to the lack of secondary contamination. The synthesized zeolites can be used to adsorb and retain radionuclides in solutions of wide range of concentrations. The application areas are from low-concentrated natural waters to high active radioactive wastes from nuclear power stations and others [2].

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[1] Kotova O.B., Shabalin I.N., Shushkov D.A., Kocheva L.S. (2016). Hydrothermal synthesis of zeolites from coal fly ash. Advances in Applied Ceramics: Structural, Functional and Bioceramics, V 115, I 3, pp. 152-157.

[2] Kotova O.B., Shabalin I.L., Shushkov D.A., Ponaryadov A.V. (2015). Sorbents based on mineral and industrial materials for radioactive wastes immobilization // Vestnik of the Institute of Geology of Komi SC of UB of RAS, № 2, pp. 32–34. (in Russian)

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MECHANISM AND KINETICS OF HEMATITE CRYSTALLIZATION IN AIR: LINKING BULK AND SURFACE MODELS VIA MESOPOROUS FILMS WITH DEFINED NANOSTRUCTURE

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The oxides, hydroxides, and oxide-hydroxides of iron belong to the most abundant materials on earth. They are highly relevant for environmental processes as co-precipitation or sorption of trace elements and nutrients [1,2], but find also widespread applications as artificial materials in medicine [3], sensing [4], and catalysis [5]. Despite the relevance of iron oxygen phases, many of the transformation processes between these phases are still under investigation. In particular, the crystallization of quasi-amorphous hydroxides and oxide-hydroxides is difficult to assess, since typical diffraction and scattering methods provide only sample-averaged information about the crystallized phases.

We report a new approach for the investigation of the crystallization of oxide-hydroxides. The approach relies on model-type films that comprise a defined homogeneous nanostructure. The nanostructure allows to link quantitatively information obtained by bulk-averaging diffraction techniques (XRD, SAXS) with locally resolved information, i.e. domain sizes (SEM, TEM, LEEM) and phase composition (SAED).

Using time-resolved imaging and diffraction we deduce mechanism and kinetics for the crystallization of ferrihydrite into hematite in dry atmosphere. Hematite forms via nucleation of hematite domains and subsequent domain growth. The Johnson-Mehl-Avrami-Kolmogorov model describes the kinetics of the observed phase transformation over a wide temperature range. The activation energy can be estimated by applying the Arrhenius equation to the temperature dependent transformation.

The contribution will discuss the detailed crystallization mechanism of ferrihydrite to hematite and will investigate carefully the kinetics of this process under dry conditions.

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[1] Brinza L., Vu H.P., Shaw S., Mosselmans J.F.W., Benning L.G. (2015). Effect of Mo and V on the Hydrothermal Crystallization of Hematite from Ferrihydrite: An in Situ Energy Dispersive X-ray Diffraction and X-ray Absorption Spectroscopy Study. Cryst. Growth Des., 15, 4768-4780.

[2] Zhu M., Legg B., Zhang H., Gilbert B., Ren Y., Banfield J.F., Waychunas G.A. (2012). Early Stage Formation of Iron Oxyhydroxides during Neutralization of Simulated Acid Mine Drainage Solutions. Environ. Sci. Technol., 46, 8140-8147.

[3] Marcu A., Pop S., Dumitrache F., Mocanu M., Niculite C.M., Gherghiceanu M., Lungu C.P., Fleaca C., Ianchis R., Barbut A., Grigoriu C., Morjan I. (2013). Magnetic iron oxide nanoparticles as drug delivery system in breast cancer. Appl. Surf. Sci., 281, 60-65.

[4] Das P., Mondal B., Mukherjee K.Y. (2014). Facile synthesis of pseudo-peanut shaped hematite iron oxide nano-particles and their promising ethanol and formaldehyde sensing characteristics. RSC Adv., 31879.

[5] Bassi P.S., Gurudayal, Wong L.H., Barber J. (2014). Iron based photoanodes for solar fuel production. Phys. Chem. Chem. Phys., 16, 11834-11842.

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COMBINED RAMAN AND EDXS ANALYSES ON DRILL CORE SAMPLES

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This presentation deals with the results of combined spectroscopic analyses performed on a sample extracted from a core drill obtained from a geological survey for raw materials mining purposes. The aim of the work was to detect the major mineral component phases following an experimental protocol setting up the bases that will be developed further within the EU-H2020 SOLSA project (http://www.solsa-mining.eu), funded by the EU-H2020 Raw Material program. In this framework, an expert system, coupling sonic drilling and combined analytical tools for automatic recognition of core minerals will be developed and tested.

In the present study, both micro-Raman as well as Energy dispersive X-Ray spectroscopy tests were carried out in a complementary way. The sample, in form of a solid bar with a very dark/black colour, was labelled as BC6 (18/84, 60 m), and, according to the provider (the French mining and metallurgical group ERAMET), it consists of sulfur minerals, mainly pyrite.

Micro-Raman spectra were carried out in backscattering geometry by means of a Horiba-Jobin Yvon apparatus (model LabRam HR), consisting of a single spectrograph an objective 80X, a notch filter and an holographic grating (600 lines/mm). The spectra here reported were excited by the 633 nm of a He-Ne laser and recorded by a CCD (256x1024 pixels) detector, cooled at -134°C by liquid N_2. The laser spot size at sample surface was about 3 µm, the laser power was 1.5 or 3 mW, and the integration time of the order of 100 s. The energy dispersive X-ray spectra (EDXS) were acquired with a system (mod. Falcon Zaphire, EDAX) attached to a scanning electron microscope (SEM- mod. XL30, FEI)) operated in a low-vacuum mode and using an accelerating voltage for the primary electrons of 20 kV. When the low-vacuum mode is used, the specimens can be observed in the as delivered conditions, with no need of surface coating with a conductive film, to prevent electrostatic charging, in case the observed sample was partially or fully non conductive. Film coating would have been unacceptable in the present case for possible interference of the X-ray lines from the film (C or Au are typically used) and those coming from the underlying sample material.

SEM images of several millimeter or sub-millimeter regions of the BC6 sample clearly show its poly-crystalline and multi-phase structure, with the presence of grains of about 100 micrometers in size. EDXS spectra of the same sample regions allow for the determination of the local relevant chemical composition. These results still do not provide precise indications on the mineral phases that are there in the analyzed sample. Phase composition is an extremely critical information, in view of the drilling conditions to be adopted and, most importantly, the extraction methodology to be used to obtain from the mined ores the metal(s) of interest. Therefore, the analytical data were cross-checked and implemented using Raman spectroscopy.

Raman spectra observed from two different micro-regions in the central region of this sample indicates in both cases a significant occurrence of microcrystalline graphite, revealed by the very strong and quite narrow D and G bands in the region of 1300-1650 cm^{-1}. In addition, a noticeable pyrite FeS_2 component is observed, in the first case, while, in the other case, dolomite ($CaMgCO_3$) with a relatively minor occurrence of pyrite FeS_2 is observed. Several additional Raman measurements on morphologically unlike micro-regions, especially on microcrystalline grains, allowed to detect, besides the always present microcrystalline graphite, also dolomite ($MgCO_3$), and, in turn, quartz SiO_2 alone or, even, accompanied by a minor amount of pyrite. Finally, in some cases microcrystalline graphite alone was observed.

These results provide now a clear picture concerning of the chemical and phase composition of the analyzed sample. For the experimental tools that we have used in this feasibility study, the sample regions are extremely small as compared to the interesting size for real mineralogical core drills. Indeed, within the SOLSA project the acquisition of analytical and crystallographic data will rely also on “larger scale” tools, e.g., X-ray diffraction and X-Ray fluorescence, carried out in a hierarchical way so to optimize the acquisition times and relevant combined data processing. As a further step forward, the whole knowledge acquired from the experimental and test strategy will be used for designing a multi-analytical instrumentation, that will render the whole data acquisition procedure and analysis protocol comparatively fast and user friendly.

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REDUCTION OF ENVIRONMENTAL IMPACT OF INDUSTRIAL AND MINING ACTIVITIES: VIABLE SOLUTIONS FOR ECO-SUSTAINABLE BUILDINGS

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Construction industry has a significant environmental impact, being responsible for energy consumption, CO_2 emissions and consuming about 50% of all materials extracted, thus depleting natural resources. The construction sector is currently required to become more sustainable and the use of secondary materials, such as wastes from both industries and construction/demolition activities, represents a viable and valuable solution for the reduction of its environmental impact. Waste generated from industrial activities (industrial by-products) are increasing substantially and such materials, for quantity, distribution, characteristics or low chances of re-use in more added-value applications, represent a serious environmental and socio-economic problem. In addition, waste resulting from construction and demolition activities (construction and demolition wastes – CDW) have been identified by the European Commission (EC) a priority target due to their large volumes and the potential for re-use and recycling. These waste materials are considered among the most significant waste streams in EU and are, therefore, available in quantities large enough for feeding the construction sector. Recycling or reutilization of industrial and construction/demolition wastes in the building sector contribute to reduce waste amounts sent to landfills or incinerators and prevent also consumption of natural resources.

This work presents the promising results of the *SUS-CON European project* (founded by 7th Framework Programme, grant agreement 285463, duration 2012-2015) [1], dealing with the valorisation of industrial wastes, and the ambitious challenges of the *RE^4 European project* (founded by Horizon 2020 Work Programme, grant agreement 723583, duration 2016-2020) [2], allowing the reduction in the use of materials from mining activities. *SUS-CON project* aimed at developing new technology routes to integrate waste materials (e.g. ashes from thermal-power plants or slags from metallurgical plants to replace cement, which production has an high environmental impact, and post-consuming plastics) in the production cycle of concretes, both for ready-mixed and precast applications, resulting in an innovative lightweight, eco-compatible and cost-effective construction material, made by industrial waste materials (up to 100% by weight) and characterized by low embodied energy and CO_2 as well as thermal insulation performance. *RE^4 project* aims at radically modify the construction process by promoting new technological solutions for the design and development of structural and non-structural, eco-compatible and cost-effective pre-fabricated elements with high degree of recycled materials from construction and demolition waste (e.g. concretes, bricks, tiles, fine fractions or lightweight materials - plastic, wood - from residential, industrial or commercial buildings demolition activities) and reused structures from the partial or total demolition of buildings (up to 65% by weight). Both projects are intended for the development of building materials with reduced environmental impact; these solutions allow, respectively, reduction of industrial wastes disposal and consumption of not-renewable natural raw materials, with positive impacts for both industrial and mining activities.

[1] SUS-CON (SUStainable, innovative and energy-efficient CONcrete, based on the integration of all-waste materials) project web-site: www.sus-con.eu.
[2] RE^4 (Reuse and Recycling of CDW materials and structures in energy efficient pREfabricated elements for building Refurbishment and construction) project web-site: www.re4.eu.

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CORROSION INHIBITION AND LIFE EXTENSION OF STEEL BY USING ORGANIC OIL EXTRACTS

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The corrosion life of steel is important consideration for marine and chemical structure used in seawater or sulfuric acid environment. For corrosion life extension of steel, anti-corrosive nano-coating, chemical painting resistance, as well as the use of non-toxic natural corrosion inhibitor such as plant oil extract have been practical approaches. In this study, the effects of eco-friendly spearmint oil extracts on corrosion resistance of steel were investigated. Inhibition efficiency (I.E) of the oil extract was evaluated by immersion test in 3.5 mass% NaCl and 1M HCl solution as a function of oil concentration (i.e., 0, 5, 10, and 15 ml), respectively. Corrosion I.E of the spearmint oil increased with increasing oil concentrations up to about 40% and 80% in 3.5 mass% NaCl and 1M HCl solution, respectively. Corrosion morphology and products on the steel surface were discussed in relation with the observed corrosion inhibition behavior.

Keywords: eco-friendly organic oil, corrosion inhibition, inhibition efficiency, spearmint oil.

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INTERFACIAL ENERGIES FOR $CaCO_3$ NUCLEATION: EFFECTS OF SUBSTRATE, STRAIN AND SURFACE CHARGE

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Through the use of optical methods or grazing incidence small angle x-ray scattering (GISAXS) in concert with classical nucleation theory and reasonable assumptions, interfacial energies for Ca carbonate nucleation on substrates have been determined for a range of materials.

For example, heterogeneous $CaCO_3$ nanoparticle nucleation on near perfect mica, quartz and feldspar substrates is associated with interfacial energies of 24, 36 and 44 mJ/m^2, respectively, while similar nucleation on organic monolayers ranges from 70 to 90 mJ/m^2, and homogeneous nucleation appears to be at about 120 mJ/m^2 [1-3].

The reasons for this spread of energies are many and would include differences in surface binding, surface charge, strain energy (when the nucleus is coherently bound to the substrate), and confounding experimental factors that alter nucleation density and thus sampling accuracy. Another complication is the notion that while calcite is the stable form of large nuclei, vaterite is believed to be the usual initial phase formed, and the possibility of amorphous calcium carbonate (ACC) as a nucleating phase cannot be discounted.

Here we discuss these various complications in interpretation of the interfacial energy and suggest approaches for evaluating strain energy. We also discuss how changes in interfacial energy affect nucleation for natural carbonate-containing liquids contacting rock materials with varied mineralogy.

[1] Fernandez-Martinez A., Hu Y., Lee B., Jun Y-S., Waychunas G.A. (2013). In Situ Determination of Interfacial Energies between Heterogeneously Nucleated $CaCO_3$ and Quartz Substrates: Thermodynamics of CO_2 Mineral Trapping. Environmental Science & Technology 47, 102-109. Please pay attention to the rules for preparing your abstract.

[2] DeYoreo J.J., Waychunas G.A., Jun Y-S., Fernandwz-Martinez A. (2013). *In situ* Investigations of Carbonate Nucleation on Mineral and Organic Surfaces. Reviews in Mineralogy and Geochemistry 77, 229-257.

[3] Li Q., Fernandez-Martinez A., Lee B., Waychunas G.A., Jun Y-S. (2014). Interfacial Energies for Heterogeneous Nucleation of Calcium Carbonate on Mica and Quartz. Environmental Science & Technology 48, 5745-5753.

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INTERACTION OF POLYHYDROXY FULLERENES WITH FERRIHYDRITE: ADSORPTION, AGGREGATION AND DEGRADATION

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The rapid development of nanoscience and nanotechnology, with thousands types of nanomaterials (e.g., carbon nanomaterials) being produced, will eventually lead to various environmental impacts [1,2]. Thus, understanding the behavior and fate of these nanomaterials is of great importance. As iron (oxyhydr)oxides are ubiquitous in the environment and contain abundant surface active groups (e.g., Fe-OH), they have been considered as an important family of geosorbents that can significantly affect the environmental behaviors of various chemicals (e.g., heavy metal ions, oxyanions) [3,4]. Therefore, iron (oxyhydr)oxides are expected to play important role in the geochemical process of nanomaterials.

This study focused on the interaction of polyhydroxy fullerenes (PHF) with ferrihydrite (Fh), a wide-spread iron (oxyhydr)oxide nanomineral in the environment. The obtained adsorption isotherm for PHF on Fh could fit the D-R model well, with the calculated adsorption mean free energy of 10.72 kJ/mol. A rapid increase of solution pH and a decrease of the Fh surface zeta potential were observed after the adsorption of PHF on Fh. FTIR detected a red shift of C–O stretching from 1075 cm^{-1} to 1062 cm^{-1} and a decrease of Fe-O bending, implying the interaction between PHF oxygenic functional groups and Fh surface hydroxyl. In addition, vibration of nitrate at 1384 cm^{-1} indicated that nitrate could also be adsorbed on Fh, and the adsorption amount decreased (i.e., decreased absorption intensity) with the increasing loading amount of PHF. In this term, anion exchange combining with anion exchange contributed to the adsorption of PHF on Fh. The adsorbed PHF could trigger the aggregation of the Fh particles by changing their surface physicochemical properties, since an aggregation of PHF and Fh with the detected particle size increasing from ~2 nm to larger than 5 nm were measured by AFM. The TEM imaging showing rather evenly distribution of C and Fe further suggested the aggregation of Fh was possibly bridged by PHF. In addition, the degradation of PHF under simulated solar irradiation as shown by the degradation rate of TOC were accelerated from 5% to 30% in the presence of Fh, possibly due to the Fenton-like chain reaction [5].

Our results indicated that the interaction between PHF and Fh could evidently influence the migration and degradation process of PHF, and thus controlling their environmental fate and behaviors. Further investigation will be needed to elucidate interaction between PHF and Fh in a long term (e.g., effects of PHF loading on the transformation of Fh to more crystalized minerals and the release of PHF during the transformation of Fh).

[1] Wagner S., Gondikas A., Neubauer E. (2014). Spot the difference: engineered and natural nanoparticles in the environment: release, behavior, and fate. Angew. Chem. Int. Ed., 53, 12398-12419.
[2] Raghavendhran A., William A.J., Brie S. (2014). C60 Fullerene Soil Sorption, Biodegradation, and Plant Uptake. Environ. Sci. Technol., 48, 2792−2797.
[3] Schwertmann U., Cornell R.M. (1991). Iron oxides in the laboratory: Preparation and characterization, VCH: Weinheim, Germany.
[4] Moon E.M., Peacock C.L. (2012). Adsorption of Cu(II) to ferrihydrite and ferrihydrite–bacteria composites: Importance of the carboxyl group for Cu mobility in natural environments. Geo. Cosmochim. Acta, 92, 203-219.
[5] Kwan W.P., Voelker B.M. (2002). Decomposition of hydrogen peroxide and organic compounds in the presence of dissolved iron and ferrihydrite. Environ. Sci. Technol., 36(7), 1467-1476.

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INTERFACE INTERACTION BETWEEN STRONTIUM IONS AND SACCHAROMYCES CEREVISIAE UNDER CULTURE CONDITIONS

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Strontium ion is normal in many environments, but its isotopes such as ^{90}Sr and ^{89}Sr may be found in the waste from nuclear reactors or nuclear accidents. Biosorption shows attractive advantages for heavy metal and radioactive nuclides treatment. The studies on interface interaction between strontium ions and *Saccharomyces cerevisiae* cells will contribute to further understanding of biosorption mechanism. Under culture conditions, the results showed that the strontium ion bioremoval efficiency by *S. cerevisiae* could exceed 90%. The high initial concentration strontium ions may react with culture medium components, for example, SO_4^{2-}. This can be used as an artificial modulation method for strontium ion content in solution. A programmed gradient descent biosorption process was designed to utilize the biosorption capacity of microorganism for low concentration metal ions. The strontium ion bioremoval ratio reached approximately 99.9% after 3 cycles biosorption under culture conditions and the remaining strontium ions concentration in solution could meet the standard of drinking water (0.2-5.0 mg L^{-1}) or discharge standard ($\leq$ 10 mg L^{-1}). The detail adsorption and bioaccumulation analysis showed that the cell surface was the major site for biosorption and interface interaction. Adsorption quantity on yeast cell wall for strontium ion (q_{pas}) accounted for about 90% of total biosorption amount, while, it was only 10% for the quantity of strontium ions bioaccumulated in the yeast cytoplasm (q_{act}). The q_{pas} could be described as Langmuir isotherm and a mathematical model was proposed for bioaccumulation analysis. The model indicated that q_{pas} could first promote the bioaccumulation (q_{act}), then the accumulated strontium ions (q_{act}) would conversely inhibit further bioaccumulation (Δq_{act}), which may be regulated by energy-dependent efflux system. The *S. cerevisiae* cell surface contains a large number of mannoprotein, glucan and chitin. Many fuctional groups exsit in these biological macromolecules. The role of surface functional groups is to provide adsorption site for strontium ions. When modified the fuctional groups, the biosorption ratio decreased greatly. The order of fuctional group for biosorption of strontium ions was amino group > carboxyl group > ester group. The Fourier transform infrared spectroscopy (FTIR) suggested that the O or N of –COOH, –OH and $–NH_2$ groups formed –O-Sr, –N-Sr, or –CO-Sr coordination binding states when strontium ions interacting with these functional groups. The main binding form can be described as a mononuclear six- (or four-) coordinate model. Besides these, the $–PO_2^-$ group may also participate in adsorption or transmembrane transportation. Mesoscopic analysis also indicated that the strontium ions may form some precipitates on surface besides adsorption and bioaccumualtion. So, the interface interaction between strontium ions and *S. cerevisiae* cells included three mechanisms: adsorption with surface functional groups, bioaccumulation in cytoplasm and precipitation on surface.

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THE APPLICATION OF NATURAL DIATOMITE AS CATALYST SUPPORT FOR THE OXIDATION OF TOLUENE

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Diatomite, known as diatomaceous earth or kieselgur, is a fine -grained and low-density biogenic sediment. Diatomite frustules are mainly composed of amorphous hydrated silica ($SiO_2 \cdot nH_2O$), which is categorized as non-crystalline opal-A according to the mineralogical classification. Diatomite is inexpensive and readily available, because diatomaceous silica is an abundant form of silica on earth and there are many diatomite reserves worldwide. With several unique physical and chemical characteristics, e.g., highly developed mesoporosity and/or macroporosity, strong acid resistance, thermal stability, and high mechanical strength, diatomite is a nice choice as support in the fabrication of catalyst.

Herein, through the application of diatomite-supported manganese oxide as catalysts for thermally toluene oxidation, three aspects were focused on: (i) the valence, microstructure, and distribution of MnO_x on diatomite, (ii) effect of supported MnO_x content on catalytic performance, (iii) the reaction mechanism, structure-activity relationship, and application prospect of the prepared catalyst. The fundamental information derived from this study is important for the application of diatomite as catalyst support and the development of novel catalysts for toluene abatement.

In this work [1], the catalytic oxidation of toluene over manganese supported on diatomite catalysts was studied. The following findings can be derived from the present investigation. (i) The manganese species are mainly in the phase of amorphous MnO_2 and Mn_2O_3 on the diatomite, accompanied with low content of $MnCO_3$. The Mn oxides gradually aggregate on diatomite as the increase of Mn content. (ii) The manganese-supported on diatomite catalysts show excellent activity and high selectivity to CO_2 for toluene oxidation. With the increase of Mn content, the catalytic activity becomes better. The catalysts also show high activity toward toluene oxidation even after a week of test, indicating strong stability. (iii) The reaction mechanism in this study follows the Mars-Van Krevelen (MVK) mechanism. With higher adsorption-reaction sites associated with surface oxygen, the catalytic activity of manganese-supported on diatomite catalysts improves. Moreover, the superior catalytic activity is ascribed to the excellent reducibility of Mn^{4+}.

[1] Liu P., He H., Wei G. et al. (2017). An efficient catalyst of manganese supported on diatomite for toluene oxidation: Manganese species, catalytic performance, and structure-activity relationship. Microporous and Mesoporous Materials, 101-110.

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SPECIFIC ION EFFECTS ON MM-SIZE ALUMINA PARTICLES: A SURFACE COMPLEXATION TO DESCRIBE SHIFTS OF ISOELECTRIC POINTS AND LEVELS OF ZETA-POTENTIALS

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Experimental data on surface charge densities in NaCl and zeta-potentials in various monovalent salts for µm sized spherical alumina particles. Experimental data were obtained by classical potentiometric titrations (relative surface charge densities) and streaming potential measurements (zeta-potentials) in the absence of carbon dioxide. The surface complexation model successfully describes the data including the observed shifts of the isoelectric point in different monovalent salt solutions. Observed isoelectric points shift with varying salt concentration for a given salt and at constant salt concentration they change with the nature of the salt. The pristine point of zero charge of the particles is obtained in the absence of added salt (i.e. in a titration starting from MilliQ water).

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AN EXPERIMENTAL INVESTIGATION OF PD NANO-CATALYSTS PERFORMANCE IN GREEN CATALYTIC REACTIONS

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In this study, an investigation of employment of metal nanoparticles as catalysts in different green catalytic reactions was reported. Improvement in catalytic properties due size of catalyst reduced in situ is discussed and the dependence of nano- and micro-structural morphology on different parameters (temperature, reducing agent, presence of a phase transfer agent) is emphasized. A catalyst obtained by copolymerization of the metal-containing monomer Pd(AAEMA)2 [AAEMA− = deprotonated form of 2-(acetoacetoxy) ethyl methacrylate] with ethyl methacrylate as co-monomer, and ethylene glycol dimethacrylate as cross-linker, was used in two catalytic reactions: Suzuki-Miyaura cross-coupling of aryl bromides in water and oxidation of benzyl alcohols to the corresponding benzaldehydes under sustainable conditions. The reduction in situ of Pd (II) to Pd(0) forming the real active nano-species was confirmed through TEM analyses. In addition, the capacity of polymeric support in enhancing the stability of nanoparticles for several catalytic cycles was also demonstrated through TEM and IR analyses.

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USE OF MINERAL ACIDS FOR NEUTRALISATION OF BAUXITE RESIDUE PRIOR TO METAL RECOVERY BY ACIDIC LEACHING

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Bauxite residue (also called red mud) is a waste product produced in the industrial production of alumina. Storage of bauxite residue may be harmful to the environmental due to the presence of residual alkalis. However, some of the bauxite residues represent an attractive resource for scandium, yttrium and lanthanides not only by the presence of those elements in this material, but also due to the high amount of bauxite residue produced each year [1,2]. Nowadays, there are several methods available to extract those elements from the bauxite residue; however, those processes have presented some limitations (e.g. large reagent consumption, long residence time, high energy consumption) hindering their application at industrial scale. The alkalinity of the bauxite residue represents the most significant issue during direct acidic leaching or during safe disposal. In acid leaching, part of the acid is consumed for the neutralisation of alkaline waste products remaining from the Bayer process (aluminium hydroxide production).

In the current work, “neutralization with mineral acids” has been proposed as alternative for neutralisation of bauxite residue before acidic leaching. The bauxite residue alkalinity has been reduced during neutralisation by the partial dissolution of calcium-aluminate and calcium-silicate compounds. Concurrently, Na and Ca were readily dissolved in hydrochloric and nitric acid.. After leaching, an increase in the dissolution yield of major elements, e.g. Al, Fe, Ti, has been observed. However, silica has demonstrated a high polymerization rate (gel formation) when acid concentration has been increased. The recovery of selected rare earths, e.g. Sc, Y, La, Nd, is subjected to the co-dissolution of Al and Fe.

[1] Binnemans K., Jones P.T., Blanpain B., Van Gerven T., Pontikes Y. (2015). Towards zero-waste valorisation of rare-earth-containing industrial process residues: a critical review. Journal of Cleaner Production 99, 17–38.
[2] Evans K. (2016). The history, challenges, and new developments in the management and use of bauxite residue. J. Sustain. Metall. 2, 316-331.

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THE STUDY OF ALKALI-SILICA REACTION BY MEANS OF SYNCHROTRON X-RAY MICROTOMOGRAPHY AND DIFFRACTION TOMOGRAPHY

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The investigations of cement based materials affected by Alkali-Silica Reaction (ASR), as a weathering phenomenon in building materials, has attracted much attention. The ASR consists of chemical reactions between silica aggregate affected by different degrees of structural disorder (i.e. quartz crystals, opal, chert, etc) and the alkali and hydroxide ions in the pore water of concrete [1]. The ASR results in the precipitation of a gelatinous product (commonly reported as ASR gel), rich in silica, calcium-, sodium-, potassium-oxides and water that surround the aggregate. The expansion of ASR gel, because of the osmotic pressure due to the imbibition of pore solution, promotes cracks and fractures through concretes [1].

The ASR mechanism is poorly understood. There has been debate as to which mechanism is dominant in the ASR gel growth at the cement-aggregate interface. Hence, several authors assume that ASR products are gel whereas others report a “crystallised gel”, but this is still an open debate [2]. Lots of studies have been performed to highlight concrete structures affected by ASR, using traditional analytical techniques such as optical and electron microscopy.

For the first time, we have investigated ASR-affected cement based materials by means of X-ray diffraction microtomography combined with transmission microtomography using synchrotron radiation. In particular, several samples were prepared by mixing an aggregate of quartz grains reactive towards ASR and Ordinary Portland cement. The specimens were demoulded in a solution of 1M NaOH to enhance the ASR products formation.

The research aim was to monitor the weathering of the quartz crystals as the ASR proceeds. The quartz-XRD-peak based image reconstruction by X-ray diffraction microtomography combined with transmission X-ray microtomography allowed to assess ubiquitous distribution of this phase as well as by the line shape analysis on XRD-quartz-peaks we extracted microstructural information (domain size and microstructure) for clarifying how the ASR affects quartz crystals [3]. From the image reconstruction, the shape analysis of quartz crystals gave useful data for building mathematical model for quantifying the ASR in cement based materials. Furthermore, the X-ray diffraction microtomography provided fundamental information about the spatial distribution of the ASR gel. The analysis of the powder pattern allowed to clarify the true nature of the ASR gel (is it an amorphous and/or crystalline?). The ASR gel position was mapped by a selected portion of the measured powder pattern data containing its relevant scattering. The ASR gel distribution will also mapped by means of X-ray microtomography. In particular, the small differences in mass absorption coefficients of the gel filling the fractures and the cement phases during normal absorption contrast imaging technique could not provide the visualization of the complete microcracks framework present in the sample, thus requiring the use of the phase contrast X-ray microtomography. All the data allowed to quantify the ASR weathering in cement based materials. Finally, the spatial distribution of the weathering products (i.e. voids, fractures, etc) in the ASR-aged samples will be assessed by means of monochromatic phase-contrast X-Ray microtomography. A quantitative analysis of these weathering products (size, distribution, etc) was assessed by using the digital image analysis.

[1] Stanton T. (1940). Expansion of concrete through reaction between cement and aggregate. Proc Am Soc Civ Eng 66:1781–1811.
[2] Hobbs D.W. (1988). Alkali-silica reaction in concrete. Thomas Telford, London.
[3] Marinoni N., Broekmans M.A.T.M. (2013). Microstructure of selected aggregate quartz by XRD, and a critical review of the crystallinity index. Cement and Concrete Research 54, 215-225.

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COMPETITIVE ADSORPTION OF VOCS AND HUMIC MONOMERS FROM WATER ON HIGH-SILICA ZEOLITES

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The carboxylic acid and phenolic functional groups are abundant in natural organic matter and are present in the molecular structures of many natural and synthetic compounds released to water, including plant exudates, lignin derivative, and environmental contaminants. The aim of this study is to characterize the adsorption of selected monomer of humic acid by zeolites as part of a broader study on the adsorption of organic pollutants from dilute solution onto zeolites [1-5]. In order to evaluate the influence of natural organic matter on the removal of contaminants from water we studied sorption of caffeic acid (CA) and p-hydroxyl benzaldehyde (p-HBA) to commercial ZSM-5 zeolite. Both CA e p-HBA are low molecular weight compounds secreted into soil by plant tissues and/or decay of plant residues and play an important role in agricultural and ecological dynamics.

TOL (toluene, purity 99.9%), CA (purity 99.8%), p-HBA (purity 99.8%) were obtained from Sigma-Aldrich (Steinheim, Germany). The zeolite sample used in this study is a hydrophobic ZSM-5 (CBV28014, Zeolyst International) characterized by $SiO_2/Al_2O_3 \sim 280$, Na_2O content <0.05% w/w, NH_4^+ content <0.1% w/w, and surface area of 400 $m^2\ g^{-1}$. The concentration of contaminants in the aqueous solution was determined by Headspace Gas Chromatography coupled to Mass Spectrometry (HS-GC-MS) and by HPLC-DAD. Adsorption isotherms were determined using the batch method. X-ray diffraction experiments were carried out with a Bruker D8 Advance diffractometer equipped with SOL-X detector. Rietveld refinements were carried out by the EXPGUI interface, for General Structure Analysis System (GSAS). Harmonic vibrational frequencies were computed for CA e p-HBA in their Density Functional Theory (DFT) optimized geometry, and compared to experimental IR spectra. The adsorption of both CA and p-HBA on ZSM-5 has been investigated as a function of pH of the aqueous solution. Rietveld structure refinements provided information about the position of CA and p-HBA molecules inside the ZSM-5 structure after adsorption. Thermogravimetry data confirm the adsorption of CA from acid solution (pH=4).

In the presence of TOL, the adsorbed caffeic acid was replaced at pH 4, in contrast, the TOL adsorption was slightly affected by the presence of CA. The higher selectivity of ZSM-5 for TOL *vs* CA was also observed in the competitive adsorption of TOL and p-HBA aqueous mixtures. Similar results were also obtained for the p-HBA-TOL system. This finding was confirmed from structural investigation of ZSM-5 loaded with single component solution of TOL and CA and from a binary mixture containing both the chemicals (i.e. CA and TOL). Strong similarities between the X-ray powder pattern as well as FTIR spectra of ZSM-5 after adsorption of the mixture and after only TOL adsorption, indicate that ZSM-5 adsorbs preferentially and selectively toluene, also in the presence of CA or HBA. From this finding and from the results obtained by Rietveld structure refinements it was possible to assess that TOL is preferentially adsorbed onto ZSM-5 when it is present in solution with CA.

On the basis of these results we can conclude that zeolites may be suitable for integration into drinking water and wastewater treatment systems and in environmental remediation projects concerned with removal of emerging organic contaminants

[1] Martucci A., Rodeghero E., Pasti L., Bosi V., Cruciani G. (2015). Adsorption of 1, 2-dichloroethane on ZSM-5 and desorption dynamics by in situ synchrotron powder X-ray diffraction. Microporous and Mesoporous Materials, 215, 175-182.

[2] Rodeghero E., Martucci A., Cruciani G., Bagatin R., Sarti E., Bosi V., Pasti L. (2016). Kinetics and dynamic behaviour of toluene desorption from ZSM-5 using in situ high-temperature synchrotron powder X-ray diffraction and chromatographic techniques. *Catalysis Today*, *277*, 118-125.

[3] Pasti L., Martucci A., Nassi M., Cavazzini A., Alberti A., Bagatin R. (2012). The role of water in DCE adsorption from aqueous solutions onto hydrophobic zeolites. Microporous and Mesoporous Materials, 160, 182-193.

[4] Martucci A., Braschi I., Bisio C., Sarti E., Rodeghero E., Bagatin R., Pasti L. (2015). Influence of water on the retention of methyl tertiary-butyl ether by high silica ZSM-5 and Y zeolites: a multidisciplinary study on the adsorption from liquid and gas phase. RSC Advances, 5(106), 86997-87006.

[5] Braschi I., Martucci A., Blasioli S., Mzini L.L., Ciavatta C., Cossi M. (2016). Effect of humic monomers on the adsorption of sulfamethoxazole sulfonamide antibiotic into a high silica zeolite Y: An interdisciplinary study. Chemosphere, 155, 444-452.

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APPLICATION OF SCANNING LASER-INDUCED BREAKDOWN SPECTROSCOPY IN DRILLING CORE ANALYSIS

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Scanning Laser-Induced Breakdown Spectroscopy (LIBS) is an upcoming technology that is relatively unknown in geosciences. It has potential for rapid non-destructive and in-situ multi-element geochemical mapping, which could in particular be useful for relatively large and unpolished samples, e.g. drilling cores. It is a type of atomic emission spectroscopy that uses a laser-generated plasma to ablate, atomize, and excite material from a sample surface. Plasma variations due to physical and chemical matrix effects, however, influence the LIBS signal, which means that raw LIBS data are to be considered primarily qualitatively. In order to achieve reliable (semi-)quantitative results, appropriate classification and calibration strategies have to be developed.

LIBS can be used to rapidly map a large number of chemical elements. In contrast to XRF, LIBS can also be used to measure light element such as Li. Furthermore, optically non-obvious but chemically significant patterns, such as element ratios (e.g. Fe/Mg) in individual mineral grains, can be recognized that can be used to reconstruct crystallization histories. Characteristic examples of LIBS applications in drilling core analysis will be presented.

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AUTOMATED MINERALOGY: COMPARISON BETWEEN E-BEAM AND MICRO-XRF TECHNOLOGY

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Automated mineralogy has been successfully used in the mining industry since the 1970s. Since that time a variety of companies have developed competing technologies with a range of capabilities, however, with one aspect in common in that they are all based on an electron beam (e-beam) system (e.g. scanning electron microscope (SEM) with energy dispersive spectrometers (EDS)). Recent technological advancements mean it is now possible to focus X-rays using a polycapillary lens to a spot size of less than 20 micrometers. Accordingly, a micro-XRF system can be operated using similar parameters as an e-beam system and thus yield results compatible with traditional automated mineralogical analysis. The advantages and limitations of each technique are discussed, incorporating aspects such as sample preparation, analytical conditions, sample information and processing.

In general, the advantages of the micro-XRF include simpler sample preparation and the ability to analyse large samples, for example an analytical area of 20 cm by 16 cm. In addition, the x-ray source yields a spectral excitation with significantly lower limits of detection. The advantages of the e-beam based systems are the smaller beam size and excitation volume, as well as the ability to interactively use high magnification interactive imaging (for example, secondary electron or backscattered images). Whilst both systems are generically referred to as surficial analytical techniques, it should be noted that the micro-XRF has a greater depth penetration and excitation volume, and thus some differences can be expected. This can be an advantage or disadvantage depending on the objectives of the analysis. The interaction of the x-ray beam or electron beam with the sample yields different resultant spectra. Generally the x-ray beam will typically have an energy of 50 kV enabling higher energy lines to be detected with a maximum signal intensity for the transition metals. In contrast, the electron beam will typically have an energy of 25 kV, but yield a better x-ray signal for lighter elements such as Na, Mg, Al, and Si. In terms of practical analysis, it is possible to raster an electron beam over a low magnification area, thus limiting stage movement, and mosaic the analysed fields into a final image for processing. In contrast, a micro-XRF is fixed and all 2-D information is dependent on the stage movement. Both systems use energy dispersive silicon drift detectors (SDD) and thus have similar capabilities in this regard. The automated mineralogical systems, there are fundamental parameters that impact on the mineralogical classification and analytical time; this includes (but is not limited too) x-ray beam excitation (kV and μA), detector active areas (mm^2), pixel spacing (μm), and dwell time (ms).

A variety of case studies are used as the basis for comparison, including samples from exotic-Cu deposits in Chile, epithermal Au-Ag deposits in New Zealand, diamond deposits in South Africa, and REE deposits in Chile. Each of the case studies has been the subject of detailed investigations and thus a wealth of information exists to support the evaluation of the automated mineralogy results. The results are based on a Bruker M4 TORNADO^{AMICS}micro-XRF and a Zeiss based EVO QEMSCAN E430. In addition, it is also possible to attach a micro-XRF source to a SEM. To supplement the aforementioned comparisons a Bruker XTrace has been attached to a QEMSCAN, thus allowing the exact same points to be analysed by an electron and x-ray beam.

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NANOSTRUCTURED MATERIALS FOR GREEN CATALYSIS

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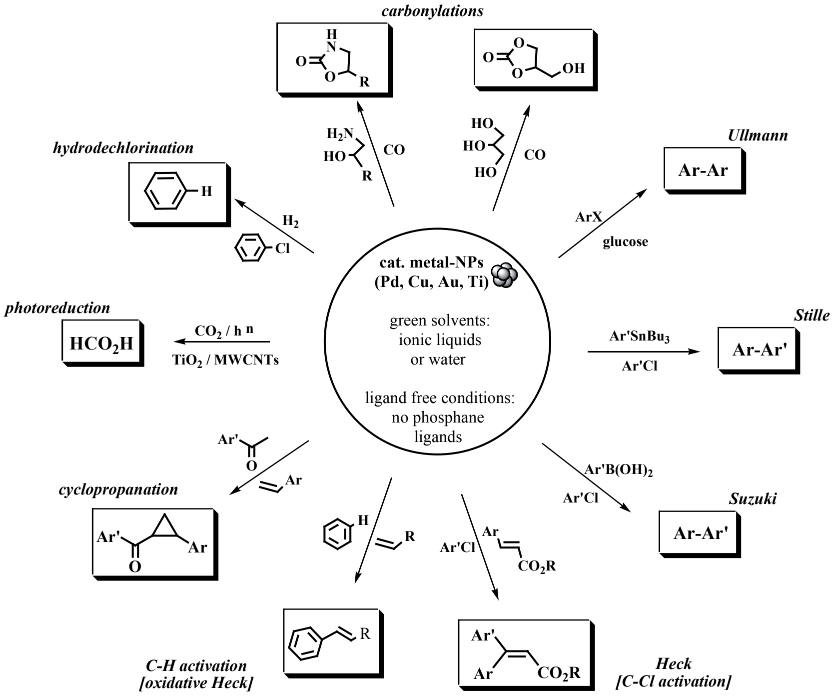
Transition-metal nanoparticles (NPs) are attracting a great deal of attention in almost any scientific and technological field, including catalysis, where nanoscale materials are becoming more prevalent in a wide range of applications such as fuel conversion, pollution abatement and fine chemical production [1]. Nowadays, many researchers are exploiting the high activity and selectivity of nanocatalysts to develop greener and waste-minimized processes.

During the last decade, we exploited nanostructured metal catalysts based on Pd, Cu, Au and Ti to perform a wide range of organometallic reactions (Heck, Suzuki, Ullmann, Stille, carbonylations, cyclopropanations, hydrodehalogenations and CO_2 photoreduction) under environmentally friendly conditions given by the absence of phosphane ligands and using neoteric solvents (ionic liquids, water and so on) as green reaction media [2].



This communication deals with our recent advances in controlling the catalyst performances by choosing properly the nature of both the reaction medium and nanocatalyst [3].

[1] Astruc D., Lu F., Aranzaes J.R. (2005). Nanoparticles as recyclable catalysts: the frontier between homogeneous and heterogeneous catalysis. Angew. Chem. Int. Ed. 44, 7852.

[2] Pârvulescu V.I., Hardacre C. (2007). Catalysis in Ionic Liquids. Chem. Rev. 107, 2615.

[3] a) Monopoli A., Cotugno P., Palazzo G., Ditaranto N., Mariano B., Cioffi N., Ciminale F., Nacci. A. (2012). Ullmann Homocoupling Catalyzed by Gold Nanoparticles in Water and Ionic Liquid. Adv. Synth. & Catal. 354, 2777, b) Cotugno P., Monopoli A., Ciminale F., Milella A., Nacci A. (2014). Palladium-Catalysed Cross-Coupling of Styrenes with Aryl Methyl Ketones in Ionic Liquids: Direct Access to Cyclopropanes. Angew. Chem. Int. Ed., 126, 13511.

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MINERAL FORMATION PROCESS IN AUTOCLAVED BINDERS BASED ON ALUMINOSILICATE GEOMATERIALS PRODUCED BY HYDROTHERMAL SYNTHESIS

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Inorganic binding systems «$CaO–SiO_2(Al_2O_3)–H_2O$», produced by hydrothermal synthesis and modified with reactive micro- and nanosized components are the base of many construction materials characterized by improved thermo-resistance, corrosion stability and biopositivity vs. traditional analogues as well as have high performance characteristics. Final properties of these materials directly depend of chemical composition and properties of new mineral phases, as products of phase formation processes. Thereby, investigation of processes of hardening and mineral formation in these binding systems is the key factor to produce the high-performance construction composites.

This study is important when using of virgin geomaterials with different composition and origin. In this paper the authors submit application of nanostructured modifier as reactive component. Nanostructured modifier is aluminosilicate polydispersed sedimentation stable system containing reactive amorphous (colloid) component and produced when wet mechanoactivation.

Goal of this work is study of phase- and structure formation of model system «$CaO–SiO_2(Al_2O_3)–H_2O$» containing modifiers based on different types of crystal raw materials such as silicates (quartz sand) and aluminosilicates (granite) when hydrothermal synthesis (increased pressure and temperature, saturated steam).

The typical phenomenon in these binding systems is supposed to be a superposition of the followings hardening mechanisms: hydration leading to *C–S–H* phase formation and geopolymerization leading to zeolite phase formation. Understanding of phase transformation mechanisms in the system «$CaO–SiO_2(Al_2O_3)–H_2O$» taking into account chemical composition of modifiers and regime of hydrothermal synthesis allows manipulation of structure formation processes to provide the best values of performance characteristics for final materials having optimal structure.

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ADSORPTION OF SELENIUM AND STRONTIUM ON GOETHITE: SURFACE COMPLEXATION MODELING OF THE TERNARY SYSTEM

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The geochemical behaviour of selenium and strontium is critical for the disposal of radioactive wastes. It is of great significance that goethite as one of the most thermodynamically stable and commonly occurring natural iron oxy-hydroxidespromisinglyimmobilizesthese elements.Here we present a comprehensive study on the ad sorption of Se(IV) and Sr(II) on goethite. Starting from zeta potential measurements, the binary and ternary adsorption systemsare investigated and systematically compared via batch experiments, EXAFS analysis and CD-MUSIC modelling.

EXAFS indicates that Se(IV) formsbidentate inner-sphere surface complexes, while Sr(II) may form outer-sphere complexes at low and intermediate pH and inner-sphere complexes at high pH. Instead of a direct interaction between Se(IV) and Sr(II),our results indicate an electrostatically drivenmutual enhancement of adsorption.In the presence of Se(IV), the adsorption of Sr(II) is promoted overall by an average factor of five in pH range 6-8, typical for groundwater. Furthermore, Se(IV) promotes Sr(II) outer-sphere adsorption, but competes for inner-sphere adsorption sites.

The present workgains even more environmental significanceif the similarity of selenite and Sr(II) to ubiquitous carbonate and Ca(II), considered.The complexity of surfaces is highlighted by the inability of adsorption models to predict zeta potentials without additional constraints.

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COUPLED MINERALOGY AND CHEMISTRY ON DRILL CORE SAMPLES: BENCHMARKING ON-LINE-REAL-TIME ANALYSES

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Drill core materials from contrasting lithologies (sandstone, coarse granite, peridotite and siliceous breccia), were analysed to benchmark analytical conditions for XRF, XRD, hyperspectral and Raman spectrometers for on-line-real-time-on-mine analyses in the frame of the SOLSA project (http://www.solsa-mining.eu) sponsored by the EU-H2020 Raw Material program. We tested: (1) a multi-technique approach on sample surfaces (20 x 20 mm^2); (2) surface roughness effects on the different analyses. Five surface states were selected: (1) sonic and diamond drilled, (2) diamond-saw cut, (3) 6 µm polished, (4) 0.25 µm polished (5) powdered (< 80 µm). The following techniques were used: (1) portable X-ray fluorescence spectroscopy (pXRF), (2) portable infra-red spectroscopy (pIR), (3) Raman spectroscopy (4) laboratory XRD. The results obtained on the selected lithologies can be summarised as follows: **Peridotite** hosts 57 wt.% serpentine, 29 wt.% forsterite, 11 wt.% enstatite, 3 wt.% talc and traces of amphibole (XRD), while pIR only indicate serpentine. Raman spectroscopy clearly detects the ubiquitous presence of lizardite and forsterite. Grains of enstatite, quartz, anatase, rutile, pyrite, magnetite, maghemite and goethite were detected in selected regions. pXRF analyses on powders indicate 22 wt.% Si, 21 wt.% Mg, 6 wt.% Fe, 90 ppm V, 40 ppm Ti, 2200 ppm Ni, 1400 ppm Cr, 40 ppm Zn and 900 ppm Mn. Analyses on the drilled, cut and polished surfaces show higher values for Si, Mg and Ti, similar contents of Fe, Ni, Zn, Mn, and variable contents of V and Cr compared to those on the powder sample. **Granite** (XRD) is composed of 27 wt.% quartz, 20 wt.% microcline, 28 wt.% albite, 24 wt.% mica and/or illite and 1 wt.% chlorite. pIR shows the presence of bound water and illite, in agreement with XRD analyses. Raman spectroscopy confirms the presence of quartz, albite, precises muscovite as mica, and detects gypsum, magnesium sulphate, rutile, anatase, calcite and hematite. pXRF on powder surface indicate 39 wt.% Si, 9.2 wt.% Al, 0.55 wt.% Ca, 4.2 wt.% K, 95 ppm Zr, 60 ppm Sr, 300 ppm Ba, 43 ppm Zn, 38 ppm Pb, 0.9 wt.% Fe, 136 ppm V, 960 ppm Ti. Analyses on drilled, cut and polished surfaces show higher Si contents (42-46 wt.%), and variable contents of the other elements. Cr was detected during polished surface analyses (235–324 ppm). These heterogeneous results are due to the coarse grain size. **Sandstone** is composed of 100 wt.% quartz (XRD). pIR indicates the presence of bound water, illite or montmorillonite. Raman spectroscopy, besides quartz, detects anatase, pyrite, maghemite, goethite and zircon. pXRF on powder shows 55 wt.% Si, 132 ppm Zr, 0.02 wt.% Fe, 55 ppm V, 358 ppm Ti and traces of Ca and K. Analyses on the drilled, cut and polished surfaces give lower concentrations, in particular for Zr (50-100 ppm), Ti (99-256 ppm). Fe, heterogeneously distributed (260-600 ppm), is related to iron oxihydroxides. **Breccia** contains 100 vol.% of quartz with traces of hematite and goethite (XRD). pIR shows water molecules and goethite. Raman spectroscopy confirms quartz, and hematite and goethite, and adds hedenbergite, forsterite, calcite, magnetite and maghemite. pXRF on powder indicate 53 wt.% Si, 1.7 wt.% Fe, 3700 ppm Ni and 780 ppm Cr. Sawn surfaces give lowest trace element values. As for sandstone, analyses on the drilled, cut and polished surfaces give generally lower concentration and highly variable (241-1520 ppm Ni; 12 ppm–1.2 wt.% Fe, 86-480 ppm Cr). The major challenges of combined on-line sensor are the different sizes probed by techniques (from cm (IR) to mm (pXRF) down to micron (Raman spectroscopy)). Heterogeneous and coarse grained materials need a high number of analyses to give reliable results (time consuming). Methods, such as IR and XRF, need a surface proximity. in order to have maximum signal output. Major technological developments are needed for optimizing the on-line setup. Finally, it is recommended to build-up an adequate Raman database.

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RAPID PARTICLE SIZE AND SHAPE CHARACTERISATION OF FINE GRAINED IRON ORES: OPTIMISING COMMINUTION PARAMETERS

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Iron ore from banded iron formations (BIF) is fine-grained and composed of a complex iron-oxyhydroxide mineralogy. These characteristics lead to significant metal, energy and water loss during beneficiation, such as comminution, gravity and magnetic separation. Routine grain shape characterisation, not yet done by the industries, allows defining optimal grinding parameter and follow-up beneficiation methods, which will significantly reduce OPEX. We present a case study on particle size distribution and morphologies of a low-grade iron ore (14-42 wt.% Fe) from a drill core at Aguas Clara Mine, Minas Gerais (Brazil). These samples were priorly studied for mineralogy and bulk chemistry. We chose two types of samples: (1) iron oxide-carbonate rich and quartz poor sample (Fe_2O_3 ≈40 wt.%, SiO_2 < 1 wt.%; CO_2 ≈30 wt.%) and (2) an iron oxide poor, quartz and dolomite rich sample (Fe_2O_3≈14 wt.%; SiO_2≈32 wt.%, Al_2O_3< 1 wt.%, $CO_{2\approx}$24 wt.%). The samples are composed of dolomite-quartz bands alternating with massive hematite bands. Raman spectroscopy, XRD and FIB-TEM analyses show that the dolomite bands host micro- and nanometric hematite and minor goethite inclusions, partly occurring as clusters in voids, and aggregated specular hematite. The dolomite/quartz locks up ~ 30% of the iron minerals. After dry ball and rod milling (< 100 µm), the QICPIC particle analyser (Sympatec) was used in dry mode for particle size distribution to analyse at high-speed a high number of particles (2.5 million particles after dry rod milling; 4.3 million particles after dry ball milling). Ball milling for 10 min gives 50% lower particle sizes compared to rod milling. QEMSCAN analyses showed that ball milling favorises liberation of fine grained iron-oxides compared to rod milling. The average shape factor (aspect ratio) is 0.7 independant on the milling type and the grain sizes. At the same grinding conditions, dolomite rich ore shows a 30 to 50% lower particle size distribution for the 50 and 20 µm fractions respectively, than the quartz rich ore. This contrasting behaviour is related to the lower Mohs hardness of dolomite (3.5-4) compared to quartz (7). Grinding times and steps, including energy consumption, can be reduced while removing this overground material prior to further milling down to 10-20 µm, which is necessary to liberate the iron-oxide inclusions. This study gives hints to define optimal comminution parameters for the upgrading of these low-grade iron actually considered as "waste" to about 65% Fe.

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IN-SITU ANALYSES OF CARBONACEOUS MATTER IN METAL-RICH BLACK SHALES: IMPLICATIONS FOR ORE PROCESSING

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In low grade metal bearing carbonaceous matter black shales, an upgrading beneficiation step is needed prior to further metallurgical processing. However, the presence of abundant carbonaceous matter (CM) in these shales is known to be adversary for metal recovery. The detailed characterization of the CM and its textural relationship with the economic metal bearing phases is thus important in order to develop an appropriate process design. We studied Mn-rich black shales from COMILOG drill-cores (exploration drilling campaign 2012, 2013). These shales hosting about 23 wt.% Mn are the protore of the world-class Mn-oxide deposit in Moanda (Gabon), which is twofold enriched in Mn. The shale is very fine grained and has a laminated texture. The laminae are composed of biogenically formed Mn-carbonates, showing variable compositions (rhodochrosite, kutnhorite, dolomite). The carbonates have different textures, varying from bacterimorphous structures composed of micrometric carbonate particles to recrystallized grains of a few tenth to hundred microns. The carbonates alternate at certain levels with biogenically formed pyrite laminae. Minor minerals are quartz, muscovite, illite and apatite, occasionally Ti-oxides occur. Rock-Eval analyses of representative Mn-rich black shales indicate a total organic carbon content between 6 to 8 wt.%. Optical reflected light microscopy, SEM, FIB-TEM, QEMSCAN show that CM range in grain size from micrometric to ≈ 100 µm. It occurs interstitially associated with phyllosilicates. This interstitial CM host about 1.6 wt.% S and 0.2 wt.% of Mn (EMPA). FIB-TEM detected nanometric carbonaceous matter bound to Mn-carbonates (and pyrite). This type of organic matter (comprising roughly about 2 wt.%) cannot be detected by SEM or QEMSCAN, and cannot be separated from the carbonates without including a recrystallization step of the carbonates prior to e.g. a flotation process.

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SYNTHESIS, CHARACTERIZATION OF RARE EARTH-ALKALINE EARTH OXIDE COMPOUNDS

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Crystalline compounds with form $AREE_2O_4$ (A = Ca, Sr, Ba and *REE* = Rare Earth Element), often referred to as the $CaFe_2$O4 structure type, are becoming increasingly important in the field of material science due to its potential to be used as high temperature ceramic super conductors, superfine phosphors when doped with REE and electrode/electrolyte in solid oxide fuel cells (SOFCs) [1-4].

The abstract reports on the results concerning the sol-gel preparation of $SrREE_2O_4$ and $BaREE_2O_4$. The following REE were used: dysprosium, europium, neodymium and ytterbium. The synthesised compounds are studied by powder X-ray diffraction analysis, IR, TG, REM and calorimetry.

Rare earth-alkaline earth oxide compounds are synthesised by Pechini method. The gels were prepared using stoichiometric amounts of analytical-grade $Sr(NO_3)_2$, $Ba(NO_3)_2$, Eu_2O_3, $Yb(NO_3)_3{\cdot}5H_2O$, Dy_2O_3 and $Nd(NO_3)_3{\cdot}6H_2O$. Additionally citric acid as a complexing agent and ethylene glycol as a dispersing agent was added to form the gel. The annealing temperature was between 1000 and 1300 °C.

The synthesis results are given in Figure 1. $SrREE_2$O4 and $BaREE_2O_4$ belong to the orthorhombic space group Pnma. The effects of the lanthanide ionic radius on crystallographic parameters are studied.

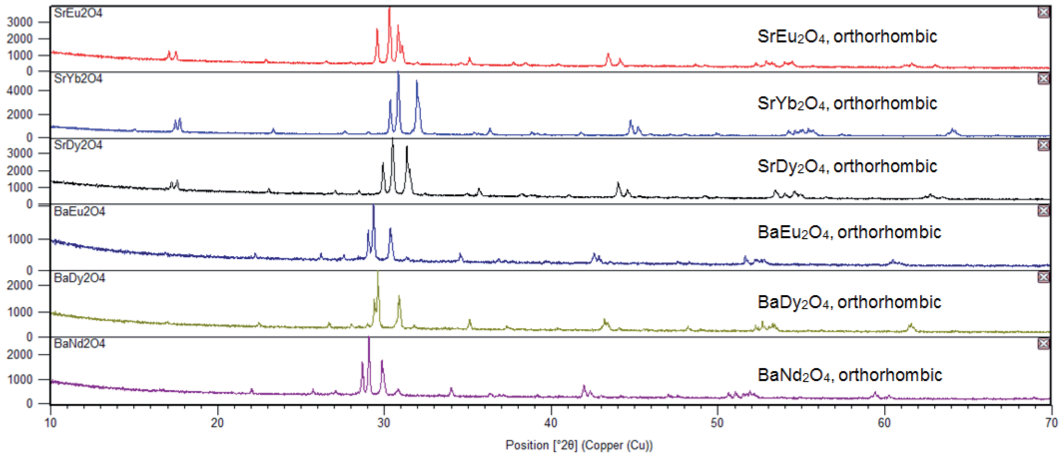

Fig. 1. XRDs of $SrEu_2O_4$, $SrYb_2O_4$, $SrDy_2O_4$, $BaEu_2O_4$, $BaDy_2O_4$ and $BaNd_2O_4$

The present study demonstrates the versatility of the Pechini method to yield monophasic compounds earth alkaline rare-earth oxides at low sintering temperature (1300 °C, 2h) when compared to the temperature required for solid state synthesis (≥1400 – 1600 °C, over 48 h) [5].

[1] Pollmann H., Kaden R. (2014). X-ray Investigations of solid solutions of Monocalcium Aluminate and Monostrontium Aluminate Important Phases in Cement and Phosphorescence Materials. Powder Diffraction. 37-47.
[2] Bednorz J.G., Müller K.A. (1986). Possible high Tc superconductivity in the Ba-La-Cu-O system. Condensed Matter, 189-193.
[3] Zhou L., Shi J., Gong M. (2005). Synthesis and photoluminescence properties of SrLu2O4:Eu3+ superfine phosphor. Materials Research Bulletin, 1832-1838.
[4] Minh N.Q. (1993). Ceramic Fuel Cells. Journal of the American Ceramic Society, 563-588.
[5] Karunadasa H., Huang Q., Ueland B.G., Lynn J.W., Schiffer P., Regan K.A., Cava1 R.J. (2005). Honeycombs of triangles and magnetic frustration in SrL2O4 (L=Gd, Dy, Ho, Er, Tm, and Yb), Physical review, 144414-8.

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HOT-STAGE CARBONATION: FOR CO2 SEQUESTRATION AND BOF SLAG STABILISATION

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Carbon capture, utilization and storage (CCUS) are a group of technologies which consider carbon dioxide (CO_2) as an important carbon feedstock for a future green economy. In order to reduce CO_2 emissions, these technologies are dedicated to effectively capturing CO_2 from emission sources, transporting it, and then using it or storing it into a suitable and permanent sink. Industrial solid wastes such as steelmaking slag and incineration ashes which are typically inorganic may be an alternative feedstock for CO_2 capture. The utilization of alkaline solid wastes has several benefits: a low cost of sequestration, close proximity to energy and industrial sites where CO_2 is emitted, and minimal environmental impacts through the resulting stabilisation (IPPC, 2005) [1]. So CCUS do not only permanently store CO_2 but also provide sustainable, environmental and economic benefits for further use of CO_2. CCUS face the challenges to improve the reaction efficiency and the material properties for utilization, to reduce the energy consumption. The present research makes a contribution to this area.

This study focuses on a specific CO_2 sink called BOF slag which is a by-product of a steel making plant employing the Basic Oxygen Furnace (BOF) process. The presence of residual free lime (CaO) in the BOF slag is one of the major obstacles to its sustainable re-use as an aggregate in construction practices. Because of the short term hydration and the long term carbonation of free lime, BOF slag aggregates present a potential for problematic volume expansion (swelling) resulting in rapid deterioration of the material.

Hot-stage mineral carbonation may be a promising stabilisation treatment route, as reported by Santos et al. 2013 [2]. This novel approach takes advantage of the heat source of the slag during slag cooling to allow rapid and low-cost mineral carbonation (given the favourable kinetics and freely available thermal energy) at elevated temperature. In addition, this high temperature gas/solid carbonation overcomes the disadvantages of conventional liquid/solid mineral carbonation such as the high energy requirement for milling, prolonged mixing, pressurization, and the generation of products (water with salts and heavy metals) having low market demand, for instance.

The stabilization of BOF slag via hot-stage carbonation treatment is studied in this paper. Lab-scale experiments have been designed to simulate the hot-to-cold stage path of the molten slag and investigate the susceptibility of the slag to carbonate along this route. This work investigates the carbonation of the free lime (CaO) contained in the BOF slag in the temperature range 700-300 ºC. The influence of different process parameters (the residence time, the solid-gas contact method, the particle size) on the carbonation conversion is highlighted in order to identify the key parameters for developing the envisioned ‘’carbonation during granulation’’ route.

This study gives the following important preliminary insights: the carbonation conversion is the fastest during the first minutes of cooling; it is directly proportional to the gas/solid contact, and inversely proportional to the particles size. These promising results show that the hot stage carbonation presents a double benefit: to sequester CO_2 and to stabilize BOF slag.

[1] IPCC, 2005. IPCC special report on carbon dioxide capture and storage. In: Metz, B., Davidson, O., Coninck, H., Loos, d., Meyer, M.L. (Eds.), Intergovernmental Panel on Climate Change, Cambridge.
[2] Rafael M. Santos, Da Ling, Amin Sarvaramini, Muxing Guo, Jan Elsen, Faïçal Larachi, Georges Beaudoin, Bart Blanpain, Tom Van Gerven, “Stabilization of basic oxygen furnace slag by hot-stage carbonation treatment’’, Chemical Engineering Journal 203 (2012) 239–250.

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SELECTIVE TRANSFER HYDROGENOLYSIS OF AROMATIC ETHERS PROMOTED BY BIMETALLIC PD/FE CATALYST

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One of the major challenges in the catalytic valorization of lignin is the selective cleavage of the C–O bond preserving its aromatic nature [1,4].

The Pd/Fe catalyst (prepared by the co-precipitation technique), in the last years, has shown excellent performance in several catalytic reactions including the catalytic transfer hydrogenolysis (CTH) of lignocellulosic platform derived molecules [5,7].

In this contribution, the selective cleavage of the C–O bond of benzyl phenyl ether (BPE), 2-phenethyl phenyl ether (PPE) and diphenyl ether (DPE) – as model compounds of lignin linkages – promoted by the Pd/Fe catalyst, with a nominal palladium loading of 5 wt%, was investigated under CTH conditions using 2-propanol as the H-donor [8].

On using the coprecipitated Pd/Fe as catalyst, an appreciable BPE (0.1 M) conversion (19.7%) was achieved at a temperature as low as 180 °C. The conversion of BPE increases by increasing the reaction temperature and, at 240 °C, it is fully converted (100% conversion) into phenol and toluene as the only reaction products (100% aromatic yield) clearly indicating that the cleavage of the etheric C–O bond occurs as the primary reaction route under CTH conditions. The low tendency of the coprecipitated Pd/Fe catalyst to hydrogenate the aromatic ring was confirmed with crosscheck experiments in which phenol and toluene were subjected to the same reaction conditions as employed for BPE. In both cases, products derived from aromatic ring hydrogenation were not observed.

In the next step, the H-donor ability of simple primary (methanol, ethanol, 1-propanol, 1-butanol and 1-pentanol) and secondary (2-butanol, 2-pentanol and 3-pentanol) alcohols with different carbon chain lengths was tested. A tight relationship between the moles per l of aldehyde or ketone formed (H-donor ability) and the amount of BPE converted (moles per l) was observed.

Reaction of PPE at 240 °C shows a lower conversion (22%) and 100% selectivity of aromatics. On the contrary, DPE was not converted at all. Interestingly, a linear correlation of the bond strength and the ability of the Pd/Fe catalyst in the CTH of aromatic ethers was found.

Therefore, the Pd/Fe catalyst is able to cleave the C–O bond of benzyl phenyl ether (BPE) and 2-phenethyl phenyl ether (PPE) under CTH conditions and, at the same time, it avoids parallel hydrogenation reactions of the aromatic ring, being one of the most selective heterogeneous catalysts in the production of arene derivatives.

[1] Besson M., Gallezot P., Pinel C. (2014). Conversion of Biomass into Chemicals over Metal Catalysts. Chemical Reviews, 1827–1870.
[2] Tuck C.O., Peŕez E., Horváth I.T., Sheldon R.A., Poliakoff M. (2012). Valorization of biomass: deriving more value from waste, Science, 695–699.
[3] Zhou C.-H., Xia X., Lin C.-X., Tong D.-S., Beltramini J. (2011). Catalytic conversion of lignocellulosic biomass to fine chemicals and fuels. Chemical Society Reviews, 5588–5617.
[4] Xu C., Arancon R.A.D., Labidi J., Luque R. (2014). Lignin depolymerisation strategies. Chemical Society Reviews, 7485–7500.
[5] Musolino M.G., Scarpino L.A., Mauriello F., Pietropaolo R. (2009). Selective transfer hydrogenolysis of glycerol promoted by palladium catalysts in absence of hydrogen. Green Chemistry, 1511–1513.
[6] Cozzula D., Vinci A., Mauriello F., Pietropaolo R., Müller T.E. (2016). Directing the cleavage of ester C-O bonds by controlling the hydrogen availability on the surface of coprecipitated Pd/Fe_3O_4. ChemCatChem, 1515–1522.
[7] Mauriello F., Ariga H., Musolino M.G., Pietropaolo R., Takakusagi S., Asakura K. (2015). Exploring the catalytic properties of supported palladium catalysts in the transfer hydrogenolysis of glycerol, Applied Catalysis B: Environmental, 121–131.
[8] Paone E., Espro C., Pietropaolo R., Mauriello F. (2016). Selective arene production from transfer hydrogenolysis of benzyl phenyl ether promoted by a co-precipitated Pd/Fe_3O_4 catalyst Catalysis Science & Technology, 7937-7941.

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A NEW LOOK AT BIO-KAOLINITE FORMATION AT ROOM TEMPERATURE

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The interactions between microorganisms and minerals in low energy systems have a long history, as they are incessantly occurring for at least 3 billion years (Lower et al., 2001). Number of mineral species of different origin, chemistry, structure and chemical reactivity is continuously interacting with an undefined number of microorganisms displaying a host of phenotypic, genotypic, biochemical and surface properties.

The authigenic clay formation is a matter of great interest from both geological and pedologic standpoints. An impressive amount of scientific literature is available on this topic. Three main hypotheses were proposed to explain the clay formation in low energy systems: a) the process is completely driven by inorganic mechanisms (e.g., Waroszewski et al., 2015); b) the process is a phenomenon under both microbial and inorganic control (Cuadros et al., 2013); c) the process is mainly biologically driven (Fiore et al., 2011).

Kaolinite, a very common and interesting clay mineral from both basic science and practical interest standpoints, plays a relevant role in both soil ecosystem and in the industrial sector. Even though the kaolinite formation in high energy environments is a well-known phenomenon (Huertas et al., 1999), kaolinite precipitation from Al and Si at ambient temperature was obtained only by Linares and Huertas (1971) and Fiore et al. (2011). Linares and Huertas (1971) focused their work on the abiotic synthesis of kaolinite thanks to humic acids as complexing agents able to put Al in octahedral coordination. Fiore et al. (2011) speculated on the microbially induced precipitation of this mineral: they documented the formation of few crystals of kaolinite in gels precipitated from solution containing Al, Si and microflora extracted from a peat soil. An axenic solution, containing the same concentrations of Al and Si, failed to produce the same result.

Extending the incubation over 5 years produced some crystals of low crystalline kaolinite and highly mineralized bacterial cells. The use of complexant agents, as oxalic acid, alpha-ketoglutaric acid, EDTA and humic acids failed to precipitate kaolinite in axenic solutions of $Na_2SiO_3•5H_2O$ and $Al(NO_3)_3•9H_2O$.

In this work we report an experiment aimed at obtaining kaolinite from Al and Si solution in presence of fungi. Solutions containing Si, Al and a selected fungal species produced single crystals and packets of kaolinite from few nm up to 2 microns.

This surprising result casts a new light on the process of kaolinite formation in low energy environments. Maybe the role of bacteria has been overestimated compared to the fungal action.

[1] Cuadros J., Afsin B., Jadubansa P., Ardakani M., Ascaso C., Wierzchos J. (2013). Microbial and inorganic control on the composition of clay from volcanic glass alteration experiments. American Mineralogist 98, 319–334.
[2] Fiore S., Dumontet S., Huertas F.J., Pasquale V. (2011). Bacteria-induced crystallization of kaolinite. Applied Clay Science, 53, 566-571.
[3] Huertas F.J., Fiore S., Huertas F., Linares J. (1999). Experimental study of the hydrothermal formation of kaolinite. Chemical Geology, 171-190.
[4] Linares J., Huertas F. (1971). Kaolinite: synthesis at room temperature. Science, 896-897.
[5] Lower S.K., Tadanier C.J., Hochella M.F. (2001). Dynamics of the mineral–microbe interface: use of biological force microscopy in biogeochemistry and geomicrobiology. Geomicrobiology Journal 18, 63-76.
[6] Waroszewski J., Egli M., Kabala C., Kierczak J., Brandova D. (2015). Mass fluxes and clay mineral formation in soils developed on slope deposits of the Kowarski Grzbiet (Karkonosze Mountains, Czech Republic/Poland). Geoderma 64, 363–378.

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CHARACTERISATION OF OCHREOUS AND VITREOUS GOETHITE IN IRON ORE USING REFLECTANCE SPECTROSCOPY AND HIGH-RESOLUTION X-RAY COMPUTED TOMOGRAPHY

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Goethite is one of the most ubiquitous minerals on the Earth's surface and it is also a significant mineral in economic deposits such as iron ore. Goethite was named in 1806 after the German poet, philosopher and naturalist Johann von Goethe. In iron ore, the two main goethite subtypes are ochreous and vitreous, respectively defined by texture and colour. Ochreous goethite is friable and yellow whereas vitreous goethite is hard, glassy and brown. These two subtypes have different processing and metallurgical behaviour and their discrimination is a challenge for the iron ore mining industry. The main goal of this paper is to offer characterisation techniques that provide objective means of discriminating the two subtypes even when they occur together. The two methods used to achieved discrimination are; (1) reflectance spectroscopy in the visible, near and short wave infrared (VNSWIR) wavelength range (380 to 2500 nm) and (2) high-resolution X-ray computed tomography (HRXCT).

Ochreous and vitreous goethite subtypes are spectrally different in the VNSWIR range. The crystal field absorption feature at around 900 nm (CFA900) for ochreous goethite is sharp and symmetric whereas vitreous goethite shows a broad, asymmetric CFA900 feature. The development of a spectral index related to the width of the CFA900 provides a way of discriminating between ochreous and vitreous goethite.

HRXCT offers three-dimensional (3D) characterisation of both ochreous and vitreous subtypes at a spatial resolution down to 0.7 µm providing not only striking 3D images but also unique, 3D mineralogical and textural measurements. It provides (1) an assessment of the degree of heterogeneity of the ores, (2) the quantification of the mineral proportions and their 3D textural relationships and, (3) the topology of the pore spaces and the quantification of the nano-porosity that provide the difference between ochreous and vitreous goethite.

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ADVANCES MINERAL CHARACTERIZATION BY HYPERSPECTRAL, LIBS AND EDXRF DATA MERGING

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Two dimensional scanning by LIBS (Laser Induced Breakdown Spectroscopy with 200 µm resolution), EDXRF (Energy dispersive X-Ray Fluorescence Spectroscopy with down to 20 µm resolution) and Hyperspectral imaging (VNIR, SWIR, both 1400 - 25 µm, and LWIR 1400-400 µm resolution) provides both chemical pattern as well as chemistry and hyperspectral based mineralogical information. Since neither method provides all information needed, their combination opens up new perspectives for scientific data acquisition. Evaluation and cross validation can be performed on a continuous basis or for selected targets in detail. Information of individual mineral grain sizes, shapes and orientations, paragenetic assemblages, vein types can be obtained and objectively be correlated with neighboring cores.

Based on the identified chemical anomalies and characteristic mineral assemblages sub-samples can be selected for further detailed geochemical, mineralogical and textural investigations.

Future perspectives are partial automatization of the data analyses and evaluation process.

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“BROTHERS IN ARMS” – HIF HIGH-SPEED PIXE AND MEGA SPECTROMETER

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In a fast growing world with increasing demand on resources like high-tech metals as In, Ga, Ge, or rare earth elements (REE), mineralogists and economic geologists need faster and automated analytical tools to explore mineral deposits, make them accessible and define necessary initial data for all subsequent processing steps. Next to the necessary knowledge in which phases the elements of interest, ecotoxical as well as deleterious elements are concentrated, it is important to determine structural parameters like grain sizes and possible intergrowths relations of these minerals. These are typical geometallurgical analytical tasks, which are so far routinely performed by electron beam based methods of automated mineralogy, like MLA (mineral liberation analysis) or QEMSCAN, with their advantages and disadvantages. The methodological problems of these type of methods are, for example, the necessary measurement time, insufficient limits of detection (no trace element detection) and high background (electron Bremsstrahlung).

Some of these hurdles can be overcome by using alternative excitation radiation, like ions, known as particle-induced X-ray emission (PIXE) or X-rays, known as X-ray fluorescence (XRF). Combining these with a full-field detection system, such as the so-called SLcam® [1], allows the determination of trace element distributions in reasonable time over a large field of view.

The SLcam® consists of a 12 x 12 mm², X-ray sensitive pnCCD chip with 69696 pixels. A high read-out speed of up to 1000 Hz, allows the acquisition of complete X-ray spectra (2-20 keV) on each pixel simultaneously, with an energy resolution of around 160 eV (@ Mn-Kα), even for high photon fluxes. A poly-capillary lens is used to guide the X-rays from their point of origin on the sample to the corresponding pixel on the detector-chip. Usage of a straight 1:1 lens results in a lateral resolution better than 100 µm.

The MEGA spectrometer is equipped with a laboratory-scale X-ray tube. XRF is used for the determination of major and trace element data. It’s “small”, table-top like size would in principle allow to use the set-up directly at the mining site. The so called High-Speed PIXE [2] uses a broad proton beam to excite the fluorescence radiation. Samples with a total weight of up to 10 kg and a maximum size 25 x 25 x 2.5 cm³ can be mounted in a dedicated vacuum sample chamber. The instrument is installed at the Ion Beam Center at the Helmholtz-Zentrum Dresden-Rossendorf. The advantages and disadvantages of both instruments will be presented, as well as first results of combined qualitative studies of the distribution of trace elements in representative samples to demonstrate the importance of these innovative concepts for geometallurgical research.

[1] Scharf O. et al. (2011). Compact pnCCD-Based X-ray Camera with High Spatial and Energy Resolution: A Color X-ray Camera. Analytical Chemistry, 83(7), 2532–2538.

[2] Hanf D. et al. (2016). A new particle-induced X-ray emission set-up for laterally resolved analysis over wide areas. Nuclear Instruments and Methods in Physics Research B, 377, 7-24.

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PLOTTING PHYSICAL PROPERTIES AGAINST 2D PROJECTIONS OF THE WHOLE MINERALOGICAL SYSTEM

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The mineralogical system can be projected into two dimensions, and the data accumulated in the process have shown a number of interesting relationships [1,2]. Besides, the 2*D* projections can also be used for plotting scalar physical properties as a third dimension. To illustrate the potential and the risks of doing so, three physical properties were selected: (i) mean refractive index, (ii) density, and (iii) mean reflectance.

All plots indicate a positive correlation between the physical property and the mean atomic number of elements present (four different functions of atomic numbers were tested). The density and the reflectance also show a negative correlation with the *InfEnt,* the information entropy [3], which “measures” the complexity of the stoichiometry of a mineral formula.

The data used, both chemical and physical, were excerpted from several sources [4,5,6], and their suitability for the purpose is variable, to say the least. Most homogeneous is the set of refractive indices, but they only represent oxidic compounds, and the points crowd in a relatively small area of the projection quadrangle - not a best setup for numerically stable regressions. In contrast, the data for reflectance (another homogeneous set, even if mostly for opaque phases) yield both a linear and a quadratic term for the *InfEnt.*

The scatter dominating some of the plots leaves something to be desired, and it is a consequence of several causes. Whether these causes can be controlled, or to what extent, may be a subject of discussion, but the fact that there are visible tendencies running across the vast diversity of the whole mineralogical system makes a project like this well worthwhile.

[1] Rieder M. (2014). The mineralogical system: 2*D* projections and their potential in mineral identification. *Eur. J. Mineral.* 26, 703-710.
[2] Rieder M. (2016). The mineralogical system: Can global plots teach us something new? *Mineral. Mag.* 80, 239-248.
[3] Shannon C.E. (1948). A mathematical theory of communication. *The Bell System Technical Journal* 27, 379-423.
[4] Shannon R.D., Fischer R.X. (2016). Empirical electronic polarizabilities of ions for the prediction and interpretation of refractive indices: Oxides and oxysalts. *Amer.Mineral.* 101, 2288-2300.
[5] Ralph J., Chau I. (1993-2013). Mindat.org – the mineral and locality database. www.mindat.org.
[6] Criddle A.J., Stanley C.J. (1993). Quantitative data for ore minerals, Third edition, 635 pp.

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HEALING AND EDIBLE CLAYS. PAST, PRESENT AND FUTURE

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Clays have been subject of an increasing interest fromindustries, notably pharmaceuticals and cosmetics. Clay minerals are being included in formulations, as active or excipients. There are various aspects related to their peculiar crystal-chemistry, that condition their use, therefore justifying a deepening of studies, in particular the mobility of the elements and the controlled release of species, under specific conditions (such as pH and/or temperature differentials) or by the action of electric field.

Concerning rehabilitation and balneology, these minerals have shown beneficial effects for the treatment of rheumatic diseases, dermal or musculoskeletal. In this context, clays are used for relief of symptoms of rheumatic diseases, dermatological and orthopedic (in the form of peloids). Clay particles possess ability to absorb and excrete toxins from the body, as well as incorporate and release toxic elements, heavy metals, among others, via ingestion or dermal application.

Clays for thermal application and/or rehabilitation areas must be submitted to artificial maturation with selected mineral/thermal (usually under light conditions and shaking). These geomaterials can also be applied as transdermal devices which allow the release of therapeutic species (ions/compounds and pharmaceuticals) directly on the area to deal with promoting a more effective reception of these elements and your most efficient use.

As active ingredient, namelly as dermal or gastrointestinal protectors, laxatives and antidiarrheals [1,2]; as excipients, supporting various substances with bioactivity, improving organoleptic characteristics, facilitating the preparation and/or promoting the disintegration of the active product [3,4]. Clays are described as modulators of several systems of release of drugs, e.g. ibuprofen [5,6]. The inclusion of clays in (nano-) composites reveals improvements of mechanical properties and polymer materials, opening ways for development of new materials for biomedical applications [7].

Clays have also been traditionally used as food supplements and dressings (primarily for gastrointestinal problems) and continue to be so in many contemporary societies; this is commonly known as Geophagy [1].

[1] Abrahams P.W. (2012). Involuntary soil ingestion and geophagia: A source and sink of mineral nutrients and potentially harmful elements to consumers of earth materials. Applied Geochemistry, 27: 954-968.
[2] Carretero M., Pozo M. (2010). Clay and non-clay minerals in the pharmaceutical and cosmetic industries Part II. Active ingredients. Appl. ClaySci. 47: 171–181.
[3] López-Galindo A., Viseras C., Cerezo P. (2007). Compositional, technical and safety specifications of clays to be used as a pharmaceutical and cosmetic products. Appl. Clay Sci., 36: 51-63.
[4] Viseras C., Aguzzi C., Cerezo P., Lopez-Galindo A. (2007). Uses of clay minerals in semisolid health care and therapeutic products. Appl. Clay Sci., 36: 37-50.
[5] Dziadkowiec J., Mansa R., Quintela A., Rocha F., Detellier C. (2017). Preparation, characterization and application in controlled release of Ibuprofen-loaded Guar Gum/Montmorillonite Bionanocomposites. Appl. Clay Sci.,135: 52–63.
[6] Mansa R., Quintela A., Rocha F., Detellier C. (2016). Preparation and Characterization of Novel Clay/Scleroglucan Nanocomposites. Appl. Clay Sci.,126: 235 – 244.
[7] Mishra R., Ramasamy K., Lim S.M., Ismail M.F., Majeed A.B. A. (2014). Antimicrobial and in vitro wound healing properties of novel clay based bionanocomposite films. Journal of Materials Science: Materials in Medicine 25(8):1925-1939.

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DESIGN OF SPECIAL CLAYS PASTES BLENDED WITH ADDITIVES TO IMPROVETHEIR PROPERTIES AS HEALING CLAYS

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Clays and clayey materials are used for a large range of applications, being commonly used for cosmetic and pharmaceutical formulations as well as for application on aesthetic medicines. For these purposes, new formulations of different special clays are being developed, blended with additives in order to improve their relevant properties.

The aim of this study is to design several new blends of special clays (bentonites and kaolins) to be used as healing clays, and to analyze the influence of the addition of glycerol, hidrogel, calcium and kaolin on the properties relevant for that applications, such as: abrasivity, plasticity, viscosity, cooling time, pH, cation exchange capacity (CTC) and adsortion.

We studied several formulations using bentonites from Avis and Montargil (South Portugal) and from Porto Santo (Madeira archipelago) and blended with variable but always minor quantities of kaolin from Vila Chã (North Portugal); glycerol, hidrogel, calcium were also blended in variable proportions.

Mineralogical characterization was performed by X-ray diffraction; grain size analysis was carried out by wet sieving (for fraction >63 µm) and for fraction <63 µm was used a X-ray grain size analyzer (Micromeritics® Sedigraph 5100). Technological properties followed protocols described on Quintela et al. (2012) and Rebelo et al. (2011). Results were submitted to statistical analysis, namelly Principal Components Analysis.

Concerning the different proportions of bentonite: kaolin, the increase of kaolin implies the increase on cooling time, mean grain size, viscosity and abrasivity and a decrease on pH, plasticity, CTC and adsorption.

Concerning the additives, their influence on the different properties varies strongly. The results obtained so far allowed to put forward some preliminary statements. Formulation combining saturation with calciumand hydrogel improves plasticity, followed by hydrogel added ones whereas glycerol has a strong negative effect on plasticity. Glycerol addition increases cooling time, which is a positive effect, but has a negative effect on abrasivity, which increases. Hydrogel addition shows similar effects, slightly less evident in what concerns abrasivity increase. Calcium saturation increase also abrasivity, but not cooling time, and reduces a little CTC. Concerning exchangeable cations, in general, all formulations show an enrichment in Ca andNa whencomparedwiththeinitial raw samples.

[1] Quintela A., Terroso D., Ferreira da Silva E., Rocha F. (2012). Certification and quality criteria of peloids in use for therapeutic purposes. Clay Minerals, 47(4):441–451.

[2] Rebelo M., Viseras C., López-Galindo A., Rocha F., Ferreira da Silva E. (2011). Characterization of Portuguese geological materials to be used in medical hydrology. Applied Clay Science, 51: 258-266.

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STRUCTURAL CHARACTERIZATION OF NaX ZEOLITE EXCHANGED WITH Y AND Nd ELEMENTS

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Thanks to their properties, REEs are extensively used in many daily commodities. Unfortunately, the REEs resources are finite and the access to the supplies is uncertain. For this reason, it is necessary produce and use the REEs in a sustainable manner [1]. Moreover, the widespread use of these elements has resulted in an increasing of REEs contamination in environmental matrices, creating problems to humans and ecosystems due to their bioavailability [2]. Despite of vast efforts in research about rare earth elements recycling a very low percent of these elements was recycled during the last years. This is mainly due to inefficient collection, technological problems and, especially, a lack of incentives. As a matter of fact that the most of conventional methods nowadays used for the extraction, recovery and separation of REEs have need a high consumption of energy and often given rise to secondary pollutants [3]. An eco-friendly and low cost alternative to recycle REE is the adsorption [4,5,6] process using zeolites [7]. Indeed, the properties of these sorbent materials to capture and concentrate significant quantities of species make them ideal candidates not only for the development of recycling but also for remediation processes, separation, environmental monitoring and resource recovery processes. However, at the best of the Authors' knowledge, the adsorption mechanism and selectivity of REEs on zeolites has not been extensively treated in literature. To fully understand the adsorption mechanism and selectivity of zeolites a key aspect is to implement studies on adsorption capacities and on the distribution of distinct cations on adsorbent materials. In fact, the partitioning of ions and the distribution of bulk phase at the interface between minerals and aqueous solution, involves a complex interplay of chemical, electrostatic and crystallographic factors. For this reason, in this work NaX zeolite ion exchanged with Y and Nd (from liquid solutions) were studied by X-ray diffraction in order to locate the Rare Earth cations in the zeolite framework and the resulting changes in its structural properties. The Nd-exchanged NaX-XRD pattern has clearly showed the occurrence of a new diffraction peaks, which are absent in the Y-exchanged NaX. Moreover, Rietveld refinement also has indicated variations in the unit cell parameters, suggested the incorporation of REEs in the structure. According to the literature [7] the analysis of the difference Fourier map has allowed us to recognize a maximum three-fold coordinated to framework oxygen which can be assigned to Al extraframework ion.

[1] Zhanheng C. (2011). Global rare earth resources and scenarios of future rare earth industry. Journal of Rare Earths, 1-6.

[2] Ichihashi H., Morita H., Tatsukawa R. (1992). Rare earth elements (REEs) in naturally grown plants in relation to their variation in soils. Environmental Pollution, 157-162.

[3] Massari S., Rubert M. (2013). Rare earth elements as critical raw materials: Focus on international markets and future strategies. Resources Policy, 36–43.

[4] Qing C. (2010). Study on the adsorption of lanthanum(III) from aqueous solution by bamboo charcoal. Journal of Rare Earths, 125-131.

[5] Xu S., Wang Z., Gao Y., Zhang S., Wu K. (2015). Adsorption of Rare Earths(III) Using an Efficient Sodium Alginate Hydrogel Cross-Linked with Poly-γ-Glutamate. Plos one, 1-12.

[6] Johnson B.E., Santschi P.H., Chuang C.Y., Otosaka S. (2012). Collection of Lanthanides and Actinides from Natural Waters with Conventional and Nanoporous Sorbents. Environmental Science & Technology, 11251−11258.

[7] Nery J.G., Giotto M.V., Mascarenhas Y.P., Cardoso D., Zanon Zotin F.M., Sousa-Aguiar E.F. (2000). Rietveld refinement and solid state NMR study of Nd-, Sm-,Gd-, and Dy-containing Y zeolites. Microporous and Mesoporous Materials, 281-293.

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CHROMATOGRAPHIC AND STRUCTURAL STUDY OF THE ADSORPTION/DESORPTION PROCESS OF ZSM-5 LOADED WITH VOLATILE ORGANIC COMPOUNDS

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The water contamination has increased significantly in recent years due to a very fast development of industries as well as of intense agricultural practices. As a matter of fact that the development of progress has given rise to a general improvement of the standard of living, but it had increased the environment pollution through the wide release of contaminants of emerging concern (CECs) [1]. In particular, the presence of these chemicals at ultra-trace levels causes the development of sublethal toxic effects in aquatic organisms and in human health [2]. Nowadays, the traditional wastewater treatments (*i.e.*, vaporization, dilution, decomposition, and reactions to sunlight action) designed to degrade or remove these pollutants or reduce the levels of their concentrations are not completely effective. To support the traditional methods, new technologies which employ different types of materials have been developed. Among these technologies, adsorption method based on the use of adsorbent materials have been shown to be an effective and eco-friendly alternative. In particular, hydrophobic zeolites have proven to be very promising materials, which have been employed as adsorbents for the removal of contaminants from water bodies [3,4]. Indeed, zeolites represent an important adsorbents for the recovery of groundwater polluted by organic complexes and can be easily regenerated by thermal processes without changing their initial adsorption features [3,5].

On the basis of the above statements, the combination of chromatographic, diffractometric and thermogravimetric techniques has been employed to investigate the adsorptive-desorptive properties of hydrophobic synthetic zeolite as well as the temperature dependence of the desorption processes. Specifically, time-resolved high-temperature synchrotron X-ray powder diffraction was used as a tool to understand the behaviour of hydrophobic ZSM-5 zeolite ($SiO_2/Al_2O_3 \sim 280$) during the desorption of 1,2 dichloroethane, toluene, and methyl tert-butyl ether (adsorbed both as single component as well as binary mixtures). The structural modifications of ZSM-5 zeolite are monitored through thermal treatment from room temperature to 600 °C. The results achieved by means of Rietveld refinements of the investigated compounds highlight the “out-of-equilibrium effects” that govern the adsorption/desorption dynamic conditions in ZSM-5 powders.

[1] Perego C., Bagatin R., Tagliabue M., Vignola R. (2013). Zeolites and related mesoporous materials for multi-talented environmental solutions. Microporous and Mesoporous Materials, 37 – 49.
[2] Raghav M., Eden S., Mitchell K., Witt B. (2013). Contaminants of Emerging Concern in Water. The Arroyo, 1 – 12.
[3] Rodeghero E., Martucci A., Cruciani G., Bagatin R., Sarti E., Bosi V., Pasti L. (2016). Kinetics and dynamic behaviour of toluene desorption from ZSM-5 using in situ high-temperature synchrotron powder X-ray diffraction and chromatographic techniques. Catalysis Today, 118–125.
[4] Pasti L., Rodeghero E., Sarti E., Bosi V., Cavazzini A., Bagatin R., Martucci A. (2016). Competitive adsorption of VOCs from binary aqueous mixtures on zeolite ZSM-5. RSC Advance, 54544–54552.
[5] Martucci A., Rodeghero E., Pasti L., Bosi V., Cruciani G. (2015). Adsorption of 1,2-dichloroethane on ZSM-5 and desorption dynamics by in situ synchrotron powder X-ray diffraction. Microporous and Mesoporous Materials, 175-182.

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CATALYTIC ACTIVITY AND RECYCLABILITY OF POLYMER SUPPORTED PALLADIUM NANOPARTICLES IN HYDROGENATION REACTIONS IN WATER

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An insoluble palladium catalyst (Pd-pol) was obtained by copolymerization of the metal containing monomer $\mathrm{Pd(AAEMA)_2}$ [$\mathrm{AAEMA^-}$ = deprotonated form of 2-(acetoacetoxy)ethyl methacrylate] with ethyl methacrylate (co-monomer) and ethylene glycol dimethacrylate (cross-linker), followed by in situ reduction of Pd(II) to Pd(0), to give polymer stabilized metal nanoparticles [1].

The good swellability in water exhibited by Pd-pol rendered it an ideal potential catalyst for reactions carried out in a green solvent, such as water, since the migration of the reagents to the active sites would not be hampered by the solid support.

With the aim to develop innovative catalytic processes that enable chemical transformations to be performed under mild and sustainable conditions with high efficiency, we decided to evaluate the catalytic activity of Pd-pol for hydrogenations using water as solvent. Pd-pol resulted highly active and selective in catalysing the reduction of quinolines and nitroarenes by H_2 or $NaBH_4$ [2,3].

Pd-pol was recyclable for several consecutive runs; for example in the nitroarene reduction up to twelve times. TEM analyses carried out on the catalyst showed that the active species were supported palladium nanoparticles having a mean size of 4 nm, which did not aggregate with the recycles.

All these results proved that the proposed Pd based composite material is an excellent hybrid structure as efficient and reusable catalyst.

[1] Dell'Anna M.M., Romanazzi G., Mastrorilli P. (2013). Polymer supported catalysts obtained from metal-containing monomers. Current Organic Chemistry, 17, 1236–1273.

[2] Dell'Anna M.M., Romanazzi G., Intini S., Rizzuti A., Leonelli C., Piccinni A.F., Mastrorilli P. (2015). A polymer supported palladium(II) β-ketoesterate complex as active and recyclable pre-catalyst for selective reduction of quinolines in water with sodium borohydride. Journal of Molecular Catalysis A: Chemical, 402, 83–91.

[3] Dell'Anna M.M., Intini S., Romanazzi G., Rizzuti A., Leonelli C., Piccinni F., Mastrorilli P. (2014). Polymer supported palladium nanocrystals as efficient and recyclable catalyst for the reduction of nitroarenes to anilines under mild conditions in water. Journal of Molecular Catalysis A: Chemical, 402, 307–314.

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A NEW NMR SPECTROSCOPY APPROCH TO CHARACTERIZE DIFFERENT BITUMEN'S

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Bitumen is a complex system of different components, made of aromatic / aliphatic hydrocarbon and heteroatoms. The constituent molecules, classified based on their solubility parameters, are divided into two principal class: malthenes and asphaltenes.

The asphaltenes are present in the bitumen in a percentage of between 5% and 25% by weight and are composed of polynuclear aromatic molecules with attached alkyl chains. They are grouped into a structure composed of different molecular units organized in layers surrounded or immersed in the malthene fluid. The malthene fluid is composed of free saturated, mono- and diaromatics and resins which may be associated with the asphaltenes. For thermodynamic reasons, various units of these systems, asphaltenes sheets immersed in malthenes, lead to formation of macrostructures or "micelles".

Recently, hydrogen nuclear magnetic resonance (1H NMR) spectroscopy has emerged as a very powerful and versatile tool for bitumen characterization [1]. It is possible with a single 1H NMR spectrum to simultaneously detect and quantify a large number of components. The direct 1H NMR spectrometry quantitative method presents advantages over some routine methods: simplicity, rapidity, selective recognition, and quantitative determination of aliphatic and aromatic hydrogens in bitumen. Besides applying the 1H NMR technique to bitumen as such, it is possible to separate the asphaltenes fraction from malthenes and analyze separately the two class of compounds, with the aim of standardizing bitumens from different sources to obtain a specific ligand with required characteristics.

Moreover, this research provides new insights into the chemical composition of the bitumen in order to correlate the chemical composition to its rheological properties.

Tables, figures and photographs should preferably not be included in the abstract.

[1] Sciri N., Song S., Kim N., Cho N. (2014). Chemical Characterization of Gilsonite Bitumen. J. Pet. Environ. Biotechnol 5: 193. doi:10.4172/2157-7463.1000193.

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THE USE OF MICRO-CT SCANNING IN THE RECOVERY OF SCHEELITE FROM THE RIVIERA DEPOSIT, SOUTH AFRICA

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The granite-hosted Riviera W-Mo-REE deposit is an approximately 40 million ton low grade (~0.2% WO_3) endoskarn resource located in the Boland Terrane of the Neoproterozoic Saldania Belt, South Africa. Disseminated scheelite is the principle ore mineral but, disseminated molybdenite and allanite offer additional economic potential. These minerals are intergrown with a diversity of skarn minerals such as diopside, garnet, epidote, titanite and carbonates as well as the products of the pervasively hydrothermally altered granite host. Scheelite is strongly zoned and has a molybdenum-rich core and depleted rim [1,2]. Separation of the high demand low molybdenum scheelite core to upgrade the deposit does not appear possible at this stage.

The high density contrast between scheelite (ρ 6.1) and gangue (ρ 2.7) allows separation by gravity on tables, wet or dry spirals and heavy medium liquids. In the present laboratory study the latter method was used as a pre-concentration stage. An approximately 40 kg sample was collected from split diamond drill core with a WO_3 grade representative of the ore body. The core was crushed into four size fractions and the high density fraction separated with TBE (ρ 2.89). Results showed that the -1 mm size fraction yielded the best but, a disappointing scheelite recovery of ~50%. To explain this poor result, X-ray micro computed tomography (microCT) of sinks and floats of the various size fractions as well as the -45 µm fines was conducted to assist the study [3,4]. This relatively new application of the method allowed quantification of scheelite grain size variation and calculation of WO_3 content of the various size fractions. In addition it provided 3D images of textural relationships between the ore and gangue minerals. Results show that the heavy medium separation was successful. The fine grain size of scheelite in effectively all floats and slimes are responsible for the poor recovery. The finer grains remain as lockings intergrown with gangue and report to the floats. Increased density of the heavy liquid to ρ 3.5 will upgrade the scheelite concentrate. The friable nature of scheelite (two distinct cleavage directions) resulted in the considerable loss of liberated grains to the -45 µm fraction. This also contributed to the low overall recovery.

The study demonstrated that MicroCT scanning can be effectively applied to geometallurgical challenges and offers 3D and quantitative data that can contribute to improved mineral beneficiation.

[1] Rozendaal A., Boshoff R. (2011). Rare earth element mineralogy and its recovery from the Neoproterozoic Riviera W-Mo deposit, South Africa. Proceedings of the 10th International Congress for Applied Mineralogy Trondheim, pp. 605-612.

[2] Rozendaal A., Theart H.F.J. (2013). Technical review of the Riviera Tungsten Deposit, Western Cape Province, South Africa. Internal report by SRK consulting for Bongani Minerals Pty (Ltd), p 634.

[3] Le Roux S.G., Du Plessis A., Rozendaal A. (2015). The quantitative analysis of tungsten ore using X-ray microCT: Case study. *Computers & Geosciences*, *85*, pp.75-80.

[4] Du Plessis A., le Roux S.G., Guelpa A. (2016). The CT Scanner Facility at Stellenbosch University: An open access X-ray computed tomography laboratory. *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms*, *384*, pp.42-49.

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CHROMIUM AND ARSENIC REMOVAL FROM CONTAMINATED WATERS: ENVIRONMENTAL APPLICATION OF MAGHEMITE NANOPARTICLES – PRELIMINARY RESULTS -

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Toxic metal release, transport and dispersion into the biosphere have a direct impact on the environment and on human health. Arsenic and hexavalent chromium are highly toxic agents that act as carcinogens, mutagens, and teratogens in biological systems, so the reduction of these pollutants in soils and waters to acceptable levels is of great importance. The selection of the most suitable treatment techniques depends on some basic parameters such as pH, initial contaminant concentration, environmental impact and economic parameters such as capital investment and operational costs. Traditional remediation methods are problematic in terms of high operational costs, large consumption of reagents and significantly large volume of sludge generation, furthermore, for industrial application these methods seems unsuitable due to large areas required. In this field nanoparticles emerge as one of the most promising new techniques for soil and water remediation. In this work a new type of iron nanoparticles called SAMNs (Surface Active Maghemite Nanoparticles) is used. It's a novel superparamagnetic nanoparticle constituted of maghemite [1] characterized by specific surface chemical behaviour, without any coating or superficial modification, high surface-area-to-volume-ratio, low toxicity, strong absorption ability and are stable in water for months as colloidal suspensions.

The removal efficiency of SAMNs in respect of hexavalent Chromium ~~it~~ was tested in laboratory solutions, suitably prepared, with variable testing conditions in terms of pollutant concentrations, temperature and pH of the solution.

From these tests emerged that SAMNs are able to remediate water also with high concentrations of hexavalent Chromium (~22 mg/L) with a strong pH dependence; they are able to bind 99% Cr(VI) at pH 3.0, while this amount decreased to about 40% at pH 9.0 [2]. SAMN@CrVI complex was also characterized, as well as the covalent nature of the absorption was unequivocally proved [3].

For Arsenic removal the same methodology is applied, supported by several studies that demonstrate the ability of iron nanoparticles to reduce arsenic concentration in groundwater [4].

For the application of SAMNs in the environment the site Stoppani S.p.A located in Arenzano (Genova, Italy) was chosen. The Stoppani S.p.A industry transformed Cr-III from chromite ($FeCr_2O_4$), a mineral naturally present in the territory, into Cr-VI as sodium dichromate ($Na_2Cr_2O_7$, a known carcinogenic). The purpose of the industry was to produce chromic acid for galvanic processes or basic chromium sulphate [$Cr(OH)SO_4$] for the tanning industry. At the beginning of 2003 the industry ceased any activity. The area of Stoppani S.p.A. has been included, with DM n.468/01, into the national program of environmental remediation and restoration. The application of SAMNs (100mg mL^{-1}) on water samples coming from this area have demonstrated the ability of SAMNs to remediate heavy polluted waters with concentrations of Cr^{VI} between 527 and 232000 µg/l.

Further experiments are in progress to validate the efficiency of SAMNs for the removal of Arsenic from groundwater.

[1] Magro M., Valle G., Russo U., Nodari L., Vianello F. (2010). "Maghemite nanoparticles and method for preparing thereof" International Patent Application WO/2012/010200.

[2] Salviulo G., Magro M., Baratella D., Bonaiuto E., Carbone C., Dinelli E., Vianello F. (2015). "Removal of Cr(VI) in contaminated water of Stoppani S.p.A. site (Liguria, Italy) by surface active maghemite nanoparticles" – Congresso congiunto SIMP-AIV-SoGeI-SGI, Firenze 2-4 Settembre 2015.

[3] Magro M., Domeneghetti S., Baratella D., Jakubec P., Salviulo G., Bonaiuto E., Venier P., Malina O., Tuček J., Ranc V., Zoppellaro G., Zbořil R., Vianello F. (2016). "Colloidal Surface Active Maghemite Nanoparticles for Biologically Safe CrVI Remediation: from Core-shell Nanostructures ti Pilot Plant Development, Chem. Eur. J., 2016, 22, 14219-14226.

[4] Tuutijarvi T., Lu J., Sillanpaa M., Chen G. (2009). "As(V) adsorption on maghemite nanoparticles" J. Hazard Mater., 166,1415-1420.

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PHOSPHATE ADSORPTION BY LAYERED DOUBLE HYDROXIDES TYPE MATERIALS: EFFECT OF MATRIX COMPOSITION AND COMPETITIVE ANIONS

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LDHs, also called hydrotalcites, are a class of clay minerals having positive layers and negative exchangeable interlayer species. They occur naturally and may be easily synthesized in laboratory. The structure of these materials arises from the one of brucite ($Mg(OH)_2$) in which a divalent Mg^{2+} cation is isomorphously substituted by a higher charge cation, such as Al^{3+}, generating positive brucite-type layers. These positive layers are electroneutralized by anions, which together with the crystallization water molecules, are located in the interlayer gallery.

The LDH-type materials are generally described by the chemical formula $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2]^{x+} (A^{n-}_{x/n})$ mH_2O, where: M^{2+} are divalent cations (Mg^{2+}, Zn^{2+}, Ca^{2+}, etc.), M^{3+} are trivalent cations (Al^{3+}, Fe^{3+}, Mn^{3+}, etc) and An- are interlayer anions (CO_3^{2-}, NO_3^-, etc).

These materials may be used as suitable sorbents for phosphate uptake due to their large surface areas, high anion-exchange capacity, and flexible interlayer region accommodating various anionic species. Moreover, their chemical composition can be easily tuned allowing not only a high ion exchange capacity but also high selectivity towards the phosphate ions.

The composition of the brucite-like layers, the interlayer exchangeable anions, the calcination treatments and competitive anions in the polluted aqueous solutions are among the factors that may affect the sorption capacity as well the selectivity towards phosphates when dealing with LDH-type materials.

This study investigates the sorption behavior of phosphates on LDHs and their derived mixed metal oxides having different matrix compositions, such as different intercalated anions (Cl^-, NO_3^- or CO_3^{2-}) or different metal cations within the brucite-like network (Mg^{2+}, Zn^{2+}, Ca^{2+} and Al^{3+}). The selectivity as a function of LDH composition is evaluated towards phosphates adsorption in the presence of competitive anions, such as carbonates, sulphates, nitrates and chlorines.

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REUSE OF DISCARDED MEDICAL EQUIPMENT AS A KEY FOR HEALTH CARE SUSTAINABILITY: A LCA PERSPECTIVE

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In 2012 in the European Union there were 11,000 hospitals and 68,000 medical institutions (including long-term care facilities, clinics, specialized clinics, laboratories, etc.), with about 3,000,000 beds for acute illnesses.

The supply of healthcare services is highly dependent on the use of medical equipment, whose employ is continuously increasing. Moreover, the use phase of the life cycle of medical equipment is very short. In fact, the adoption of new standards, the need to improve safety and functionality of the equipment and also marketing purposes contribute to a continuous renew of the medical equipment: It is estimated that in European hospitals a medical equipment is averagely used only for 5 years. This brings to an increasing amount of medical equipment disposed.

Once disposed, most of the medical equipment become a WEEE, i.e. a Waste of Electrical and Electronic Equipment, which represents both a serious risks for the environment, primarily due to their content of hazardous materials, and at the same time, if properly managed, a valuable resource.

Considering healthcare institutions, scientific literature highlight that not enough attention is payed to medical WEEE, which are often neglected, stored in basements or in unused premises or donated to charity organization for their shipment in poor Countries without any warranty on their real destiny. Therefore, it is very important to promote a proper management of medical WEEE within healthcare institution.

In this work, a comparative life cycle assessment is performed to assess the environmental implications of different realistic solutions for the end of life medical equipment.

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COAL. ARTIFACTS AND PROPERTIES

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The development of dry mineral process is a priority issue in the mining industry aimed at saving raw materials and energy resources. The transition to dry beneficiation of high-ash coal is a highly promising trend in this respect. The development of an efficient dry coal beneficiation technique becomes possible on the condition of preliminary heat treatment of coal without the access of air and subsequent ash removal through dry electromagnetic separation. Heat treatment at 450–550 °C causes a drastic change in both the internal coal structure and the surface structure of its lumps. At this temperature, coal turns into so-called semicoke. Coal porosity increases, while the ratio of amorphous and crystalline phases in coal changes, thus creating favorable conditions for further dry beneficiation. At the same time, thermochemical modification of coal significantly changesits physical and mechanical properties, in particular through reducing its mechanical integrity. This drives down specific power consumption in the crushing process by 20–30% and also increases the calorific value of coal.

The structure study was carried out using a sample of Kuzbass coal. Macrophotographing and X-ray shadow graphing of the initial and heat-treated coal were performed using the SkyScan 1173 tomography scanner. The initial coal is dark gray, dense, laminar, fractured, with a matt cleavage surface. The surrounding coal mass consists of dispersed dark gray material of a massive texture. Layers (0.7–4 mm thick) are black, with irregular shiny cleavage surfaces, striated sections, and sections with gray-colored crystals measuring up to 0.025 mm. The coal samples are brittle; they break down along micro cracks under slight stress to produce sharp-cornered particles of 1–2 mm. They contain gelified bitumoids that make the fine powder (up to 20–40 μm) reddish-brown in color upon abrasion. In terms of petrography, the coal sample was composed predominantly of vitrite and lesser amounts of fusain. The ash portion made up 15% and consisted of aluminosilicates and minor amounts of pyrite. During heat treatment, the material'sgrains can be observed breaking up into smaller pieces, while the adhesion of coal particles with mineral components decreases as compared with the initial coal. Heat treatment significantly affects the pore structure of coal. At a moderate processing temperature of 450–500 °C, empty cavities and cracks grow larger letting out volatile coal components. As the temperature rises further above 550 °C, they are partially filled with organic matter degradation products. Overall, while the initial coal porosity ratio was 2%, it reached14% for semicoke and therefore the porosity ratio increased sevenfold.

In addition, the relief surface structure (roughness) of coal and its change as a result of heat treatment were studied. The surface roughness was quantitatively assessed with a laser scanning 3D microscope, Keyence VK-x200. This device provides a surface roughness measurement protocol for a set of parameters, which are used in international practice for evaluating various materials' (metal, wood, stone) surface properties, mainly subjected to mechanical treatment. The roughness of semicoke after heat treatment 5–7% lower than that of the initial coal. Visual assessment of the laser images and their 3D models'surface roughness demonstrates another interesting fact: the surface roughness of the initial coal is mainly related to sharp-cornered micron-sized bumps, while the roughness of the coal modified thermally at 550 °C is largely due to holes. Moreover, semicoke shows marked surface bitumization. The study of crystal (mineral) structure of the initial coal and samples after thermochemical treatment at 500–550 °C using the Rigaku SmartLab X-ray diffractometer with a rotation range of 5–100 degrees demonstrated the following: the initial coal's ash fraction consists mainly of kaolinite $Al_4[Si_4O_{10}](OH)_8$ with small inclusions of calcite $CaCO_3$, which is typical for coal as a geological material of sedimentary origin. The initial coal also contains a minorinclusion of chloro-bromo-organic compounds, which, based on the fundamental concepts of paleontology, were accumulated by initial plants (algae) up to the stage of their conversion into coal. Sulphur in the initial coal consists predominantly of typical inclusions of pyrite FeS_2. At 500–550 °C, bromo-chloro-organic compounds evaporate, and kaolinite decomposes first into cryptocrystalline quartz SiO_2, which at 550 °C turns into amorphous silica. At 550 °C,there are signs of the initial coking stage, which is established by graphite formation peaks.

The study of the coal heat treatment process with the use of modern instrumental methods of analysis showed what happens in the temperature range of 500–550 °C: the opening of incombustible mineral fraction particles along borders adjoining to the carbonic portion due to differences in physical and chemical properties during heat treatment; the decomposition of the ash portion, the kaolinite actively swelling in water with the formation of simple oxides, which practically do not swell and do not absorb air moisture, creates favorable conditions for subsequent dry beneficiation of coal; graphitization, which is undesirable from the standpoint of further use of the raw materials as energy, is not taking place in the given temperature range yet; the heat treatment range of 500–550 °Cis preferable from the standpoint of disintegration processes and classification in terms of size as it enables the formation of the favorable physical raw material structure and the high yield of ash content in small size classes.

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SPECIFIC ION EFFECTS ON OSCILLATORY HYDRATION FORCES, PROBED BY ATOMIC FORCE MICROSCOPY

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Short-range repulsive forces are fundamental to our understanding of the behavior and stability of a wide range of systems, from DNA and proteins to minerals and colloidal particles. Close to the solid – water interface, short range forces such as oscillatory hydration forces are observed which continues to be a topic of interest in the physical chemistry community. Ions affect the mobility of water and when adsorbed to an interface, ions influence the hydration and therefore these short range oscillatory forces [1]. How different types of ions, their hydration and mobility, contribute to the structural hydration force remains unclear. By the use of sub-nanometer oscillation amplitude modulation AFM and ultra-sharp tips, we are able to investigate the structural hydration force on muscovite mica interfaces, in the presence of electrolyte solutions without lateral confinement. We study the oscillatory hydration force in the presence of LiCl, KCl and CsCl in a concentration range from 0.05 to 4 M. Up to 3 oscillations are observed in our experiments indicating 3 stable hydration layers on the muscovite mica interface. The number of oscillations changes by changing the salinity and the type of ion (Li^+, K^+ or Cs^+). Our results show that small, highly hydrated ions such as Li^+ and K^+ are stabilizing the hydration layers on the muscovite mica interface while large, less hydrated ions such as Cs^+, destabilizing the hydration layers resulting in only one oscillation in the force profile.

[1] Martin-Jimenez D., Chacon E.,. Tarazona P, Garcia R. (2016). Atomically resolved three-dimensional structures of electrolyte aqueous solutions near a solid surface. Nat Commun, 7, 07/15/online 2016.

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A CRYSTAL-CHEMICAL INVESTIGATION ON NATURAL ZN-CLAYS FROM NONSULFIDE ORE DEPOSITS

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Zn-bearing clay minerals occur worldwide in several supergene nonsulfide ores, where they may represent an important metal source [2,3,4]. In the present work a crystal chemical investigation, by means of XRPD, WDS, ICP-MS/OES and FTIR, has been undertaken on two trioctahedral Zn-smectites, belonging to the supergene nonsulfides of the Skorpion (Namibia) and Yanque (Peru) deposits.

The Skorpion mineralization is the largest supergene nonsulfide zinc deposit in the world. It is hosted in Neoproterozoic rocks that are part of a volcano-sedimentary sequence within the Gariep Belt in the southern part of the country. In this deposit sauconite predominates over the other Zn-oxidized minerals, mainly represented by smithsonite, hemimorphite and Zn-bearing phosphates [5,6].

The Yanque prospect is a (Zn)-Pb nonsulfide concentration located 20 km north of Santo Tomás village in Peru [7]. The deposit consists of several sub-horizontal stratabound bodies that extend in depth to more than 100 m. Yanque is hosted by a sedimentary breccia with lateral facies variations, which stratigraphically comprehends parts of the Mara and Ferrobamba Formations [8]. Sauconite is the most abundant economic Zn mineral in the Yanque deposit.

The first studies on the composition and thermal properties of sauconite from different localities were provided by [9, 10]. Recently, mineralogical studies on this Zn-clay were carried out by various authors, i.e. [3, 11-13], but structural data on sauconite are scarce. The XRDP pattern of the Skorpion sample exhibits broad diffraction maxima indicative of the lack of perfect long-range order due to stacking faults and/or fine grained crystallite dimension. The (001) basal reflection is positioned at about 14.7 Å, whereas the diagnostic peak d_{060} is at 1.533 Å. For the Yanque sample XRPD data indicate the presence of minor amount of quartz, illite, kaolinite, chlorite, K-feldspar and goethite. Both sauconites show variable contents of Al and Zn, as well as Fe and Mg. The IR spectra show a distinctive band at about 3644 cm^{-1}, assigned to the $Zn(OH)_3$ stretching vibrations.

[1] Boni M., Mondillo N. (2015). The "Calamines" and the "Others": the great family of supergene nonsulfide zinc ores. Ore Geology Reviews, v. 67, 208-233.
[2] Boni M., Balassone G., Arseneau V., Schmidt P. (2009). The nonsulfide zinc deposit at Accha (Southern Peru): geological and mineralogical characterization. Economic Geology, 104(3), 267-289.
[3] Mondillo N., Nieto F., Balassone G. (2015). Micro- and nano-characterization of Zn-clays in nonsulfide supergene ores of southern Peru. Am. Min., 100, 2484–2496.
[3] Borg G., Kärner K., Buxton M., Armstrong R., van der Merwe S.W. (2003). Geology of the Skorpion non-sulphide deposit, southern Namibia. Economic Geology, 98, 749–771.
[5] Kärner K. (2006). The metallogenesis of the Skorpion Non-sulphide Zinc Deposit, Namibia. Unpublished Ph.D. Thesis, Martin-Luther-Universität Halle-Wittenberg (Germany), 133 pp.
[6] Zincore Metals, Inc. (2013). AZOD Zinc Oxide project, NI 43-101 Technical Report on a Preliminary Feasibility Study: Zincore Metals, Inc., Vancouver, Canada (http://www.zincoremetals.com/_shared/pdf/170848_Zincore_PFS_Tech Report_AZOD_26August2013_Final.pdf).
[7] Pecho V., Blanco E.Z. (1983). Geología de loscuadrángulos de Chalhuanca, Antabamba y Santo Tomás: Instituto de Geología, Minería y Metalurgia, Boletín, Lima, Peru, 35, 97 p.
[8] Mondillo N., Boni M., Balassone G., Villa I.M. (2014). The Yanque Prospect (Peru): from polymetallic Zn-Pb mineralization to a Nonsulfide deposit. Economic Geology, 109, 1735-1762.
[9] Ross C.S. (1946). Sauconite—a clay mineral of the montmorillonite group. American Mineralogist, 31, 411–424.
[10] Faust G.T. (1951). Thermal analysis and X−ray studies of sauconite and of some zinc minerals of the same paragenetic association. American Mineralogist, 36, 795–822.
[11] Kaufhold S., Färber G., Dohrmann R., Ufer K., Grathoff G. (2015). Zn-rich smectite from the Silver Coin Mine, Nevada, USA. ClayMinerals, 50, 417-430.
[12] Choulet F., Buatier M., Barbanson L., Guégan R., Ennaciri A. (2016). Zinc-rich clays in supergene non-sulfide zinc deposits. Mineral. Deposita 51, 467–490.
[13] Buatier M., Choulet F., Petit S., Chassagnon R., Vennemann T. (2016). Nature and origin of natural Zn clay minerals from the BouArhous Zn ore deposit: Evidence from electron microscopy (SEM-TEM) and stable isotope compositions (H and O). Applied Clay Science, http://dx.doi.org/10.1016/j.clay.2016.07.004, 1-14.

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USE OF ALKALI-ACTIVATED BINDERS FOR SOIL STABILISATION

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KAOLINITE-BASED RENAISSANCE CERAMICS: THE HIDDEN PHASE OF BERNARD PALISSY

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The ceramics earthenware of Bernard Palissy (1510-1590) rank amongst the most outstanding technical and artistic masterpieces of the European Renaissance period. The polychromic clay-based substrates and the glazes are assembled with a precision that still remains unequalled. The issue of the still unknown thermal processes is the focus point of a research program developped at the *Centre de Recherche et de Restauration des Musées de France* of the Louvre museum, Paris, France, based upon a corpus of ceramics shards collected during the excavations of Palissy's workshop in the Louvre's courtyard.

As shown by our analyses, the white paste, very common in his ceramics, results of the annealing of a kaolinite ($Al_2Si_2O_5(OH)_4$)-rich clay mixed with quartz. The thermal transformations of these pastes can be used to assess the heat treatments more surely than the colored ones, in which the transition metals oxides (Fe, Co, Cu, Mn, …) are known to foster the formation of mullite ($\sim Al_4SiO_8$). In parallel with X ray diffraction and scanning electron microscopy on a dozen of authentified samples, mock-ups were synthesized starting from pure kaolinite and a natural clay, chemically similar to the one used by Palissy, and originating from the same Provins deposit. The effect of the (t, T) parameters on the mineralogic composition and the microstructure was studied, then the so-obtained samples were compared to Palissy's own ones.

At this point, and in spite of a consistent literature, our works evidenced wide gaps in the knowledge of the themal transformations of kaolinite. The main cause was the lack of knowledge of the quantitative assessment and the nature of the metastable nanophase known since 1959 as the "Al-Si spinel", but never characterized to this date. The Al-Si spinel occurs in the 950-1070 °C range before collapsing into mullite. A crystallization process starting from sol-gel and the use of neutron diffraction (in collaboration with the PEARL diffractometer, Delft TU, The Netherlands) revealed for the first time the composition and the monoclinic crystal structure of this key phase, one of the rare definite compounds of the Al_2O_3-SiO_2 pseudo-binary system. The thermal evolution of the concentrations of the various decomposition products of kaolinite, the Al_2O_3:SiO_2 ratio in mullite and its microstructure were finally established using Rietveld quantitative phases analysis, allowing a significant breakthrough in the knowledge of the thermal transformations of Al-rich clays.

As composite ceramics, Palissy's white paste appears to be made of undigested quartz, nanocrystalline Al-Si spinel and poorly-crystallized mullite in various amounts, the whole being cemented by a silica-rich amorphous phase with low modifiers ratios. On the basis of a heat treatment reasonably estimated at 10-24 hours, this typical composition of the first stage of the transformation of kaolinite seems to indicate that the Renaissance master's kilns were operating around 1000 °C, clearly below the temperature range commonly used for the elaboration of Al-rich pastes like porcelaines (around 1200 °C). Nevertheless, the remarkable mechanical properties and the absence of cracks of Palissy's ceramics led us to investigate also the thermomechanical properties of these poorly-known earthenware composites.

High-temperature X ray diffraction revealed that, in spite of a high Al:Si ratio, the thermal expansion of the Al-Si spinel is moderate ($\alpha_l = 7.4\ 10^{-6}$ °C^{-1}, versus $9.3\ 10^{-6}$ °C^{-1} for α-Al_2O_3). The thermal libration of the SiO_4 tetrahedra that link the layers of AlO_6 octahedra are indeed responsible for an inflection of the expansion curve around 600 °C. This allows to conclude that the four constitutive phases of Palissy's white ceramics exhibit very similar coefficients of thermal expansion, in agreement with their high toughness.

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GRAZING-INCIDENCE EXAFS ANALYSIS OF SORPTION ON MICA EDGE PLANES: RESULTS FOR Pb^{2+} AND AsO_4^{3-}

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Mica edges appear to behave chemically much like oxide surfaces, but studies that focus uniquely on the edge planes themselves are extremely limited. For example, most studies of sorption consider the entire mica surfaces, which are usually dominated by basal planes. Hence the reactions of the edges are difficult to extract from the data.

In our studies we emphasize the mica edge planes by using specially prepared single crystal mica samples with extended edge plane surfaces of up to 1 cm^2 in area. The edge planes can be prepared by chemical-mechanical polishing to a roughness less than 1 nm by slow processing. With such samples it is possible to use grazing-incidence x-ray methods to obtain enhanced EXAFS signals from the edge planes in several x-ray electric vector polarizations. This allows three-dimensional information on the geometry of sorption and any possible clustering of sorbed species.

Initial work has been done both with muscovite and phlogopite surfaces using arsenate and divalent lead as sorbates. While arsenate sorbs as an inner sphere complex on the edges, divalent lead may sorb as some combination of inner and outer sphere complexes. Determination of second shell neighbors is difficult but may be possible with additional data. In particular it is of interest to see if sorbed ions prefer binding to silicate or aluminate polyhedra, and whether edge sites have distorted metal oxygen polyhedra (e.g. with five-fold coordination) as suggested by edge plane simulations. Although preliminary work has been confined to solution conditions affording maximal sorption, we ultimately wish to study a range of solution compositions and edge plane charge states.

We discuss both the grazing incidence approach and aspects of data reduction as well as the significance of the findings for environmental chemistry and crystal chemistry.

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AG$_3$PO$_4$ IMMOBILIZED ON HYDROXY-METAL PILLARED MONTMORILLONITE FOR THE VISIBLE-LIGHT-DRIVEN DEGRADATION OF ACID RED 18

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Ag_3PO_4 is considered to be an ideal candidate for water photooxidation and organic contaminant decomposition under visible light due to its appropriate band gap position, nontoxicity, and high quantum yield [1]. However, pure Ag_3PO_4 may decompose to metallic Ag during the catalytic degradation of organic contaminants and generally has a small specific surface area (SSA) [2]. Some studies have shown that coupling Ag_3PO_4 with other semiconductors or metals to form composite photocatalysts can largely increase its stability in resisting recombination of photogenerated and electron–hole pairs [3,4]. Hydroxy-metal pillared montmorillonite (Mt), such as hydroxyl-iron–aluminum pillared Mt (Fe–Al/Mt), due to their large SSA, low cost, and high adsorption capabilities, have been used as an adsorbent for oxyanions and metal cations [5]. As such, hydroxy-metal pillared montmorillonite may effectively load Ag_3PO_4. On the other hand, considering that some metals (e.g., Fe^{3+}) can act as electron acceptors, the corresponding pillared Mt may be used as a support material to suppress the charge recombination of Ag_3PO_4. Hence, we expect that some hydroxy-metal pillared Mts may be an ideal support and at the same time can act as an electron acceptor for Ag_3PO_4 to suppress charge recombination, and the resulting composites with a high SSA can effectively degrade organic pollutants under visible light irradiation and have better stability.

In the present work, hydroxy-aluminum pillared Mt (Al/Mt) and Fe–Al/Mt were selected as hydroxyl-metal pillared Mts and used as support materials to load Ag_3PO_4, with the purpose of synthesizing new materials (i.e., Ag_3PO_4/Al/Mt and Ag_3PO_4/Fe–Al/Mt) with high photocatalytic activity and good stability. The structural characteristics of the resulting materials were studied using XRD, SEM-EDS, XPS, ICP, nitrogen adsorption-desorption isotherms, and UV–vis diffuse reflectance spectra; the photocatalytic activity of the obtained catalysts was tested using acid read 18 (AR18) as a model contaminant under visible light irradiation.

The obtained results illustrated that high dispersity and smaller size of Ag_3PO_4 was successfully loaded on hydroxy-metal pillared Mts. The photocatalytic activity and structural stability of the three synthesized catalysts were in the order Ag_3PO_4/Fe–Al/Mt>Ag_3PO_4/Al/Mt>Ag_3PO_4. The efficiency of 98.5% was achieved for AR18 degradation by Ag_3PO_4/Fe–Al/Mt after seven times of recycling, while only 54.9% for Ag_3PO_4. Superoxide radical anion ($O_2^{\bullet-}$) was confirmed to be the dominant reactive species in all the three degradation systems, and the Ag_3PO_4/Fe–Al/Mt system formed the largest amount of $O_2^{\bullet-}$. The possible reasons for the enhanced photocatalytic activity and stability of Ag_3PO_4/Fe–Al/Mt may originate from two aspects. The first one may be the high dispersity and smaller size of Ag_3PO_4 in Fe–Al/Mt. The other aspect may be attributed to the Fe–Al/Mt support, which can result in the efficient separation of photogenerated electron–hole pairs by Ag_3PO_4 and high $O_2^{\bullet-}$ generation from the reduction of dissolved oxygen. When Ag_3PO_4 is irradiated by visible light, electron–hole pairs are generated. In the absence of electron acceptors, the transformation of Ag^+ into metallic Ag usually takes place during the photocatalytic process. The presence of Fe^{3+} in Ag_3PO_4/Fe–Al/Mt, which can act as an electron acceptor for the photo-induced electrons from Ag_3PO_4 during the photocatalytic process and then inhibit the transformation of Ag^+ into metallic Ag.

[1] Yi Z., Ye J., Kikugawa N., Kako T., Ouyang S., Stuart-Williams H., Yang H., Cao J., Luo W., Li Z. (2010). An orthophosphate semiconductor with photooxidation properties under visible-light irradiation. Nat. Mater., 9, 559-64.

[2] Bi Y., Hu H., Ouyang S., Lu G., Cao J., Ye J. (2012). Photocatalytic and photoelectric properties of cubic Ag_3PO_4 sub-microcrystals with sharp corners and edges. Chem. Commun., 48, 3748–3750.

[3] Yao W., Zhang B., Huang C., Ma C., Song X., Xu Q. (2012). Synthesis and characterization of high efficiency and stable Ag_3PO_4/TiO_2 visible light photocatalyst for the degradation of methylene blue and rhodamine B solutions. J. Mater. Chem., 22, 4050–4055.

[4] Yu H., Cao G., Chen F., Wang X., Yu J., Lei M. (2014). Enhanced photocatalytic performance of Ag_3PO_4 by simutaneous loading of Ag nanoparticles and Fe(III) cocatalyst, Appl. Catal., B, 160–161, 658–665.

[5] Zhu R., Zhu J., Li M., Ge F., Xu Y., He H. (2014). Co-sorption of Cd and phosphate on the surface of a synthetic hydroxyiron-montmorillonite complex. Clays Clay Miner., 62, 79–88.

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DEGRADATION BEHAVIOR OF FLUORINE-DOPED TIN OXIDE FILM EXPOSED AT HIGH TEMPERATURE

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Fluorine-doped tin oxide (FTO) having excellent electrical conductivity and transparency has received great attention as a transparent conductive material to replace indium tin oxide (ITO). Its heatable characteristics make FTO versatile in many applications such as heating glass and thin film ceramic heaters. However, during prolonged use of FTO film at high temperature, its heating ability can decrease due to microstructural degradation. In this study, the performance degradation of FTO thin film exposed to high temperatures and its microstructural mechanisms were evaluated. FTO thin films deposited on a Si glass substrate by using nano-spray pyrolysis deposition (SPD) process were isothermally exposed to 500 °C, 600 °C and 700 °C for various durations up to 7 days, respectively. Interface delamination and formation of internal defects such as pin hole and hill-rock were examined by flash thermography technique. The surface/cross-sectional microstructures including grain growth and phase were analyzed by SEM and XRD, respectively. Electrical sheet-resistance measured by 4-point probe method was observed to increase with increasing temperature and exposure time. This performance degradation was rationalized in terms of the structural changes observed after thermal exposure.

Keywords: FTO, thin film, degradation, heatable characteristics.

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MICRO RAMAN STUDY OF *PIETRA OLLARE* ARTIFACTS: AN INSIGHT ON MEDIEVAL COMMERCIAL ROUTES OF NORTH ITALY

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Pietraollare indicates a group of several Alpine metamorphic rocks, prevalently constituted by talc, magnesite and dolomite, with other accessory minerals. However, the term *pietraollare* has no specific petrological meaning and derives from the Latin word *olla*, which means “container”. In fact, these rocks combine good thermal stability, usually up to 1000 °C, high resistance to temperature changes, low porosity, and low hardness, thus providing an easily processable material, perfect for stoves and cooking utensils. Consequently, *pietraollare* has been exploited since the prehistoric age, and from the Roman Empire to the Middle Age it was part of everyday life, being widespread throughout Italy and Central Europe.

Pietraollare have been classified into 11 groups with different composition and origin [1]. In particular, light green-grey magnesite talc schists and chlorite schists are typical of the quarries of Valchiavenna and Valmalenco, whereas green garnet chlorite schists come from Valle d’Aosta and Val di Lanzo. This specificity in the mineralogical composition of the different outcropsrepresents a fingerprint that can be exploited to determine the provenance of archaeological findings. This identification has been usually accomplished by standard petrological studies, often combined withother techniques such as x-ray diffraction, e.g. [2], and more recently micro Raman spectroscopy [3]. In particular, this non-destructive technique allows to identify mineralogical species with high sensitivityby measuring their vibrational spectra.

Here we present an extensive micro-Raman study on a set of specimens coming from twoMedieval sites nearby Verona, Nogara [4] and Illasi [5], dating back to the 9th- 11th century.Measurements were carried out in backscattering geometry byusing a Horiba-JobinYvonLabRam HR, a single spectrograph with a notch filter and an holographic grating (600 lines/mm). As light source we used the 633 nm line of a He-Ne laser and spectra werecollected with a 80x objective, spot-size of about 4 μm^2, and acquired by a CCD detector (256x1024 pixels), cooled at -134 °C by liquid N_2.Average information were obtained by mapping the samples with several punctual measurements.

The so-obtained spectra were then compared to those measured on reference samples coming from ancient quarries distributed throughout the Alps. This allows to identifythe provenance of each specimenand addsa tile to the map of trading routesduring the Middle Ages in the north of Italy.

[1] T. Mannoni, H.R. Pfeifer, V. Serneels (1987).“La pietra ollare dalla preistoriaall’età moderna” conference proceedings, Como, October 16–17 1982, 7–45.

[2] P. Santi, A. Renzulli, F. Antonelli, A. Alberti (2009). J. Archaeol. Sci. **36**, 2493-2501.

[3] C. Baita, P.P. Lottici, E. Salvioli-Mariani, P. Vandenabeele, M. Librenti, F. Antonelli, D. Bersani (2014). J. Raman Spectrosc. 45, 114–122.

[4] G. Varanini, F. Saggioro, F. Scartozzoni (2009). “Il castello di Illasi. Storia e archeologia”, Giorgio Bretschneider, Roma.

[5] F. Saggioro (2011). “Nogara: archeologia e storia di un villaggio medievale”, Giorgio Bretschneider, Roma.

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POROUS COAL FLY ASH FOR ANIONIC SURFACTANTS REMOVAL

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This work concerns the synthesis of a sustainable porous material, obtained by an industrial by-product and a food material, for anionic surfactants removal.

Anionic surfactants are widely used in many applications and are present in both industrial and domestic wastewater. Surfactants can create environmental problem such as foam formation, eutrophication and increase the solubility of some pollutants in water [1]. For these reasons it is important remove them from water. Many treatments are available for their removal such as membrane filtration [2], oxidation [3] and adsorption [4]. One on the common method to remove surfactants from water is to use adsorption technology. Nowadays, activated carbons are the adsorbent widely used in water purification. The disadvantage in the use of these materials are the high cost of production (they are natural resources) and the thermal regeneration process. Therefore, the research of low cost adsorbent is today quite desirable. The challenge of this work is to select a new porous adsorbent, mainly in term of high adsorption capacity but with great attention of its costs and sustainability. Porous material have been proven invaluable for use as adsorbent for their property: due to their unique properties such as low density, high porosity and high specific surface area.

To evaluate the environmental sustainable of this material, the CO_2 footprint and embodied energy were selected (CES Edu'13) as main parameters to consider. In particular, the coal fly ash (CFA) was found to be a promising alternative to activated carbon. CFA is an industrial by-product derived from coal combustion in thermal power plants. This abundant and low cost waste is generally reemployed as additive in the building industry or for soil amendment [5]. Therefore, the porosity of the material was obtained by the use of egg white as environmentally-friendly binder and pore former.

The porosity of the obtained composite was analyzed by mercury intrusion porosimetry method. Structural and morphological characterization of adsorbent were performed by Scanning Electron Microscopy (SEM) and X-Ray Diffraction (XRD). The adsorption efficacy of porous material was evaluated using Sodium Dodecyl Sulfate (SDS) as model surfactant.

The obtained results revealed good adsorption capacity of porous material up to 60%. This material may be used in a pre-treatment phase, to optimize chemical and/or biological treatment and to achieve the required level of water quality at low costs. Furthermore, the material float on the solution, so it could be easily removed from wastewater, after the pollutants adsorption.

For material recovery two solutions are proposed: the regeneration of porous material, by thermal treatment and its reuse in the concrete production. Indeed, recent works show that surfactants improve the resistance of concrete toward degradation [6].

[1] Mukherjee B., Nivedita M., Mukherjee D. (2010). Plankton diversity and dynamics in a polluted eutrophic lake, Ranchi. J.Environ.Biol. 31, 827-839.
[2] Qin D., Liu Z., Bai H., Sun D.D., Song X. (2016). A new nano-engineered hierarchical membrane for concurrent removal of surfactant and oil from oil-in-water nanoemulsion. Sci.Rep. 6, 24365.
[3] Lechuga M., Fernandez-Arteaga A., Fernandez-Serrano M., Jurado E., Burgos A., Rios F. (2014). Combined use of ozonation and biodegradation of anionic and non-ionic surfactants. J.Surfactants Deterg. 17, 363-370.
[4] Goyal M., Dhawan R., Bhagat M. (2008). Aspects Adsorption of dimethyl sulfide vapors bi activated carbons. Colloid. Surf. A. 322, 164-169.
[5] Yao Z.T., Ji X.S., Sarker P.K., Tang J.H., Ge L.Q., Xia M.S., Xi Y.Q. (2015). A comprehensive review on the applications of coal fly ash. Earth Sci. Rev, 141, 105-121.
[6] Jolicoeur C., To T.C., Nguyen T.S., Hill R., Page M. (2009). Mode of action of anionic surfactants for air entrainment in cement pastes w-w/o fly ash. World of coal ash conference may 4-7.

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IN-HOUSE REFERENCE MATERIALS FOR THE DETERMINATION OF LOW TITANIUM CONCENTRATION IN SIO_2 BY SECONDARY ION MASS SPECTROMETRY (SIMS)

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SIMS (Secondary Ion Mass Spectrometry) is a routinely used analytical technique for geochemical and mineralogical applications. Nevertheless, quantification is still the major challenge of this method. Due to the fact, that each analysed matrix needs its own matrix-matched reference material (RM), the list of available reference materials is short compared to the needs of the analysts. A current evaluation of the GeoReM database [1] shows a strong focus on using the well-known NIST SRM 610-617 glasses for trace element analysis and several zircons for isotope analysis.

One approach for the production of suitable RMs is the use of ion implantation to introduce a known amount of an isotope into a matrix-matched material. This approach is widely-used for SIMS applications in materials science, but rarely used for geochemical problems. Bumett et al. (2014) [2] demonstrated the principal appropriateness of this method and ways to calibrate nominal implant fluence. We choose the more elaborate way of implanting a box profile to allow a homogeneous distribution of the respective isotope in all three dimensions.

The mineralogical and chemical "simple" SiO_2 system entails many interesting scientific challenges like the Ti-in-quartz geothermometer [3,4]. We implanted ^{47}Ti respectively ^{48}Ti into synthetic ultra-high purity silica glass. Several box profiles with concentrations between 10 and 1000 ppm and a maximum depth of homogeneous $^{47/48}Ti$ distribution between 200 and 500 nm were produced at the Ion Beam Center in Dresden-Rossendorf. The single implantation steps with different ion-energies and –doses were simulated with the SRIM (Stopping and Range of Ions in Matter) software [5] and optimized to the necessary concentrations, implantation-depths and limits of the implanter. After the implantations, the surface-roughness of the implanted glasses was measured using atomic force microscopy (AFM). The roughness is still in the range necessary for SIMS measurements.

We characterized several implanted test-samples with different concentrations and maximum implantation-depths by means of SIMS and other analytical techniques. It has been shown, that Ti is dissolved in the glass structure. The homogeneity of the Ti-concentration is within ± 5% uncertainty in all 3 dimensions.

[1] http://georem.mpch-mainz.gwdg.de.
[2] Bumett D.S., et al. (2014). Ion Implants as Matrix-Appropriate Calibrators for Geochemical Ion Probe Analyses. Geostandards and Geoanalytical Research, 39(3), 265-276.
[3] Wark D.A., Watson E.B. (2006). TitaniQ: a titanium-in-quartz geothermometer. Contributions to Mineralogy and Petrology, 152(6), 743-754.
[4] Thomas J.B., Watson E.B., et al. (2010). TitaniQ under pressure: the effect of pressure and temperature on the solubility of Ti in quartz. Contributions to Mineralogy and Petrology, 160(5), 743–759.
[5] Ziegler J.F. (2004). SRIM-2003. Nuclear Instruments and Methods in Physics Research Section B, 219-220, 1027-1036.

INDEX OF AUTHORS

NOTICE. THE NAMES OF SOME OF THE AUTHORS WERE NOT ERRONEOUSLY OMITTED BUT THEY WERE NOT AVAILABLE SINCE THEY HAD NOT BEEN INSERTED DURING THE ABSTRACT SUBMISSION PROCEDURE.