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PLENARY LECTURES

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ADVANCED ECOMATERIALS BASED ON FUNCTIONAL CLAY NANOARCHITECTURES

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Clay minerals are exceptionally abundant and widely distributed raw materials in Nature. They have been used since antiquity in pottery and building elements as for instance adobe, bricks and tiles. Currently, this natural resource attracts a great interest in view to prepare advanced nanostructured materials contributing at the same to reduce environmental impact. Clays, by themselves, and most of clay derivatives, are safe materials useful for multipurpose applications in strategic sectors ranging from energy storage to biomedical uses under nanotechnology approaches. Beside, the use of clay-based nanostructured materials for detection and removal of pollutants from air, water and soils is becoming a topic of increasing research activity.

Functional nanoarchitectures based on silicate clays of different composition and structure, showing layered, tubular or fibrous morphologies, have been designed in view to applications as adsorbents, catalysts, membranes, gas-barriers, polymer-clay nanocomposites, electrical and electrochemical devices, photoactive systems or even as additives for vaccines and non-viral vectors for gene delivery and transfection of last generation. Assuming that advanced technologies will require in a near future the use of low cost, widely distributed and no-pollutant resources such as clays and other abundant raw ecomaterials, recent examples of advanced materials based on smectite type, such as montmorillonite, or prepared from fibrous clays such as sepiolite, will be introduced and discussed here. It will be shown, for instance, applications on materials based on clays as superparamagnetic adsorbents, supported graphenes and materials for biomedical purposes, which have been developed in our laboratory in recent past years.

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ENGINEERING OF MAGNETIC PROPERTIES OF AMORPHOUS AND NANOCRYTALLINE MICROWIRES

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Amorphous and nanocrystalline thin ferromagnetic microwires (typically of 1-30 μm in diameter) have attracted growing attention in the last few years owing to excellent magnetic properties, fast domain wall dynamics and Giant Magnetoimpedance, GMI, effect [1,2]. The principal advantages of these materials are unexpensive fabrication method allowing preparation of long and continuous microwires. Moreover these microwires can exhibit either unusual and extremely good soft magnetic properties and GMI effect interesting basically for applications for low magnetic field detection or extremely fast domain wall propagation suitable for magnetic memories or logics [3].

Generally soft magnetic properties of amorphous ferromagnetic microwires are affected by the magnetoelastic energy related to the presence of glass coating. Spontaneous magnetic bistability and fast domain walls, DW, propagation are reported for microwires with positive magnetostriction constant exhibiting rectangular hysteresis loops. GMI effect and best soft magnetic properties are usually reported in amorphous microwires with vanishing magnetostriction constant [1,2, 4]. Aforementioned magnetoelastic energy depending on magnetostriction constant, λ_s, as well as on stresses, σ (applied, σ_{app} and internal, σ_i) affects both domain wall dynamics and GMI effect [2,5]. The magnetostriction constant depends mostly on the chemical composition of amorphous metallic alloy and is vanishing in amorphous Fe-Co based alloys with Co/Fe ≈70/5 [4].

The necessary condition for observation of fast DW propagation is the magnetic bistability typically observed in Fe-rich microwires with rectangular hysteresis loops [1]. On the other hand the condition for achievement of considerable GMI effect is high magnetic permeability usually observed in Co-rich microwires with low and negative magnetostriction constant [2]. Consequently GMI effect and fast DW propagation related to magnetic bistability are two mutually exclusive features in the case of glass-coated microwires. Until now high GMI effect and fast DW dynamics simultaneously have not been observed.

We demonstrate that in Co-rich amorphous microwires with vanishing magnetostriction coefficient conventional annealing is quite efficient method for tailoring of magnetic properties. We found the annealing conditions at which we can observe induced magnetic bistability allowing observation of fast DW propagation and GMI effect simultaneously in the same sample. For interpretation of observed changes of hysteresis loops by annealing we consider stress dependence of the magnetostriction.

For amorphous microwires with high magnetostriction coefficient most efficient methods of tailoring of magnetic properties are either stress (or magnetic field) annealing or nanocrystallization of amorphous microwires. Stress annealing of glass-coated composite microwires results in re-distribution and even drastic decrease of the longitudinal stress component and even in the appearance of the compressive longitudinal stresses (so-called "back stresses"). Consequently very interesting magnetic behavior, i.e. stress impedance effect or extremely soft magnetic properties can be realized [5].

Finally, nanocrystallization allows obtaining of the structure consisting of the nano-grains and amorphous matrix. Presence of the remaining amorphous phase gives a good balance of positive and negative magnetostriction λs, resulting finally in a very low net magnetostriction coefficient in some particular compositions. Considerable magnetic softening and as enhancement of the GMI effect in Finemet-type FeCuNbSiB with nanocrystalline structure have been observed [1].

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INNOVATIVE METHODOLOGIES IN NANOTECHNOLOGY FOR SENSORS AND BACTERIAL DISEASES

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In the last decades, research has been devoted to the development of new products for enhancing the quality of human life. Two are considered the main interests in this field, the inspection of the environments by means of sensors and the antimicrobial agents, generally used to avoid the increase of potential health risks. It is well know that nanomaterials are of particular interest for these applications due to their important properties to have most of the atoms at the surface, that is the carrier by which the material interacts with the external ambient. Various techniques distinguished in chemicals (electrosynthesis, chemical reduction) [1-3], or physicals (evaporation-condensation and laser ablation) [4-6] have been used to realize nanomaterials.

In this work a new approach is presented to prepare devices combining a physical method with a chemo-physical one. A synergy of an Ion Beam Sputtering (IBS) with a Spray technique allowed to match bulk- or nano-materials with nanoparticles.

The advantage of IBS with respect to other sputtering deposition techniques is the independent control of the energy, the current density and the direction of the gas ions that give rise to the sputtering process. Moreover, due to the low work pressure, thermalization of sputtered species can be avoided, then the energy and uniformity of the deposited particles is expected to be higher than in plasma sputtering. With this technique it has been possible to grow both metal that semiconductor or polymer films [7-9]. In cosputtering configuration composites of nanoparticles of metals or oxides in a polymer matrix were also grown [10].

The Spray method allowed to easily deposit layers on large area, with a very good adhesion starting from a powder of the material to grow [11,12].

The greatest potential of the two technique and of their combination will be further showed presenting some of the results obtained in the field of:

- antibacterial treatments of textile materials [13];
- sensors for gases and vapors [14].

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MECHANISTIC INSIGHTS ON THE ANTI-INFLAMMATORY ACTIVITY OF NATURALLY-OCCURRING TUBULAR AND FIBROUS CLAYS

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This paper reports on the anti-inflammatory activity of tubular (halloysite) and fibrous clays. Fibrous clays, produced at 1.2 m tons per year worldwide, have an ample range of industrial applications, from the production of pet littler, animal feed stuff to roof parcels, and construction and rheological additives, and other applications needing to replace long-fibre length asbestos. Yet, the effect of these materials on health remains scarce and inconclusive. This paper reports on the anti-inflammatory, anti-bacterial, and cytotoxic activity by sepiolite (Vallecas, Spain) and palygorskite (Torrejon El Rubio, Spain), as evidenced by the TPA and MPO models, nitric production inhibition, MTT assay, and screening *in vitro* against human cancer cell lines (colorectal, mammary, prostatic, and lung adenocarcinoma; chronic myelogenous leukemia, glioblastoma). As indicated by nitric oxide inhibition, peritoneal cells showed decreases in viability after exposure to sepiolite, yet when present at high concentrations only. That was not the case for when exposing cells to palygorskite or halloysite. On the other hand, as confirmed by primary screening in cancer human cells in suspension, exposure to sepiolite or palygorskite led to growth inhibition. Exposure of cells U251 to sepiolite or palygoskite showed highest mortality levels *ca.* 50%. Most notably, the mortality of cells SKLU-1 increased by 7 times after palygorskite-for-sepiolite replacement. Palygorskite presented a higher frequency in the periodic inversion of the apical oxygen of the tetrahedral sheet. Higher values for early edema inhibition by palygorskite *vs* sepiolite were explained because disruptions of inversion sites by organic or inorganic solutes. Resulting from inversions was the formation of octahedral cations, generating additional sites for adsorption at the clay-water interface. In suspension, ageing of fibrous clay surfaces limited the migration of neutrophils. When intact, such surfaces restrained the migration of neutrophils by physical means. Although, the secretion of neutrophils appeared to depend on the structure of the clay surfaces, cellular-level signals, however, responded strictly to early exposure. Binding specificity was sought to control the anti-inflammatory activity by fibrous clays. ^{29}NMR evidence showed increases in the electron density at $(SiO_4)^+$ tetrahedrons at external surfaces, strongly suggesting their role as adsorption and reaction sites. In this tenor, (i) the prolonged anti-inflammatory activity by halloysite only was explained because concentric dissolution, resulting in a continuous production of highly-reactive sites (kinks, edges, sites), generating silanol groups. Likewise, (ii) the early anti-inflammatory activity by sepiolite and palygorskite was explained because cleavage of polysomes at inversion sites, which generated binding surface sites (e.g. coordination sphere of octahedral cations), *albeit* to a lesser extent than in (i).

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PROPERTIES, MANUFACTURE AND USE OF ALKALI-ACTIVATED MATERIALS

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In 1940 the synthesis of construction materials by alkaline activation of high-calcium blast furnace slags was firstly proposed. Relevant changes took place in the 1970s when the term ‘geopolymer’ was coined by Joseph Davidovits who studied the alkali activation of low calcium aluminosilicate.

The alkali-activated material synthesis takes place by polycondensation and can start from metakaolinite or many natural and artificial silico-aluminates by reaction with alkali metal (Na or K) silicate. When in contact with the high pH alkaline solution, the starting materials dissolve and the polycondensation takes place. Amorphous materials are obtained at temperatures from 20 to 90 °C, while crystalline ones are formed in autoclave at 150-200 °C..

Alkali activated building materials are attractive because excellent mechanical properties, durability and thermal stability can be achieved. In the case of geopolymer, due to lower Ca content, they are more resistant to acid attack than those based on Portland cement. They are of great interest also because of the reduced energy requirement for their manufacture. In fact, the reaction pathway requires either metakaolinite, (kaolinite calcined at 600-700 °C), or raw silico-aluminates. Then, green house gas emission can be strongly reduced in comparison to traditional cement-based materials.

Applications of alkali activated materials in the fields of new ceramics, cements, matrices for hazardous waste stabilization, fire-resistant materials, asbestos-free materials and high-tech materials have been documented..

Among the wastes of silico-aluminate nature non-hazardous ones such as reservoir clay sediments, excavated clay residues and sludge are worthy of consideration as precursors. Most of these contain a diverse set of clay minerals, mostly illites, smectites, chlorites and kaolinites and are available in huge amounts. In addition, when pollutants are present in contaminated clay waste (e.g. marine sediments) they can also be stabilized into the polycondensated 3-D network..

This presentation summarize a number of solid waste recycling processes based on alkali activation that have been studied for applications in the manufacture of bricks, binders, artificial aggregate, panels, etc..

Handbook of Alkali-activated Cements, Mortars and Concretes. (2015). Edited by F. Pacheco-Torgal, J. A. Labrincha, C. Leonelli, A. Palomo and P. Chindaprasirt. Woodhead Publishing Series in Civil and Structural Engineering: Number 54.Elsevier. ISBN 978-1-78242-276-1.

BIOMATERIALS

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EFFECT OF TI-MO DIFFUSION COATING ON CORROSION BEHAVIOR AND SURFACE PROPERTIES OF STAINLESS STEEL AISI 316L FOR DENTAL APPLICATIONS

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The pack cementation method was used to generate titanium- molybdenum diffusion coating on stainless steel alloy AISI 316L. Some surface properties (micohardness, surface roughness and adhesion test) and corrosion resistance were investigated in this study. The corrosion behavior was assessed by using potentiodynamic polarization method in 0.1 M NaCl solution containing varying concentrations of fluoride ions. The results indicated that microhardness and surface roughness markedly increased after coating, while the adhesion strength depend on the temperature and diffusion coating time. Moreover, the corrosion reistance was signficantly improved by applying Ti-Mo coating compared with the uncoated specimens.

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FABRICATION OF THERMOSENSITIVE POLYSACCHARIDE INJECTABLE HYDROGELS

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Polysaccharides are nontoxic, biodegradable and biocompatible biomaterials that come from abundant natural resources. They have demonstrated potential applications in biomedical engineering and tissue engineering. Here, thermosensitive polysaccharide injectable hydrogels that could transform from sols to a gel at body temperature were fabricated by integrating polyethylene glycol and polysaccharides like carboxymethyl cellulose (CMC) with carrageenan. The viscosity of the polysaccharide sol depended on the sol composition and it was adjusted to give a suitable viscosity so that the sol did not overflow before changing into a gel and meanwhile the sol was easily injected and spread. The gelation temperature and gelation time of the sols were tuned by adjusting the concentrations of K^+ and CMC in order to obtain polysaccharide sols that could transform to gels at body temperature. As an example of applications, the function of the polysaccharides injectable hydrogels as barriers for reducing postsurgical adhesions was evaluated using a rat cecal abrasion model. The results show polysaccharides injectable hydrogels are effective barriers in reducing adhesiolysis difficulties.

Keywords: injectable, hydrogel, polysaccharides, carrageenan, anti-adhesion

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EGGSHELL AS A MULTIDISCIPLINARY BIOMATERIAL FOR VARIOUS APPLICATIONS

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Eggshell biomaterial (ES) belongs among the most abundant waste materials. Its application potential is often neglected, although it can be effectively utilized in various fields (Fig. 1). Within this presentation, the examples of its utilization will be given, including the use as an adsorbent, a source of hydroxyapatite, a fertilizer or in composite materials [1]. Moreover, the multidisciplinary utilization of proteinous eggshell membrane (ESM) will be also mentioned, including its use as a biotemplate, an adsorbent, a biosensor or in medicine [2].

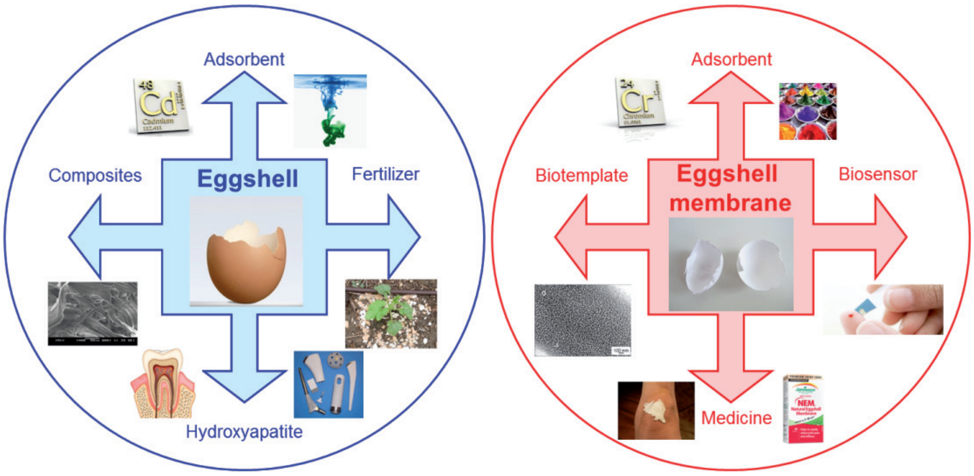

Fig. 1 Multidisciplinary application of eggshell and eggshell membrane

Finally, the potential of mechanochemical tools [3] as an effective way of treatment of ES with the aim to improve its performance for the selected application or to synthesize nanomaterials will be shown. Namely, the increase of the adsorption ability of ES towards Cd(II) and Ag(I), the possibility of simultaneous treatment polyvinylchloride and ES wastes by their co-milling and the possibility of the synthesis of semiconductor nanomaterial by co-milling ESM and lead precursor will be discussed.

This work was supported by Slovak Grant Agency (project VEGA 2/0027/14).

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SYNTHESIS OF STARCH / POLY (ACRYLIC ACID) GRAFT COPOLYMER HYDROGEL AND ITS USE FOR REMOVAL OF CADMIUM ION FROM WASTEWATER

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The redox system thiourea dioxide/potassium bromate was used in this paper to affect initiating graft copolymerization of acrylic acid monomers onto the biopolymer maize starch. The polyacrylic acid/starch copolymer resulting from this grafting process was further crosslinked to a three dimensional hydrogel by treating this graft copolymer with an alkaline epichlorohydrin solution. This resulting hydrogel was applied in removing cadmium metal from aqueous solutions via adsorption onto the hydrogel. All factors which may affect such adsorption process, like concentration of the adsorbent, hydrogel immersion duration, the adsorbent graft yield, concentration of cadmium ion and temperature of the adsorption medium were studied. The results of investigations carried out in this study demonstrated the dependence of the adsorption efficiency as a whole on the graft yield of the adsorbent hydrogel as well as the temperature of the adsorption medium. Upon fitting the adsorption data obtained from this adsorption process to different adsorption models, the results were found to fit well on both Freundlich and Langmuir adsorption isotherms. Moreover, the equilibrium data showed better mathematical fitting to the Langmuir model than Freundlich model.

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UTILIZATION OF WOOD BY-PRODUCTS AS SORBENTS FOR WATER TREATMENT

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A huge amount of wood by-products are readily available in the forest industry. For example, in sawing, a log with bark will yield approximately 50% lumber, 30 % chips, 10 % bark and 10 % sawdust. Chips are frequently utilized in pulp production and bark as an energy source. Sawdust is also utilized as an energy source and in pulp production, but also in particleboard, and as cattle bedding material. In environmental protection, sawdust has been studied as a potential material for the removal of contaminants from water. Sawdust could have major industrial markets in the water sector. Wood by-products are excellent raw materials for water treatment chemicals since they are abundant, renewable and can be modified for different purposes. The pretreatment and modification stage is, however, the key issue. A simple, low-cost and sustainable process needs to be developed while still aiming at an efficient product.

In our research, we have focused on the cationization of wood by-products in order to enhance anion removal from water. The raw materials (pine sawdust, pine bark, spruce bark, birch bark) were reacted with epichlorohydrin, ethylenediamine, and triethylamine in the presence of N,N-dimethylformamide. The quaternary ammonium groups play the main role in the uptake of anions. Maximum sorption capacities of 26.0-30.1 mg N/g were achieved for synthetic nitrate solutions [1]. In addition, modified materials worked well over a wide pH range and equilibrium was reached in 5-10 min. Regeneration with sodium chloride was studied only for modified pine sawdust: it maintained its capacity for five ion exchange and desorption cycles [1]. The multiple-use product is more ecological and, besides reuse, the recovery of wastewater components can be carried out. When temperature was studied, the modified pine sawdust worked in a wide temperature range (5-70°C) [2]. Nitrate-contaminated groundwater would be one possible application for these cationized wood by-products.

Modified pine sawdust also showed a high affinity towards vanadate: 130 mg V/g for synthetic solution and 103 mg V/g for real industrial wastewater [3]. The industrial wastewater was taken from the synthesis gas scrubber of a chemical plant and contained a large amount of vanadium (~50 mg/l) as well as nickel, sulfate, and ammonium. Sodium hydroxide was able to desorb vanadate from the material. However, nickel fouling was observed, which could be solved by acid treatment of the material. Experiments on real wastewater were valuable for the development of the modification method.

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DECOLOURATION OF TEXTILE INDUSTRIAL WASTEWATER IN PRESENCE OF ALGINATE-CHITOSAN MICROPARTICLES

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Various chemical and physical processes are currently in use for the removal of dyes by different processes. Among these numerous dye removal techniques, adsorption is considered a very important procedure for the removal of organic compounds from wastewater, and so, a useful tool for protecting the environment [1]. In this context the study of alginate microparticles, coated or not with chitosan, for dye absorption has included. Alginate, a biodegradable, biocompatible, and non toxic natural polysaccharide, is widely used in food, biomedical and pharmaceutical applications. It consists of a linear copolymer composed of two monomeric units, β-D-mannuronic (M) acid and α-L-guluronic acid (G), in varying proportions. In the presence of divalent cations, commonly calcium ions (Ca^{2+}), which bind specifically to blocks of G residues, alginate forms a physically cross-linked gel [2], then it is possible obtained gelatinous microparticles. Coating alginate microparticles with polycationic polymers, such as chitosan, has been commonly used to control the disintegration of alginate microparticles and in this specific study extend the dye adsorption. Chitosan is a derivative of chitin, one of the most abundant natural polymers in the biosphere, that represent the main component of the exoskeletons of marine crustaceans. It is considered a super high-capacity adsorbent for contaminant removal from water due to its ability of binding contaminants through hydroxyl and amino groups on the surface [3]. In particular due to the protonation of the chitosan primary amino groups by acidic media, it can strongly adsorb anionic dyes such as acid, reactive and direct dyes, by electrostatic attraction and also metal anions by ion exchange. The use of alginate and alginate-chitosan microparticles has showed a good and convenient ability in adsorption of studied dyes. In particular alginate-chitosan microparticles show a more efficient ability in textile dyes removal from aqueous solutions. The different sorbent have been added to coloured solutions under stirring and the dye concentration has been measured at selected time intervals, by means of UV-Vis spectrophotometer, in order to determine the effect of contact time. Two direct dyes, Direct Blue 78 and Direct Red 83:1, and the effect of temperature, pH, microparticles dosage and initial concentration of dye have been studied. Kinetics of adsorption has calculated using the Lagergren model, an expression adapted to general Langmuir rate equation.

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SYNTHESIS AND CHARACTERIZATION OF A NATURAL HYDROXYAPATITE (DERIVED BLACK PHOSPHATE) DOPED BY CHITOSANE FOR ENVIRONNEMENTAL APPLICATION

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The presence of organic pollutants in the environment is a major issue for ecosystems and human health. In this work, we used an adsorbant with a thermal and chemical stability remarkable. This material is the hydroxyapatite which itself comes from an Algerian mining site. it is made by the dissolution-precipitation process, followed a grafting chitosan, they are used to eliminate a phenol by adsorption method.

The prepared powders were characterized by (ATD/ATG, BET, FTIR, MEB…). The results are identical to those reported in the literature for synthetic hydroxyapatite. XRD spectra show a predominant phase of hydroxyapatite and a specific surface area estimated with BET, was about135 m^2/g. The composites obtained by grafting chitosan did not alter the hydroxyapatite crystal structure, against the FTIR analyzes reveal new characteristic bands of chitosan.

The adsorption tests were carried out in static regime by studying phenol adsorption on these adsorbents and the effects of various parameters were examined.

The modelling of the adsorption kinetic of phenol into the prepared adsorbents is fitted adequately by the pseudo second-order with an important contribution of the intra -particle diffusion.

TemkinFreundlich and Langmuir equations are tested for modelling the phenol adsorption isotherms at equilibrium and it is concluded that Freundlich model fitted the experimental data of phenol onto the prepared adsorbents.

The thermodynamic parameters suggested that the adsorption of phenol onto HAp was physisorption, spontaneous and endothermic in nature, $\Delta H^\circ = 3.65$ kJ/mol.

Keywords: Adsorption, hydroxyapatite, grafting, chitosan, phenol.

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IMPACT OF ENHANCED COAGULATION-FLOCULATION IN WASTEWATER TREATMENT PERFORMANCE

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Asset management and energy optimization in wastewater engineering is much related with aeration and sludge disposal costs and such concern is highlighted in activated sludge systems [1]. The challenge of aeration costs in activated sludge processes may be counterbalanced by anaerobic digestion gains, since electricity can be produced from sludge biomethanisation. On the contrary, conventional sludge processing remains a problem, despite some progress in order to minimize it [2]. Traditionally, the coagulation-flocculation process is not applied in wastewater treatment plants (WWTP). Indeed, WWTP are designed for removing incoming organic material in the aerobic biodegradation step on the aeration tank. However, if biodegradable polymers are used in the coagulation-flocculation process to foster primary sedimentation perfomance, the anaerobic digestion unit may degrade such organic rich primary sludge also. In that regard, *Moringa oleifera* seeds shown good properties in coagulation-flocculation and adsorption processes [3]. Therefore, the goal of the present work was to enhance the primary treatment in order to increase the sludge quality improving anaerobic digestion process and minimizing energy consumption in the overall process.

The testing of *Moringa oleifera* in sedimentation of real wastewaters samples collected from an urban WWTP displayed promising results. The turbidity, COD and TSS removal efficiencies were 86, 73 and 79%, respectively, attaining performance levels higher than the current ones. Furthermore, the organic matter flux reduction for secondary treatment signifies a lower energy requirement in the activated sludge process, because less carbonaceous oxidation is required. Thus, a reference scenario and an exploratory optimization considering future adjustments in the wastewater treatment line were sketched. The results indicate a decrease of 20% on the organic load regarding the secondary treatment, reducing energy costs for aeration and a concomitant potential increase for biogas production, about 5%. The synergistic effect of these two factors can increase energy efficiency and to provide a greener wastewater treatment plant.

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A LABEL-FREE ELECTROCHEMICAL SENSOR FOR BACTERIA DETECTION ON ORTHOPAEDIC IMPLANTS

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An early detection of pathogen bacteria is essential to ensure success of orthopaedic implants. Electrochemical approaches are widely used in the development of sensors for microbial detection. Biochemical processes of bacteria involve electron generation and/or transfer on the bacteria membranes, such as ionic transport, enzyme/cofactor interactions, and protein/metabolite secretions [1,2]. Thus, cultured bacteria on the electrodes can generate an electrochemical reaction, called oxidation-reduction (redox), at their interface. The redox reactions generate electrochemical signals or redox potentials when bacteria are on the electrodes. In the present study, microbially electrochemical characteristics of living bacteria on graphene oxide (GO) electrodeposited on titanium (Ti, smooth surface) and anodized titanium (ATi, nanotubular morphology) were investigated. Two strains of bacteria were used in the present study as models, which were *E. coli* for Gram-negative bacteria and *S. aureus* for Gram-positive bacteria. The results show the feasibility of a label-free electrochemical sensor for the detection of living *E. coli* and *S. aureus* on GO-electrodeposited Ti and ATi. Moreover, bacteria viability on the GO electrodeposited Ti and ATi were investigated after 18 h of culture. The present study shows that bacteria could be easily sensed using a label-free, GO-electrodepostied titanium, providing close to real-time bacteria dection for orthopaedic implants.

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ADVANCED CHITOSAN/NUCLEOSIDE HYBRID BIODEVICES: CHALLANGES AND PROMISES FOR THE DETECTION OF ROS

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Sulfur modified nucleic acid bases or the corresponding nucleotides have been often employed to study protein-nucleic acid interactions, with the aim of determining the substrate specificity of various enzymes involved in nucleic acid metabolism [1]. Additionally, photo-crosslinking with modified oligonucleotides has been successfully applied in the mapping of ribosomes, ribozymes, and proteins. Among other important applications of sulfur-containing nucleobases, the use of thiopurine prodrugs, such as azathioprine (Aza), 6- mercaptopurine (6-MP) and 6-thioguanine (6-TG), in the treatment of cancer, inflammatory conditions, viral diseases and in the therapy of organ transplant patients has been reported for almost five decades. In particular, in vitro and in vivo studies have recently indicated 4-thiothymidine as a promising photochemotherapeutic drug [2]. It has been also ascertained that 4-thiothymidine can be destroyed as a result of its photodynamic activity, with oxidation being the main degradative process when UV light is employed.[3] When visible light is used no significant absorption by sulfur-containing bases occurs, thus, they cannot be considered as photosensitizers, but rather as probes/quenchers to detect the presence in solution of Reactive Oxygen Species (ROS). In spite of the remarkable amount of research involving 4-thiothymidine, only limited information is available on its behavior in an aqueous environment. In the perspective of developing biodevices for the detection of ROS, based on laminated biofilms containing Chitosan and 4-thiothymidine, a comprehensive investigation on the behavior of the modified nucleotide in aqueous solution has been carried out in our laboratories using several complementary techniques, namely UV-VIS, FTIR and 1H-NMR spectroscopies and ElectroSpray Ionization Mass Spectrometry (ESI-MS). Moreover, the effect of Visible light on the 4-thiothymidine photostability has been evaluated in the perspective of using the nucleotide as a scavenger for ROS generated during photocatalytic reactions triggered by visible light. The main results of this study will be the object of the present communication.

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SILICA NANOPARTICLE FUNCTIONALIZATION FOR HUMAN HEPATOCELLULAR CARCINOMA TARGETING AND DETECTION: AN IN VITRO STUDY

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The most recent advances in cancer treatment rely mainly on the development of new diagnostic and therapeutic approaches, such as selectively targeted molecular imaging and controlled drug release, made possible by the design and synthesis of innovative smart nanomaterials [1]. Among them, silica nanoparticles (SiNP) seem to be particularly promising since of their low cost, well-documented low toxicity [2], ease of synthesis procedures as well as functionalization [3]. Moreover, owing to their acoustic properties SiNP have been demonstrated to behave as effective ultrasound contrast agents already at common diagnostic frequencies [4] and, therefore, they might be potentially employed in non-ionizing echographic molecular imaging. Aim of this work was the synthesis and functionalization of fluorescent silica nanoparticles for “in vitro” molecular imaging of hepatocellular carcinoma, using both ultrasound and laser-scanning confocal microscopy, by exploiting the particular feature of these tumor cells to express on their surface high levels of Glypican-3 protein (GPC-3). On the basis of recent literature data showing that a synthetic seven amino acid peptide exhibits high affinity in GPC-3 recognizing and binding [5], we have synthesized GPC-3 ligand peptide-functionalized fluorescent silica nanoparticles and tested them on GPC-3 positive HepG2 cells, a human hepatocarcinoma cell line. The results obtained show that GPC-3-targeted SiNP, in the concentration range used for experimental ultrasound detection, do not exert significant cytotoxic effects and seem to selectively bind to HepG2 cell plasma-membrane, as revealed by confocal microscopy and transmission electron microscopy. These results, which however require to be confirmed also “in vivo”, indicate that silica nanoparticles might be a very promising theranostic agents since of their high biocompatibility, targeting effectiveness and ultrasound enhancement power.

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THE SYNERGY OF AUTOLOGOUS BIOMATERIALS AND ARTIFICIALLY DESIGNED SCAFFOLDS IN BONE TISSUE ENGINEERING: A CONCEPT FOR THE TREATMENT OF VARIOUS DENTAL BONE DEFECTS

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Interest in applications for bone tissue engineering in dentistry continues to increas as clinically relevant methods alternative to traditional treatments. Recent progress in the studies of molecular basis of bone development and regeneration, adult stem cell biology, will provide fundamental knowledge for that. This information is already being used for the generation of dentoalveolar tissues *in vitro* and *in vivo* [1,2].

Autologous biomaterials enriched with progenitor/stem cells and growth factors can be produced from components of bone marrow, peripheral blood, adipose tissue, cancellous bone, and represent a very interesting research field for dental bone regeneration and suppose a good perspective of future in the clinical dentistry [3]. The adjunctive clinical benefit of the autologous biomaterials preparation can be explained on the basis of tissue engineering, i.e., tissue engineering generally combines three key elements for regeneration: 1) scaffolds or matrices, 2) signaling molecules or growth factors, and 3) cells. Stem cells need a scaffolds that facility their integration, differentiation, matrix synthesis and promote multiple specific interactions between cells. Synthetic or artificially designed substitutes has numerous interconnecting pathways similar to cancellous bone and facilitates bone formation by providing an exceptional osteoconductive scaffolding which results from the retention of the natural porous architecture and trabeculation of human cancellous bone. Synthetic scaffolds show resorbable characters during bone regeneration, and can be completely substituted for the bone tissue after stimulation of bone formation [4]. The use of autologous biomaterials combined with synthetic scaffolds is a recent and promising innovation in dental bone regeneration [5]. Dental bone tissue engineering could not have advanced to the current stage without the incorporation of interdisciplinary skill sets of stem cell biology, bioengineering, polymer chemistry, mechanical engineering, robotics, etc. Our experience with autologous biomaterials combined with artificially designed scaffolds in the treatment of various dental bone defects is presented. The techniques are based on stimulation of natural events continuously present in living bone, that is, the process of bone remodeling and offering both osteoinduction and osteoconductive features.

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FEASIBILITY OF USING GEOPOLYMER FOAM AS A BINDER IN WOOD LAMINATION - A REVIEW

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The use of environmentally friendly building construction materials has become increasingly important. In principle, most of the wood based construction materials were dominated by synthetic adhesives. Substitution material, especially formaldehyde-based adhesives to free formaldehyde, in wood products is vital to reduce pollutants from building materials and to control indoor air quality. Geopolymer binder has a potential to create a strong adhesion in wood bonding. In this experiment, a solid white spruce was assemble using geopolymer binder and tested. A block shear test with three different types of boards; flat grain board, rift grain board and heart board were carried out that provided evidence of good adhesion and information about the influence of the bonding on shear behavior. The results show that geopolymer binder provides good adhesion and pass the C24 (EN338) standard depend on the types of board. Fourier transform infrared spectroscopy (FTIR) measurement and scanning electron micrograph (SEM) were performed to determine the reaction mechanism. The finding shows that the geopolymer binder can be used as adhesives in wood lamination.

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THE SUITABILITY OF CALCAREOUS CLAYS FROM SOUTHERN ITALY AS RAW MATERIALS FOR GEOPOLYMERS

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The considerable growth of research on geopolymers in the last twenty years deals with the increasing interest to sustainable development and hazardous wastes recycling.

While the dehydroxylation of kaolinite clay to metakaolinite under thermal treatment is widely investigated in terms of structural changes to determine the suitability for the production of geopolymers, the use of illitic calcareous clays is still less investigated.

Pleistocene calcareous clays, occurring in Basilicata and Apulia (Southern Italy) are widely used for ceramic tile production and they have been highly characterised, in order to define the origin and nature of minerals and the related geotechnical properties. According to the results obtained from several studies on their mineralogical and chemical classification, they consist mainly of clay minerals (illite, smectite, chlorite and kaolinite), mixed with calcite, dolomite, quartz and feldspars. Similar chemical and mineralogical compositions are available in local secondary raw materials (e.g. reservoir sediments, structural ceramic wastes, etc). The SiO_2/Al_2O_3 ratio of about 3:1 makes such calcareous clays suitable for geopolymers, although the complex mineralogical composition put a problem about the processing to achieve the synthesis of geopolymers. Furthermore, the role played by Ca and Mg in the chemical and physical properties of the geopolymers is still debated.

The present study focuses on the influence of micronisation and thermal treatment in different redox conditions, on the amorphisation of calcareous clays from Southern Italy, to form geopolymers.

Two series of clay samples from Ripatetta e Lucera (FG) were analysed by XRF, XRPD and the amorphisation of mineral phases induced by both grinding and heating have been estimated by XRPD, SEM and grain size analysis.

The results obtained show the effects of particle-size and calcination conditions (soaking temperatures between 500 and 800°C) on the amorphisation of clay minerals and the reactivity of carbonates.

These preliminary data are part of a PhD research project aimed to produce geopolymers from calcareous clays combined with recycled hazardous and non-hazardous wastes.

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QUATERNARY CLAYS OF LATVIA FOR CHEMICAL AND THERMAL ACTIVATION

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Alkaline activation is a chemical process in which a powder material of an alumosilicate nature is mixed with an alkaline activator to produce a paste that is able to set and harden in a short time [1,2]. Geopolymeric materials possess excellent mechanical properties, including fire and acid resistance [3]. Mentioned properties make geopolymers as alternative construction material. Kaolinite is the most often used natural raw material because of its high content of alumina [4].

Illite clayey deposits are one of the dominating mineral raw materials in the sedimentary cover at present area of Latvia. The Quaternary clays of Latvia are useful for various kinds of traditional ceramic production such as bricks, building blocks, roof tiles as well as sorbents and precursors for promoting of sinterability of new ceramic products. Geopolymers are materials rapidly developed during last decades and they are quite new ones in Latvia. The search for alternative easily available materials in Latvia have lead among another materials to illite-based clays. From geological point of view - Latvia is rich in clay resources to be used for material production currently and at least for centuries [5].

The aim of this study was to synthesize geopolymer product from illite clays of Latvia under alkaline and thermal activation. Preliminary studies [6,7] have shown that the addition of moderate amount of calcium containing material can have a significant effect on the mechanical properties of final material. Besides illite and kaolinite mentioned clays as natural additives contain carbonates such as calcite ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$). Three Quaternary clays of Latvia (AP, SP and PR) characterised by different Si/Al ratio (from 2,8 -3,8) were used for geopolymer synthesis.

In order to investigate the effect of the activator on the mechanical properties of material obtained from AP, SP and PR clays 5 and 6 M KOH solutions were used. XRD analysis reveals the formation of new phase (CSH) - only in activated samples. Furthermore it could be noticed the decrease of intensities of the present phases - kaolinite, illite and calcite. FTIR analysis shows the difference in absorption frequencies among activated clays confirming that transformations taking place during material synthesis. It was concluded that depending on the different SiO_2/Al_2O_3 ratio in the used clays (2,8 for clay PR, 3,5 for clay SP and 3,8 for clay AP) decreases the initial rate of hardening. The best initial rate of hardening showed clay PR with smaller SiO_2/Al_2O_3 ratio. It can be also concluded that with the increase of Si/Al ratio in the source clays appears the difference in the mechanical strength measurements with the increasing of curing temperature higher than 20 ^{0}C. Curing temperature had not an essential influence on mechanical strength of activated clay AP and SP, but strength increased with increasing of curing temperature only for activated clay PR (using for activation both 5M and 6M KOH solution) reaching 60 and 65 MPa, accordingly.

IR spectra and XRD results confirmed the differences among activated clays developing the diverse final mechanical strength of the obtained samples.

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HARDENING MECHANISM OF BLAST FURNACE SLAG AS NON-OPC BINDER FOR BUILDING MATERIALS

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The purpose of this study was to analysis on the hardening mechanism of blast furnace slag (BFS) for building materials using non-OPC activation. The ultimate goal of this research would be to replace the amount of Ordinary Portland Cement (OPC) used in powder type ready-mixed OPC mortar in building construction, therefore reducing the amount of carbon dioxide emitted into the atmosphere during cement production.

This research studies the behavior of mineral binders that do not contain OPC but instead comprise BFS activated by calcium compounds and/or fluidized bed combustion (FBC) bottom ash. The information described in this paper was collected from experiments including calorimetry, which is a measure of the release of heat from a particular reaction, the determination of activation energy of cement hydration, mechanical strength determination, and pH measurement and identification of crystalline phases using X-ray diffraction (XRD). And we tested on the physical properties of Non-OPC plaster mortar using Non-OPC binder base on the result of this research

The results indicated that it is possible to produce alkali-activated binders with incorporated slag, and bottom ash, which have mechanical properties similar to ordinary Portland cement (OPC). It was determined that the binder systems can incorporate up to 40% bottom ash and calcium compounds without any major influence on binder quality.

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DURABILITY OF POROUS BUILDING MATERIALS MADE BY ALKALI ACTIVATION METHOD

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The new alkali activated materials (AAM), which could be defined as a porous building material analogue to aerated concrete, were created by using calcined illite clay from local site and aluminium scrap recycling waste (ASCW) as well as inorganic filler. Commercial silicate solution (Na_2SiO_3+nH_2O) modified by commercially available alkali flakes (NaOH) was used as an activator.

Recycling of hazardous industrial waste (ASCW) into building materials is one of the main tasks of research because it reduces possible pollution of the environment and decreases the costs of waste deposits, as well as saves resources of natural raw materials and gives economic benefits for manufacturing of new materials and building units. Other benefit of ASCW usage in the composition of AAM is its reactivity in alkaline media and gas evaporation, which promotes development of highly porous structure before AAM paste is settled.

Low-calcium alkali activated materials (AAM) have amorphous to semi-crystalline structure that are formed by transformation of alumino-silicates at low temperature in a very short time. The formation of alkali activated material involves aluminosilicate solid materials (calcined illite clay) dissolution in a highly alkaline environment; restructuring Si-O-Si and Si-O-Al bonds; appearing of three-dimensional aluminosilicate framework; and the un-dissolved solid particles bond with each other, causing hardening and formation of the geopolymer structure (van Jaarsveld et al. 2002), (Zhang et al. 2012).

Density of the obtained materials was in the range 450-550 kg/m^3, but the total porosity ranged from 70 to 80%. The compressive strength of the materials reached 2.5 MPa. The thermal conductivity of porous alkali activated building materials was between 0.14 and 0.15 ($W/(m \cdot K)$). Development of microstructure and porosity depending from composition was investigated by SEM. Detailed information of AAM was described in previous publications (Bajare et al. 2014) (D. Bajare et al. 2014).

The main focus of this study was paid to determination of durability - frost and sulphate resistance of novel building materials. Sulfate resistance test was performed according to SIA 262/1, appendix D: applicability and relevance for use in practice. Frost resistane was performed according to LVS 405:2002. The influence of curing condition and compostion of AAM to durability was clarified.

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Keywords: porous building material, durability, alkali activation

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ALKALI ACTIVATION - A NEW WAY OF RECYCLING CRT GLASS

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Cathode ray tubes (CRTs) are the video display components of televisions and computer monitors. The glass in CRTs typically contains enough lead and other hazardous elements (e.g., Sb and Ba) to require managing it as hazardous waste. In Europe, dumping this material in landfills for hazardous waste is expensive, so the CRT is typically shipped overseas (specifically to China), where it is simply landfilled. Glass-to-glass recycling has been the most common management method, but with the shift from CRT technology to flat panel technologies for video displays, the market for new CRTs is lessening. There are several ways to recycle the CRT glass, but most of these methods are either energy intensive, or the production requires expensive measures to reduce lead emissions. Some of the resulting products are incompatible with the limits for contents of toxic elements both in the dry matter and in the leachate. Promising technology is production of insulating glass fibers, foamed glass, or ceramic tiles. Anyway, each of the named methods requires relatively stable chemistry of the waste glass, which requires a thorough separation of various streams (display glass, funnel glass, solder glass) and quality control. Moreover, the demand for individual streams does not always correspond to their volumes.

A method that enables to use the whole CRT (after dismantling and separation of metallic parts) is based on the fact, that display glass and funnel glass contain heavy elements (barium and lead, respectively), which are able to effectively shield ionizing radiation. The two main CRT glass types blended as is can be used as aggregate or microaggregate for production of building materials (concrete or plaster), shielding the X-ray radiation. They could find application as masonry in radio-diagnostic laboratories and industrial radiography. Given the need to immobilize toxic elements contained in the waste CRT glass, a suitable method for production of the building materials seems to be alkali activation or production of concrete from cements more efficient in immobilization of lead than ordinary Portland cement. The binders that display such property involve calcium aluminate cement with certain additives (ashed meat-and-bone meal, raw or calcined diatomite, clinoptilolite), or a special fosfo-clinker cement. Crushed CRT glass with slag admixture (3 : 1 by weight), activated with sodium silicate solution (water glass) achieved compressive strength of almost 120 MPa. Alkali activation as well as special cements ensure that potential release of toxic elements is in compliance with pertinent building codes.

The shielding for common diagnostic rooms is 1mm thick layer of Pb and in CT rooms 1.5 mm. The same shielding effect has concrete plaster containing 30% crushed funnel glass in layer 35 mm thick and for CT diagnostics 50 mm.

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CONTROLLING THE HYDRATION KINETICS AND PHASE EVOLUTION OF ALKALI-ACTIVATED SLAG PASTE BY SEEDING WITH LAYERED DOUBLE HYDROXIDES

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Alkali-activated slags are an alternative building material formed by the reaction between blast furnace slag, which is a by-product from the steel industry, and an alkaline activator. They are environmentally beneficial compared to Portland cement due to the absence of a clinkerisation step [1]. However, the durability of reinforced alkali-activated slag concretes requires further scientific investigation to enable accurate comparisons with Portland cement, particularly in terms of resistance to carbonation and chloride ingress, which is closely linked with their binder chemistry and pore solution chemistry. To produce low-carbon alternative cements with improved performance, it is presented here for the first time the use of layered double hydroxides (LDHs) as a chemical additive to modify the binder chemistry.

Hydrotalcite-like (Mg,Al)-LDHs are commonly identified as a secondary phase in alkali-activated slag systems when the MgO content in the raw material is higher than 5 wt.%, in conjunction with the C-(A)-S-H gel, which dominates the binder [1]. Hydrotalcite has a brucite-like layered structure that allows the incorporation/ion-exchange of anions such as Cl^- and CO_3^{2-} between the positively charged layers [2], thus making hydrotalcite a potential carbonate-absorbing and chloride-binding phase. It has been proven that with higher MgO content in a slag used in alkali-activation, the hydrated paste contains a higher content of hydrotalcite. However, a higher MgO content can also extend the setting time, which is sometimes undesirable for industrial application. Therefore, it is beneficial to increase the content of hydrotalcite in the hydrated paste without delaying the formation of the main hydrate phases.

In this study, a small amount of commercial hydrotalcite was used as a chemical additive in the sodium silicate activated slag paste. The kinetic effects of different dosages of hydrotalcite addition were measured by isothermal calorimetry, and the phase evolution of pastes modified by different dosages of hydrotalcite was characterised by X-ray diffraction, ^{27}Al NMR and SEM/EDX for up to 6 months of curing. Hydrotalcite is seen to be an effective chemical additive to accelerate the polycondensation of the paste, shorten the setting time and increase the hydration degree; the seeding with hydrotalcite not only increased the total hydrotalcite content, but also altered the distribution of hydrotalcite between the regions around the remnant slag grains and the general matrix, which also resulted in a more densified and refined microstructure. These changes are expected to lead to enhanced resistance against carbonation and chloride ingress.

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ACCELERATED CARBONATION STUDY OF ALKALI-ACTIVATED SLAG PASTES PRODUCED WITH A WASTE GLASS BASED ACTIVATOR

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Alkali-activated materials (AAM) are produced through the mixing of industrial by-products such as blast furnace slag with an alkaline solution. These cements present advantageous technical properties, however, there is limited information regarding their long-term performance. Specifically, in alkali-activated slag systems it has been identified that these binders can be more susceptible to carbonation compared with Portland cements, when tested under accelerated carbonation conditions [1].

There is consensus that utilising waterglass as alkali activator promotes the formation of strong and durable binders, independent of the slag used. However, waterglass is a family of synthetic alkali silicate hydrate solutions whose manufacturing process is usually expensive and can be significantly polluting. Urban and industrial waste glasses are mainly composed of SiO_2, CaO and Na_2O, and previous studies by some of the authors [2] have demonstrated that it is possible to produce sodium silicates from this waste via chemical digestion in highly alkaline media. These silicate solutions have been successfully used as an activator for producing alkali-activated slag binders [3]; however, during the chemical digestion of the waste glass, not all the solid is fully dissolved.

In order to maximise the utilisation of the waste glass, alkali-activated slag binders were produced using silicate solutions from the alkali digested waste glass, and also the solid waste glass residue derived from this process. Carbonation resistance of these novel activated slag binders was tested under accelerated conditions using a fully controlled environmental chamber. Negligible carbonation was identified in the pastes after 28 days of exposure, however, formation of higher amounts of calcium carbonates was identified in pastes with higher contents of waste glass. Formation of calcite, vaterite and aragonite was identified, associated with the carbonation of the main binding phase forming in these systems, a calcium aluminium silicate hydrate (C-A-S-H) type gel. Minor changes in the hydrotalcite present in these pastes suggested that this phase is likely to be absorbing CO_2. These results elucidate that the waste glass based silicate activator promotes the formation of similar carbonation products to those identified in pastes produced using commercial sodium silicates; however, the replacement of slag by waste glass seems to induce formation of different carbonation products.

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EFFECT OF THERMAL TREATMENT ON THE REACTIVITY OF BIOMASS FLY ASH FOR THE PRODUCTION OF GEOPOLYMERS

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The high environmental impact associated with the combustion of coal to produce electricity, and the need to reduce the utilisation of large areas of land to dispose wastes, have motivated several nations to replacing coal combustion with renewable resources such as wood, straw, and organic wastes derived from agricultural activities. The waste generated from the combustion of biomass is referred to as biomass ash, whose chemical, mineralogical and physical properties varies depending on the initial organic waste utilised, and the combustion process adopted. Exploitation of biomass ashes as building materials has been explored over the past decades, with the continuing and rapid growth in the generation of this waste all over the world. However, the high content of heavy metals and alkalis in some of these biomass ashes make them unsuitable for utilisation as supplementary cementitious materials, as these characteristics can compromise the long term performance of blended cements, and so biomass ashes generally fall outside the scope of existing standards for cement and concrete components.

One potential alternative for utilising these biomass ashes, making the most of the properties of the wastes, is to utilise them as precursors for production of geopolymer cements. These clinker-free cements are produced via the chemical reaction between a poorly crystalline aluminosilicate source and an alkaline activator, to form a hardened solid. There are a few studies using biomass ashes as precursors for producing geopolymers, and due to the variable nature of this waste, results from different studies are not directly comparable. Despite the limited existing understanding of these systems, most of the available studies reveal that the production of geopolymers using biomass ashes is technically feasible, however, low compressive strengths have generally been achieved at early times of curing, which is usually associated with the high content of organics still present in the ashes.

In this study, biomass ashes were thermally treated at 500°C for 2 h in order to reduce the content of organics in the ash. Pastes were produced by blending the thermally treated ashes with water or an alkaline solution of sodium silicate. The kinetics of reaction were evaluated through isothermal calorimetry, and microstructural analysis of the hardened solids up to 28 days of curing was carried out via X-ray diffraction, thermogravimetry and Fourier transform infrared spectroscopy, in parallel with compressive strength measurements. Reference samples of as-supplied biomass ash were also produced for comparative purposes; thermal treatment of the ash was seen to improve the compressive strength development of the materials when activated with sodium silicate, but not when blended with water alone.

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GEOPOLYMERS FROM LOW-T ACTIVATED KAOLIN

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The feasibility of using low-grade kaolins containing sulfates to synthesize geopolymers has been assessed. In particular, alunite-containing kaolin, annealed at T = 550 °C to produce metakaolinite, has been used. Alunite is present in kaolin deposits deriving from trachyte, rhyolite, and similar potassium-rich volcanic rocks and normally hinders the use of these clays in the ceramic industry due to the release at high temperature of SO_x, which damages furnaces refractories.

First, the effects of temperature (in the range 40-90 °C) and time (in the range 1-19 h) of curing, on compressive strength and linear shrinkage of geopolymers have been studied by experimental design technique using a high-quality kaolin as starting material. Geopolymers characterized by high strength (> 60 MPa) and low shrinkage (< 1%) have been obtained when long curing times are applied at $T < 65$ °C. Then, geopolymers have been synthesized at the curing conditions suggested by the statistical model and using the alunite-bearing kaolin from Piloni di Torniella mine as starting material. The results are promising as the synthesized samples revealed to be composed mainly by an amorphous gel and characterized by high thermal stability and strength, with compressive strength higher than 80 MPa.

All samples have been characterized by thermal analysis, X-ray powder diffraction and infrared spectroscopy. A petrographic approach has been used to analyze the textural features of geopolymers at different lengths of scale by using optical and scanning electron microscopies. Finally, leaching tests have been carried out and the resulting materials as well as the leached solution have been analysed. More studies are needed in order to improve the sulfate retention as well as to identify all the silico-sulfate phases and understand the possible interactions between precipitated nanocrystalline sulfate phases and geopolymer binder.

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PREPARATION OF CLAY WASTE BASED BRICKS THROUGH ALKALI-ACTIVATION PROCESS

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Bricks are usually used in the construction of building walls, paving and finishing. They are made of a variety of materials and, particularly, concrete and clay are the most common.

Utilization of waste materials for alkali-activated brick production seems to be a logical solution that allows the conservation of natural resources, abates further pollution and preserves the environment.

This study has been conducted to produce paving blocks making use of excavated clay soil and recycled aggregates coming from a construction and demolition wastes collection and treatment plant.

The experiments were conducted on clay soil after activation by means of thermal or mechanical treatment. Thermal activation was performed by heating the soil samples at 750°C for 2 hours while the milling was conducted by means of a planetary high energy mill for periods of time varying from 20 to 120 min. The treated powders were mixed with fine recycled aggregate, granulated blast furnace slag and sodium silicate solution.

The fresh mixtures were proportioned to obtain the same consistency class of the concrete paving blocks prepared making use of commercial cement. Then, mini-slump and setting time tests were conducted. The curing of specimens was realized at room temperature for 24 hours.

The hardened samples were characterized in terms of polycondensation reaction kinetic and from physical-mechanical point of view.

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SUSTAINABILITY EVALUATION OF BRICKS MADE FROM ALKALI-ACTIVATED CLAY WASTE

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Concrete-bricks represent one of the most used materials in the constructions, but the rising demand of building materials and the increasing amount of construction and demolition wastes have encouraged the development of new blocks production processes. In fact, the traditional technologies of brick production cause several environmental and human health impacts, so there is a clear need of searching and replacing for more eco-efficient and durable alternatives far beyond the limitations of the conventional cement-based production.

The purpose of this article is to identify impacts during the entire life cycle and to describe the basic operations of alkali-activated bricks manufacturing in the Campania Region industrial district. Excavated clay soils, recycled aggregates from construction and demolition waste, sodium silicate solution were employed as source materials for bricks manufacturing.

The analysis was performed by means of the application of the Life Cycle Assessment (LCA) and Life Cycle Cost (LCC) methodologies, which are methods used to identify and quantify the environmental performance of a process or a product with "cradle to grave" approach.

Bricks manufacturing plant, sodium silicate activating solution production plant and excavated clay soils and recycled aggregate supplying firm are located in very narrow geographical area.

The results of the comparison between the traditional and new production process allow the quantitative evaluation of the environmental performance of the alkali-activated clay waste based bricks manufacturing process in terms of energy and natural raw materials consumption.

The LCA of the process that makes use of alternative more sustainable sodium silicate solution was also performed. In this case, it was possible evaluate the impacts of activating solution prepared starting from glass wastes.

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MANUFACTURE OF LIGHTWEIGHT AND HEAT-RESISTANT MELAMINE - GEOPOLYMER HYBRID COMPOSITES

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Geopolymer based hybrid materials, containing different melamine epoxy resins as organic component, with improved physical-mechanical properties in respect to the neat geopolymer, have been prepared through a synthetic approach recently developed by the authors [1]. The chemical composition of the resins has been tailored [2] to ensure a good thermal stability of the final material and in order to obtain a good compatibility with the inorganic matrix.

The simple and cost-effective synthetic approach [1,3-4] is based on the incorporation of the organic resin into the geopolymeric suspension under mechanical stirring, *when both polymerization reactions have been started but not completed yet.* In this way, the simultaneous *in situ* polycondensation reactions of the organic component and of the inorganic one were realized. Through this approach, materials showing high compatibility between the organic and inorganic phases up to sub-micrometric level have been obtained.

The preparation, the physical-mechanical and the spectroscopic characterizations are investigated. Therefore, the remarkable mechanical properties, compressive strength up to 60 MPa, and the flame resistance of composites containing up to 10% resin similar to that of plain geopolymer, make these materials optimal candidates for applications in the manufacture of lightweight, thermo-insulating, heat-resistant and acoustic insulating panels with improved toughness.

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EXPERIMENTAL STUDY OF ALKALI ACTIVATED CONCRETE: STRUCTURAL APPLICATIONS

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Alkali Activated Concrete (AAC) is an alternative kind of concrete that uses fly ash as a total replacement for ordinary Portland cement. Fly ash combined with alkali solution and cured at high temperature react to form a binder.

A four point bending test on a full scale steel reinforced beam made with AAC is described in this paper. Companion small material specimens were cast with the aim of properly characterizing this new tailored material both in compression and in tension.

The beam length was 5000 mm and the cross section was 200 mm x 300 mm.

The AAC consisted in fly ash (408 kg/m^3), water (35 kg/m^3), sand 0-4 mm (647 kg/m^3) and coarse aggregate 6-10 mm (1201 kg/m^3); alkali solution consisting in sodium hydroxide (41 kg/m^3, 8M) mixed with sodium silicate (103 kg/m^3).

The maximum aggregate size was 10 mm; fly ash was type F, containing a maximum calcium content of 2%. The ratio $l/f.a$ between liquids and fly ash was equal to 0.44.

After a rest period of 3 days, the beam was cured at 60°C for 24 hours.

Data collected and critically discussed included beam deflection, concrete strains, crack width, compressive and tensile strength, elastic modulus and free shrinkage.

Keywords: alkali activated materials, geopolymer concrete, fly ash, material characterization.

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USE OF ANALYTICAL TECHNIQUES FOR THE IDENTIFICATION OF THE MORPHOLOGY OF GEOPOLYMERS

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The present study highlights the importance of the use of analytical techniques for the identification of the morphology and structure of geopolymers. As an example, geopolymers produced from ferronickel slag and the three main components of construction and demolition wastes (CDW), namely concrete, bricks and tiles, were used.

Geopolymers were synthesized by alkali activation of the starting materials using NaOH or KOH and Na_2SiO_3 solutions. Various synthesis parameters, including particle size (<400 μm, d_{50}: 48 μm and/or <150 μm, d_{50}: 10 μm), NaOH or KOH alkalinity (8-14 M), heating temperature (60-90 ^{o}C) and setting time (7 and 28 days), were considered.

Slag, bricks and tiles were successfully geopolymerized reaching a compressive strength higher than 50 MPa, while limited geopolymerization potential was obtained for concrete-based geopolymers (compressive strength was just above 10 MPa).

The use of analytical techniques, namely X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Fourier Transform Infrared Spectroscopy (FTIR) and Thermogravimetric analysis (TG) provided significant insights on the mineralogy, the microstructure and the properties of the produced geopolymers.

XRD was used for the identification of new formed phases, the prediction of the reactions taking place and the quantitative estimation of the gel amorphicity. The composition of the geopolymeric gel and the degree of homogeneity were defined by SEM-EDS. The identification of specific molecular structures was done by FTIR. TG was used for the determination of the water evaporation in geopolymeric structures by recording the weight loss under controlled heating.

The use of analytical techniques provides very useful insights on the geopolymerization mechanisms and can indicate optimum synthesis conditions depending on the raw material used.

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RICE HUSK ASH FOR THE REPLACEMENT OF SODIUM SILICATE IN THE DESIGN OF METAKAOLIN BASED INORGANIC POLYMER CEMENT AND MORTARS

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The sodium silicate is the principal binder component used during the geopolymerization process of the amorphous to semi-crystalline aluminosilicates. The high temperature process for the preparation of the sodium silicate has appeared as limited factor for the geopolymer in the perspective of its classification as green materials. In this project, the rice husk ash is activated in sodium hydroxide solutions with various concentrations to assess the effectiveness of the rice husk-NaOH system to substitute sodium silicate in the formulations of inorganic polymer cement and composites. NMR, IR, XRD, ESEM, Flexural strength as well as DTA were used to compare the products of activation of metakaolin and metakaolin/sand with conventional sodium silicate and in-situ produced sodium silicate. It was concluded that appropriate process method applied to the geopolymerization using the system RHA-NaOH can allow the obtained products to compete with the standard metakaolin based geopolymer with sodium silicate. Products more compatible with the environmental issues with gain in sustainability.

Keywords: sodium silicate, rice husk ash, geopolymer, binding phases, sustainability.

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CA- PYROPHOSPHATE DIHYDRATE DEPOSITION DISEASE (PSEUDOGOUT) OF THE TEMPOROMANDIBULAR JOINT

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Calcium pyrophosphate dihydrate (CPPD) crystal deposition disease, also known as "pseudogout", is an artropathy caused by abnormally high concentrations of inorganic pyrophosphate in the articular cartilage and synovial fluid which eventually precipitates to form CPPD crystals. The identification of CPPD is deduced by detecting weakly birefringent crystals under polarized-light microscope, sometimes together with electron microscopic observations. CPPD demonstrates a higher predilection for fibrocartilage but CPPD of the temporomandibular joint (TMJ) is rare, with less than 30 cases reported in the medical literature. In the present contribution to AMAM 2015 there are reported results of a medical and mineralogical study on CPPD deposition in temporomandibular joint (TMJ) area.

A 63-year-old female complained of progressive mouth-opening reduction and swelling in the area of the left TMJ during the past 5 years. Her past medical history was non-contributory but reported a traumatic injury in the TMJ 10 years before. Computer tomography (CT) scan showed a calcified mass in the left TMJ. Microscopic examination of the surgical specimen revealed nodules of birefringent crystalline material and calcifications associated with reactive chondroblasts and histiocytes.

Microdiffraction and powder X-ray diffraction analyses revealed the presence of at least two dihydrate phosphates. Scanning electron microscopic observation (SEM) and microanalyses (EDS) documented that both had Ca:P ratio about 1:1, both dihydrate but exhibited different morphologies leading to a monoclinic calcium pyrophosphate (m-CPPD) and a triclinic calcium pyrophosphate (t-CPPD). The m-CPPD phase occurs as aggregates of the fine needle-shape crystals up to 15 µm in length and the t-CPPD phase as parallelogram-shaped crystals, up to 20 µm in length. According to EDS and X-ray data, the two CPPD crystals are the natural analogue of synthetic monoclinic [1] and triclinic [2] $Ca_2P_2O_7 \cdot 2H_2O$ phase. SEM observations also suggest that the monoclinic phase might be the first one to crystallize and that the triclinic larger crystals grew on the smaller monoclinic one.

Grow conditions of synthesized phosphates provide pH lower than 6 and temperature higher than 55 °C for the triclinic (t-CPPD) phase and higher than 85 °C for the monoclinic one (m-CPPD) [3]. Therefore a catalyst activity have to be led to the crystallization of these two phosphates during a human disorder: one option is to rely on the activity of the bacteria during the first stage of the growth of these minerals.

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STUDY OF THE FORMATION AND STABILITY OF A MODEL CATALYST ON MGO

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We performed the calculations and recounts the various parameters related to the first quantitative study on the nucleation and growth of a model catalyst dispersed Pd / MgO (100). The formation of small particles of palladium by vacuum deposition of epitaxial layers of MgO, prepared in situ, has been studied by transmission electron microscopy and electron diffraction at high energy. The experimental results are interpreted according to the theory of random nucleation. From this theory, the experimenters get the energy of adsorption and diffusion of palladium on MgO (100). In this study, we were able to vary the average size D of particles 8-35 Å, density n of 0.6 to 3.10^{12} cm^{-2} and the covered area A of the substrate surface of 0.4 to 15 percent.

Keywords: model catalyst, palladium, MgO, random nucleation.

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PHASE FORMATION IN THE SYSTEM BI_2O_3-SIO_2-NA_2O-H_2O

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Eulytite ($Bi_4Si_3O_{12}$) crystals are applies as a scintillator in high energy physics, computer tomography, and dosimetry.

Physicochemical basis for the phase's synthesis and growth of Eulytite structured crystals are phase diagrams of corresponding systems at high temperatures and pressures.

We studied a phase formation in the system Bi_2O_3 - SiO_2 - Na_2O - H_2O at non-equilibrium conditions at a temperature of 300ºC in the dissolution zone of the autoclave and 240ºC in the crystallization zone. The pressure was about 70 MPa. The molar ratio of Bi_2O_3 : SiO_2 in the mixture varied from 0.1 to 1. The experiments were performed in fluoroplastic settled autoclaves 30 ml volume. The NaOH at concentrations from 1 to 6 mol / l used as a solvent. The hydrogen peroxide used as an oxidant. The run duration was 10 days.

Results of the experiments we reposted on the NC - graph (Figure 1), where N is the molar ratio of bismuth and silicon oxides, and C is NaOH concentration (mol / l). As showed at the diagram, three phases are crystallizes in the given system: sodium silicate Na_2SiO_3, Eulytite $Bi_4Si_3O_{12}$ and Sillenite type structured Bismuth silicate $Bi_{12}SiO_{20}$.

Sodium silicate crystallizes in the spherulitic aggregates form. Its crystallization field depends little on NaOH concentration and it is determined mainly molar ratio Bi_2O_3: SiO_2 in the initial material mixture.

Eulytite ($Bi_4Si_3O_{12}$) crystallizes as colorless pyramidal tetrahedron. The Eulytite crystallization field at a NaOH concentration of 2 mol / l is limited by molar ratio of Bi_2O_3: SiO_2 from 0.2 to 0.6. The crystallization field of $Bi_4Si_3O_{12}$ reducing accordingly to NaOH concentration increasing up to fully disappearing at the concentration higher then 6 mol / l.

A Sillenite type structured Bismuth silicate formed as cubic shape crystals. $Bi_{12}SiO_{20}$ crystallization field increases accordingly to NaOH concentration because of the $Bi_4Si_3O_{12}$ crystallization field reduction. A $Bi_{12}SiO_{20}$ starts crystallize at conditions then a NaOH concentration higher than 6 mol / l and a molar ratio of Bi_2O_3: SiO_2 more than 0.7.

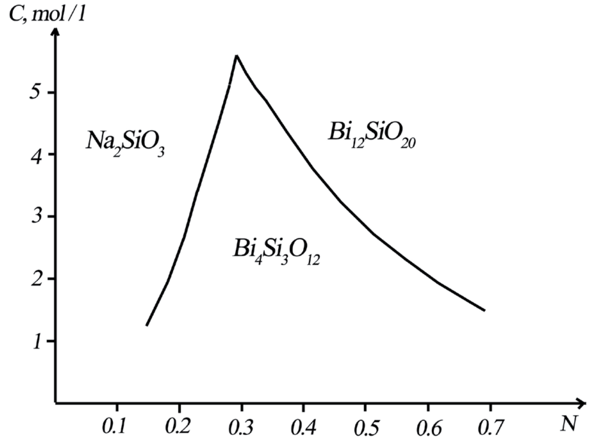

Figure 1. NC - diagram, where N is the molar ratio of Bi_2O_3: SiO_2, and C is NaOH concentration (mol / l).

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SOLID STATE TRANSFORMATION OF IRON-BEARING HYDRATED SULFATE TO α-Fe_2O_3

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Iron oxides are one of the most important transition metal oxides of technological importance. These oxides find applications as catalysts, sorbents, pigments, flocculants, coatings, gas sensors, ion exchangers and for lubrication. Synthesis of iron oxides can be performed by a variety of methods, most of which are chemical methods. Careful control of the preparation process of iron oxides is a challenging task to address the synthesis towards a particular application. Hematite, α-Fe_2O_3, can be also produced from a number of iron sulfates by heating them sufficiently in air. In this work we have employed the thermal decomposition method to obtain hematite from the dehydration of fibroferrite, $FeOH(SO_4)\cdot 5H_2O$, a secondary iron-bearing hydrous sulfate. The study was performed by Rietveld refinement based on *in-situ* synchrotron X-ray powder diffraction combined with thermogravimetric analysis and mass spectrometry. Combination of the data from both techniques allowed to study the structural changes of the initial compound, determining the stability fields and reaction paths and its high temperature products. Six main dehydration/transformation steps from fibroferrite have been identified in the heating temperature range 25-800 °C. In the last step of the heating process, above 760°C, hematite is the final phase. The temperature behavior of the different phases was analyzed and the heating induced structural changes are discussed.

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PRENUCLEATION CLUSTERS OF "HIDDEN PHASE" (QUATARONS) AS PRIMARY NANOPARTICLES FOR FORMATION OF SPHERICAL MINERAL PARTICLES

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By advanced analytical techniques globular internal structure is often found in natural nanomaterials. However the mechanism of formation the nanoparticles composing such opal-like materials, hitherto remains unclear. This report gives general principle of building amorphous particles of the type of opal-like structural units, developed on base of the quataron concept of nanoparticles genesis.

The main idea of the quataron concept is that in supersaturated media specific nanoclusters - clusters of "hidden" phase or quatarons are formed, which according to classical theory of nucleation should not be. However, quatarons are not actual new phase nuclei. They cannot be described in terms of known states of substance. Actually quatarons represent a separate intermediate phase at nanolevel. In terms of classical theory they are pre-nucleation clusters. Quatarons are the basis for all kinds of equilibrium nanoparticles from ordinary tetra- and octahedral groupings to widely known fullerenes or dense dodecahedral icosahedral clusters, colloidal particles.

The circumstance that only quatarons, which radius exceeds 4δ, where δ is diameter of cluster-forming atoms (molecules), can be potential centers of crystallization, has fundamental importance for forming amorphous nano-micro particles. Quatarons of smaller sizes represent amorphous "quasi-liquid" or "quasi-solid" objects. Exactly they are the base (primary) particles for forming structural units of opal-like materials. The main mechanism for forming self-assembled "solid" or "liquid" materials is an aggregation of quatarons sized from δ to 2δ. Quatarons in interval from 2δ to 4δ are capable to form larger secondary clusters by way of their merging.

Different variants of aggregation and interaction of quatarons are considered. It is established that forming structural units of opal-like materials is related with fractal aggregation of primary particles (quatarons). Typical sizes of structural units are reached at the third level of fractal aggregation of quatarons, more rare at the second one. This general rule for formation of spherical particles of mineral formations is confirmed by study the internal structure of the units of natural and synthetic opals, other amorphous materials.

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PHASE EQUILIBRIA IN THE CU_2SE-AG_2SE-$GESE_2$ SYSTEM AND SOME PROPERTIES OF INTERMEDIATE PHASES

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Cu- or Ag-containing ternary chalcogenides have attracted much attention, because these materials have potential applications for using as semiconductors, superionic conductors, as well as nonlinear optical and photovoltaic cell materials [1-3].

Aiming at the creation and development of modern preparative methods for controlled synthesis and growth of large single crystals of novel materials it is necessary to investigate the phase relationships in the respective systems.

In present work we report the results of investigation of phase equlibria in Cu_2Se-Ag_2Se-$GeSe_2$ quasi-ternary system and some physico-chemical properties of intermediate phases.

Initial compounds were synthesized from high purity elements in evacuated (~10^{-2} Pa) silica ampoules in the inclined two-zone furnace. The samples of the investigated system were prepared from preliminary synthesized and identified initial compounds. All samples were annealed at 800 K for 1000 h in order to achieve a equilibrium state.

Differential thermal analysis (DSC 404 F1 Pegasus Apparatus with S-type thermocouples, NETZSCH), X-ray powder diffraction (D8 Advance diffractometer, Cu-K_α radiation) and scanning electron microscopy (Philips XL_30 FEG) were used to analyze the samples.

T-x-y diagrams, a number of their polythermal sections and also isothermal sections at 300 and 800 K were constructed based on experimental results and literature data on boundary quasi-binary systems. The homogeneity and primary crystallization fields as well as the types and coordinates of non- and monovariant equilibriums were determined. It was established, that Cu_8GeSe_6-Ag_8GeSe_6 system is partly quasi-binary and characterized by formation of continuous solid solutions (δ) between high-temperature cubic modifications initial compounds and limited solid solutions (δ_1 and δ_2) based on low-temperature ones. Formation of solid solutions decreases the temperature of polymorphic transitions of both components.

Limited areas of solid solutions are formed based on Cu_2Se (α_1), Ag_2Se (α_2) and Cu_2GeSe_3 (γ) compounds.

Based on obtained data a number of samples from the homogeneity areas of γ- δ-, δ_1- and δ_2-phases are synthezed and their electrophysical properties are studied.

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NEW NON-STOICHIOMETRIC PHASES WITH Tl_5Te_3 STRUCTURE IN THE Tl_2Te-TlX-TlX' (X, X'-Cl, Br, I) SYSTEMS

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Chalcohalides of heavy p-elements and phases on their base are important functional materials. Some of them are also 3D topological insulators (BiTeI) [1] and radiation detectors at X-ray and γ-ray regimes (Tl_6SeI_4, Tl_6SI_4) [2].

In our previous studies [3, 4] it was shown that the Tl_2Te-TlX systems are characterized by formation of ternary compounds Tl_5Te_2X, with tetragonal structure such as Tl_5Te_3 (Sp.gr.I4/mcm). Tl_5Te_3 and its structural analogs $Tl_9Bi(Sb)Te_6$, $Tl_4Pb(Sn)Te_3$ are thermoelectric possess extremely low heat conductivity [5].

The results of investigations of quasi-ternary systems Tl_2Te-TlX-TlX', which formed new non-stoichiometric phases based on Tl_5Te_2X compounds are generalized in this report.

Alloys of the above-state systems were prepared by melting preliminary synthesized and identified initial compounds in quartz ampoules under vacuum (~10^{-2}Pa) with the subsequent homogenized annealing at 600K during 800h.

Differential thermal analysis and X-ray powder diffraction as well as scanning electron microscopy were used to analyze the samples.

Some polythermal sections, isothermal section at 600K and projections of liquidus surfaces of these systems were constructed. It was established, that systems are quasi-ternary plane of the corresponding quaternary systems.

There are not quasi-binary sections in investigated systems. Sections Tl_5Te_2Cl-$Tl_5Te_2Br(I)$ and Tl_5Te_2Br-Tl_5Te_2I are stable in subsolidus and characterized by formation of continuous solid solutions (γ-phase) with Tl_5Te_3 structure. The homogeneity area of γ-phase considerably falls outside the limits of above-state sections towards Tl_2Te and forms continuous strips in width ~25 mole %. Samples containing more than 95 mol% Tl_2Te are also one-phase and crystallize in monoclinic structure of Tl_2Te-type (Sp. gr. C_2/C).

Furthermore, the results of investigation of thermoelectric properties of obtained phases variable composition were presented.

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GLYCEROL STEAM REFORMING ON NICKEL LOADED APATITE-TYPE LANTHANUM SILICATES

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Being a biomass derivative, glycerol is currently produced in large quantities in the process of trans-esterification of fatty acids into biodiesel. The steam reforming of glycerol appears as a potential alternative for producing hydrogen in the near future with significant impact in the viability of numerous bio-refining processes [1,2]. Lanthanum silicates of the apatite structure have attracted considerable attention as oxygen ion conductors because of their high ionic conductivity at intermediate temperatures and low activation energy. Recently an increased interest is observed for the apatite-type lanthanum silicates in the field of catalysis, as it has been proven that substitution of Si in the apatite structure increase apatite-type lanthanum silicate activity, mainly due to oxygen excess [3,4].

In the present paper for the first time it is reported the application of apatite-type lanthanum silicates in the steam reforming of glycerol reaction. The $La_{9.83}Si_5Fe_{0.75}Al_{0.25}O_{26\pm d}$, apatite oxide prepared by solid state synthesis was applied as a supporting material for a 8wt% Ni catalyst. Apatite oxide and catalyst (fresh, reduced and used) samples were characterized by means of the XRD, SEM, TEM techniques. Catalytic testing experiments were performed using a fixed bed reactor at temperatures ranging from 400 to 750 ^oC with a feed consisting of $C_3H_8O_3$ (20% v/v.) and H_2O in the liquid phase.

Comparing with a 8%Ni/alumina the Ni/apatite catalyst exhibited a superior performance, with a glycerol conversion close to 100% for the whole range of temperatures and a higher H_2 concentration at the gaseous products even for low temperatures, ranging between 25 and 40 % v/v for 500-750 ^oC. Moreover, CO_2 and CO concentrations were rather constant having the values of 10 and 5% v/v for the aforementioned temperature range, respectively. Liquid products as acetol, acetone, allyl alcohol, acetic acid and acetaldehyde were detected only for $T<700\,^oC$ and at rather low concentrations.

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HIGH PERFORMANCE FOAM CONCRETE PRODUCED BY USING TURBULENCE MIXERS

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Foam concrete is modern building material which combines satisfactory mechanical and heat insulating properties. Technology of foam concrete allows obtaining wide range of density of light weight concrete used in building industry without additional thermal treatment.

The aim of this research is elaborating foam concrete compositions with the best relation between durability, mechanical strength, insulation properties and volume weight. Controls the technological parameters of producing process and application of different additives and admixtures allow obtaining compositions with optimal pore size distribution.

In the framework of research basic properties of foam concrete, such as water absorption, compressive strength, volume density and thermal conductivity, have been investigated in depending mixing technology, kind and amount of additive. Two kinds of high speed mixing technology with turbulence effect have been used for producing foam concrete. Different types of commercial foaming agents have been applied and one’s influences on properties of fresh mix and hardened foam concrete have been evaluated. Different kinds of additives, such as micro and nano silica fume, carbon nanotube, have been applied for improving mechanical properties of foam concrete. Obtained mechanical and physical properties of foam concrete have been compared with properties of traditionally used autoclaved aerated gas silicate concrete.

By evaluation experimental results it may be concluded that use of intensive mixers allows obtaining stable mix and high performance properties of hardened material. Application of modifying admixtures with pozzolanic effect allows increasing compressive strength and decrease value of water absorption of foam concrete.

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FINITE ELEMENT ANALYSYS ON COLD DRAWING PROCESS FOR BIOMEDICAL TUBE OF COBALT-CROMIUM ALLOY

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Recently the biomedical application parts of micro tube such as catheters, stents and operation instruments have been actively developed in advanced countries. In this study, finite element analysis on the drawing process for the micro tube of diameter 2.8 mm with CoCr alloy was conducted. The initial outer diameter and thickness of preform tube were 9.6mm, 0.5mm, respectively and drawing speed was held constantly at 10 mm/s and the total 20 drawing passes were installed for cold drawing processes. The completed tube will be used for making stents with laser cutting and polishing process and so on.

In order to make the precise simulation of drawing process, the decision for the friction coefficient of graphite lubricant should be needed. As results of the simulation and experiment, the friction coefficient of graphite was estimated as 0.298.

From pass 1 to pass 15, the tube sinking method was used and the fixed mandrel drawing method was utilized from pass 16 to pass 20. The material of the mandrel was bearing steel (100Cr6) and its material data was obtained from the material database of commercial FEA software MSC. Marc^{TM}. The tube that was sailed through each pass was annealed respectively.

As a result of the drawing simulation, the tube diameter was decreased linearly but the reduction of tube cross section was larger at the pass 18. That means the rate of drawing load' s change was large. The thickness of tube was decreased rapidly while the fixed mandrel drawing process was applied. Finally the simulation was verified making a comparison with the tube shapes obtained from the experimental results. The drawing simulation error was 2%.

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PHASE AND ELEMENTAL CHARACTERIZATION OF QUARTZ MINERALS DERIVING FROM IOS ISLAND, GREECE

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Quartz is the second most abundant mineral in the Earth's continental crust, after feldspar. It is found in nature in varying purities and forms. Commercially, quartz is traded in various qualities for different industrial applications. It can be used either for high added value applications such as silicon-metal wafers, optical glass or PV panels or for ordinary applications such as foundry sand for metal castings or as a filler for adhesives and grouts.

Quartz deposits has been found in many regions in Greece. Ios is an island belonging to Cyclades island complexity, where quartz can be found in different rock occurrences. The investigated quartz samples were detected as quartz lenses in Central and Southwestern part of the island in different rock-types within the gneiss-complex of quartz-albite gneiss and garnet-mica schist as well in metamorphosed intrusive bodies. Our results indicate the presence of pure quartz (>99 %wt) in most of the samples obtained. In some samples the elemental analysis revealed the presence of Mg, Ca which indicates that their oxides (MgO and CaO phases) possibly coexist with SiO_2.

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SONOCHEMICAL LEACHING OF CHALCOPYRITE BY USE OF FERRIC CHLORIDE AS OXIDANT

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Chalcopyrite ($CuFeS_2$) is the most abundant minerals of copper sulphide. These minerals have been commercially treated by pyrometallurgy processes since the1800s. However, pyrometallurgy processes have some disadvantages of SO2 exhaust, high construction expenses of smelter. In particular, these require high grade Cu concentrate. Therefore, several hydrometallurgical processes have been tried for recovering copper from chalcopyrite as an alternative to traditional pyrometallurgy processes. [1] However, hydrometallurgical processes have not been successfully commercialized, because chalcopyrite is one of most refractory minerals to leach. Therefore, high efficient leaching method is required for the development of chalcopyrite.

It has been found that ultrasound is a promising tool to enhance the leaching of metal ore in solution. [2, 3] Under the application of ultrasound, mass transfer is increased by disruption of the interfacial boundary layers through a process of the cavitations in the shock wave form near a surface and by a decrease in the diffusion layer thickness due to the micro-currents. In addition, interparticle collisions induce the reduction of particle size. Application of ultrasound has been tried for the leaching of metal ores.

Much study has reported that copper can be leached from chalcopyrite in acid solution by use of ferric chloride according to the following reactions;

$CuFeS_2 + 4Fe^{3+} \rightarrow Cu^{2+} + 5Fe^{2+} + 2S^0$

$CuFeS_2 + 4Cu^{2+} \rightarrow 4Cu^{+} + Fe^{2+} + 2S^0$

In the present study, the behavior of copper leaching from chalcopyrite in acid solution under ultrasound applied has been researched. The effect of ultrasound intensity on leaching of copper from chalcopyrite at various pHs, temperatures and solution compositions has been studied and sonochemical leaching reaction has been evaluated

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MINERALS AND MATERIALS PROCESSING VIA MECHANOCHEMISTRY: FROM METALLURGY TO NANOTECHNOLOGY AND MEDICINE

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Mechanochemistry, a branch of solid-state chemistry, analyzes processes which can occur in solids due to the application of mechanical energy. This energy is supplied by high-energy milling. The mechanochemical approach belongs to the group of procedures that intensify the course of processes by producing various surface and bulk defects in treated solids. The accumulated energy acquired by milling is utilized in subsequent processes. In principle, the potential of mechanochemistry can be applied in cases, where the economic demand, the high temperatures as well as wet processes are under consideration [1-3]. The environmental aspects of these processes are particularly attractive.

Several applications of mechanochemistry will be illustrated to demonstrate its potential in such apparently distinct fields like metallurgy, nanotechnology and medicine:

- Processing of enargite Cu_3AsS_4 with the aim of its dearsenification and subsequent preparation of new anticancer substance (Na_3AsS_4) and of nanocrystalline Cu illustrate the non-traditional prospect in metallurgy
- Synthesis of nanocrystalline semiconductors like ZnSe, PbSe and Bi_2S_3 contribute to efforts to prepare advanced optical materials in nanotechnology
- Enhanced in vitro activity of realgar As_4S_4 illustrates the perspective of nanomilling to prepare effective substances for cancer treatment in medicine

In all three areas the focus is aimed on scaling - up the processes where suitable large-scale processing equipment will be described.

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INVESTIGATION ON THE CREEP RESISTANCE OF TI-6AL-4V ALLOY FOLLOWING ELECTRON BEAM WELDING PROCESS

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Ti-6Al-4V alloy is the most widely used titanium alloy and excellent candidate material for the applications in aerospace, automotive, energy, and medical-implant industries due to its high specific strength, good corrosion resistance, and favourable combination of related properties [1]. The creep resistance is an important factor in design under different temperature-stress domains in the industrial applications. Recently, numerous studies have examined how particulates [2], environment [3], surface treatment processes [4], heat treatments [5] are correlated with the microstructure and creep resistance of Ti-6Al-4V alloy. It is known that successful alloy-joining methods such as welding techniques can significantly increase the utility of Ti-6Al-4V alloy in industrial applications. However, the study on the creep resistance of its weldment is still ignored.

Several common fusion-welding processes such as gas tungsten arc welding, laser beam welding, and electron beam welding (EBW) can be used on Ti-6Al-4V alloy. Among these welding processes, the high-vacuum EBW process is a promising joining method which can effectively prevent the detrimental effects produced by the reaction of alloys with atmospheric gases during the joining process. Furthermore, our previous study showed that the tensile strength of Ti-6Al-4V alloy following EBW process coupled with suitable heat treatment can be significantly enhanced up to 1223 MPa together with a comparable elongation of approximately 10% [6]. Thus, the creep resistance of the Ti-6Al-4V EBW weldment will be of interest to industrial applications.

In this study, we investigated the creep resistance of Ti-6Al-4V EBW weldments under the creep stresses of 350, 400, 450, and 500 MPa at 500 °C. It appears that when the applied stress is less than 500 MPa, the newly formed α_2-Ti_3Al and γ-TiAl phases in the fusion zone of the weldment may provide stronger resistance to dislocation climb and glide during creep, leading to superior creep resistance of present EBW weldment than the Ti-6Al-4V plate materials reported in the literature. The possible creep mechanism, microstructural evolution, and characteristics of the precipitates are also studied.

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DISSOLUTION OF MAGNETITE IN MIXTURES OF OXALIC AND SULPHURIC ACID

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The understanding of dissolution can help improve different dissolution based processes. Previous studies have shown that oxalic acid is a good leaching agent for magnetite compared to commonly used sulphuric and nitric acids [1]. However, oxalic acid can cause problems in larger applications and it is more expensive than sulphuric or nitric acids. Dissolution of iron oxides has been extensively studied in single acid systems but studies with mixtures of acids are few. Also kinetics and thermodynamics of dissolution are still not agreed on among academics. The determination of the suitable kinetic model is the first step in deepening the understanding of the dissolution mechanism. The objective of this work was to study the dissolution of magnetite in mixtures of oxalic and sulphuric acid. The work was based on performing thermodynamic and kinetic experiments at different temperatures and acid ratios.

The effect of the temperature on the equilibrium solubility was investigated with the acid mixture of 50/50 (oxalic/sulphuric). Increasing the temperature increased the solubility. However, increasing the ratio of oxalic acid from 50/50 to 70/30, the solubility was roughly same at 50 °C. This could indicate that a higher quantity of oxalic acid does not automatically result in higher solubility. The temperature had an effect on the equilibrium kinetics and solubility, which can be observed in varying shape of the dissolution curves. The shape was decelerator at 35 °C and 50 °C, but at 15 °C the shape was sigmoidal. The sigmoidal shape indicates a slow induction period at the initial stage of dissolution followed by faster dissolution period. At 35 °C and 50 °C slow induction period was not observed in the dissolution curves.

The Kabai model [2] was found the most suitable in describing the dissolution kinetics of magnetite in mixtures of oxalic and sulphuric acid. Due to faster dissolution kinetic of oxalic acid the rate of reaction was increased when the quantity of oxalic acid was increased. The solid specific constant a of the Kabai model was found to vary for the different acid ratios, which is not directly in line with the assumptions underlying the model. The reason for the differences in a might be the changes in the solid phase during the dissolution. The rate limiting step and the reaction mechanism can also be speculated on based on the constant a. The systems of mixtures of oxalic and sulphuric acids were diffusion controlled (a>1), whereas the pure oxalic acid system and the pure sulphuric acid system were controlled by the rate of chemical reaction (a≥1). The same reaction mechanism would be suggested for both the pure acid systems, named as disintegration, because the constant a>1 for both systems. The mechanism for acid mixtures would be then rounding-off, sphericalization, a<1. Empirical evidence to support these mechanisms is at this stage not yet available.

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SH-SYNTHESIS OF ALUMINOSILICATE CERAMICS: MECHANOCHEMICAL ACTIVATION AND REGULARITIES OF COMBUSTION

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Aluminosilicate materials are widely used for creation of refractories working in corrosive media, thermal insulators as well as fine pottery. These materials are produced using both conventional technologies based on a long-term firing at high temperatures and under the conditions of self-propagating high temperature synthesis (SHS) characterized by low power-intensity with a wide range of choice of the raw material [1]. The purpose of the material being synthesized is determined by its phase composition and structural characteristics of the components. Synthesis of ceramic products under the conditions of SHS is distinguished by the multifactoriness of the process and the possibility to exert a purposeful effect on its kinetic characteristics by both preliminary preparation of the charge components and changing the conditions of synthesis. Special attention is paid to combination of a complex preparation using mechanochemical treatment (MCT) of raw materials and subsequent SHS process of ceramic composition systems [2].

The results of the carried out investigations on the use of pre-activated and modified quartz have shown the possibility to decrease the temperature of the furnace heating for carrying out SH-synthesis, to produce new phases and nanosized elements of the structure. It is stated that in the regularities of MCT and subsequent SHS of ceramic systems, and important role is played by the natural state and purity of the used oxide materials, in particular quartz.

When using modifiers containing nitrogen in the process of MCT of quartz, in the synthesized SHS ceramics there forms aluminium nitride that vividly demonstrates participation of nitrogen saturating the surface layer of the particle, when modifying quartz, in the process of the subsequent combustion. Carbon- and nitrogen containing modifying additives provide the increase of the combustion temperature due to participation of carbon and nitrogen in the synthesis and contribute to maximum formation of corundum and aluminosilicate compounds.

The presented results of investigations on the combustion process show the efficiency of pre-activation of quartz resulting in the change of kinetic and temperature characteristics of the combustion process providing the completeness of conversion of initial components, when producing aluminosilicate ceramics.

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RECOVERY OF MINERAL WASTES IN THE PRODUCTION OF PIGMENTS AND FILLERS FOR THE BUILDING INDUSTRY

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The issues of tailing waste utilization mineral processing are relevant worldwide. The amount of stored waste and ensuing environmental problems are increasing with growth of mining and processing of raw materials. Nowadays the general trend consists in minimizing of mineral waste volumes by recycling with production of new materials. In order to appreciably diminish the amount of wastes, the market for the new products should have a substantial capacity. There are, indeed, industries operating with bulky material flows, namely, construction and production of paint and lacquer with an ever growing demand for pigments, pigment fillers, dispersing compounds, and thickening materials. Products with pigment properties are also indispensable in plastic, paper and rubber manufacture. In the potential developments, of special interest are composite pigments containing titanium, iron, aluminium, silicium, and calcium compounds in different combinations. As a rule, the properties of an entire composite are determined by the pigment component covering the core surface represented by known synthetic and natural fillers such as calcite, alumina, silica, talc. Products with these composites take on pigmenting or filling properties. The former is tincturing products making them more attractive; the latter - improving their technical characteristics such as stability to heat, light and aggressive media, increased impact and bending strengths, etc. Mineral composites can be produced from polycomponent mineral wastes of ore mining and dressing enterprises. This work demonstrate the possibility of apatite-nepheline and copper-nickel ore dressing wastes recycling to produce white and color pigments, weather-resistant paints and paint primers, fillers for rubber and plastic compounds and anticorrosion paint primers. The initial composition of ore wastes has been studied. The chemical process stage parameters have been established. During the kinetic studies, the operation sequence and conditions of interaction between the waste components and reagents were determined. Optimal parameters for directed synthesis of target products with tailored properties and the area of their application have been determined. The new process of ore wastes recovery is technologically attractive, considering that all steps are inter-connected and all by-products are utilized. This technology will make it possible to reduce the amount of dumped wastes by 70-80%.

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MULLITE-ZRO$_2$/Y$_2$O$_3$ BASED CERAMICS WITH SI$_3$N$_4$ ADDITIVE

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The wide use of mullite ceramics can be explained by its observable high temperatura properties such as high thermal and pressure stability in harsh oxidizing environments, favorable thermal shock, low thermal expansion and thermal conductivity. This study is focused on modification of the structure/phase composition and properties of mullite-ZrO$_2$/Y$_2$O$_3$ ceramics by Si$_3$N$_4$ additive 1 to 10 wt.% to show the effect on the thermal and mechanical properties, as well as corrosion stability to acidic and basic aqueous solutions at elevated temperatures.

The starting mixtures of powders were prepared by planetary ball-milled process, obtained grain size of particles was in range 55-100nm. Samples were prepared as disks or cylinders and subjected to sintering in nitrogen atmosphere at temperature1400°C as well as there spark plasma sintering were used. The sintering degree after firing was characterized by the density and shrinkage. Microstructure and phase composition of sintered samples was analysed using SEM (Nova Nano 650) and XRD (D8 Advance Bruker). The compressive strength was determined by Toni-technic model 2020, modulus of elasticity befor and after thermal shock - on the basis of the standard ASTM EN 1876-01. For determination of corrosion stability 1N NaOH- or H$_2$SO$_4$ solutions at temperature 60°C were used.

It was determined that microstructure of conventionally sintered at 1400^{o}C ceramic samples with 1-5 wt.% Si$_3$N$_4$ additive is dense and is formed from mullite-corundum crystals with inclusions of ZrO$_2$ cub. particles equally dispersed in mullite matrix. By increaing of Si$_3$N$_4$ additive to 5% as is shown on XRD the relative intensity of ZrO$_2$ cub. peaks decrease. Density of samples conventionally sintered in nitrogen atmosphere and by SPS differs significantly. Density of ceramic samples compacted by spark plasma sintering is in the 3.25-3.55 g/cm^3 range whereas for conventionally up to 2.5-2.9 g/cm^3.

There is shown that the Si$_3$N$_4$ additive not more than 5 wt.% to mullite-ZO$_2$Y$_2$O$_3$ ceramics lead to formation of stable ZrO$_2$ cubic phase by conventional sintering in nitrogen atmosphere at 1400°C and sequential to growth of density and compressive strength. Values of compressive strength greatly is dependent on used sintering method. Indifferently these values is in range 350-390MPa for SPS sintered samples.

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EFFECT OF ALLOYING ADDITIONS (BE AND/OR ZR) AND DUPLEX AGING TREATMENT ON MECHANICAL PROPERTIES OF CAST 7075 Al-Mg-Zn-Cu ALLOYS: EXPERIMENTAL CORRELATION USING MINITAB SOFTWARE

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The present study was undertaken to investigate the effect of aging parameters (time and temperature) on the mechanical properties of Be-and/or Zr- treated Al-Mg-Zn (7075) alloys. Ultimate tensile strength, 0.5% offset yield strength and % elongation measurements were carried out on specimens prepared from cast and heat treated 7075 alloys containing Be and/or Zr. Different aging treatment were carried out for the as solution treated (SHT) specimens (after quenching in warm water). The specimens were aged at different conditions; Natural and artificial aging was carried out at room temperature, 120^0C, 150^0C, 180^0C and 220^0C for different periods of time. Duplex aging was performed for SHT conditions (pre-aged at different time and temperature followed by high temperature aging). Ultimate tensile strength, yield strength and % elongation data results as a function of different aging parameters are analysed. A statistical design of experiments (DOE) approach using fractional factorial design is applied to acquire an understanding of the effects of these variables and their interactions on the mechanical properties of Be- and/or Zr- treated 7075 alloys. Mathematical models are developed to relate the alloy mechanical properties with the different aging parameters.

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THE THERMAL REDUCING EFFECTS OF MICA FOR CEMENTITIOUS SPRAYED FIRE RESISTIVE COATING MATERIALS

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The buildings constructed with steel structure is coated with certified Sprayed Fire Resistive Material(SFRM) to resist from fire. All the building materials lose their initial performances as time passes, so they need durability. . Steel retains approximately 50% of its strength when it reaches 1100°F (600°C). Temperatures during fires can be much hotter - a standard fire test reaches 1300°F (704°C) in the first 10 minutes. If left unprotected, the structure may collapse when exposed to fire. Building codes require certain beam, column, floor, wall and roof assemblies to have fire resistance ratings which are determined on the basis of standard fire tests. Fire resistance ratings can be accomplished with the application of sprayed fire resistive materials (fireproofing) to those assemblies.

This study is on the Mica’s effects for thermal reducing of cementitious sprayed fire resistive materials due to fire exposure. Mica is a strong heat-resistant materials. So, we expected that Mica will be effective in reducing heat of fire. We confirmed that the Mica, was used as a fire protection materials as, is to improve heat resistance

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DEEP DRAWING TEST OF AL5052 PLATE WITH ARRAY PATTERN OF PYRAMID SHAPE FOR IMPROVEMENT OF DRAWING FORMABILITY

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In recent years, in order to improve the fuel economy of the vehicle due to the strengthening of environmental regulations, the weight reduction of the vehicle is strongly required. The aluminum sheet material, lighter material, it is expected as automobile materials to substitute for steel. But the formability of aluminum sheet is low.

In this study, it was attempted to determine the extent of improvement of formability through to form an embossed pattern of pyramid-shaped in order to improve the room temperature formability in deep drawing test of the aluminum sheet. Before applying the pattern to the aluminum plate, a die was manufactured for applying a pattern on aluminum plate.

As applied pattern shape in aluminum plate, height 1.5mm in pyramid shape. It was the width 6mm, spacing 1mm between the patterns. After the pattern selected, 19 pyramids in horizontal and 19 ones in vertical direction, as plate of 120mm x120mm is formed, and pyramid aluminum plate to fabricate a pattern die which can total 361 pieces of patterns is formed. Forming speed at the time of pattern forming was applied to 1.08mm/s.

Sheet with 0.4mm thickness at Al5052 for aluminum plate was applied in the experiment. The tensile strength of the sheet was about 20.6kgf/mm^2(15mm/min experimental tensile test condition). Using the drawing ratio, the formability was evaluated through comparison with pattern applied deep drawing results and no pattern plate

The deep drawing test die had a circular punch with a diameter of 40mm, shoulder radius 3mm and clearance was selected by 0.48mm. Deep drawing test speed was adopted the same 1.08 mm/s when applied forming stage.

In the case of sheet with no patterns were formed up to the drawing ratio 1.2 at room temperature.

The fracture was occurred early stage of drawing process over drawing ratio 1.2.

In the case of sheet applied patterns was formed up to the drawing ratio 1.45. The formability of the sheet material was improved by about 20%.

Measurements of the thicknesses for the sheets after drawing tests were implemented at 2 mm intervals in diagonal direction. Usually, the thickness of the plate was reduced about 10%. The thickness of the sheet with pattern was measured 0.32mm thick in the area of fracture.

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EFFECT OF ULTRASOUND TREATMENT ON SURFACE PROPERTIES OF NATURAL ALUMINOSILICATES

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Ultrasound exposure belongs to environmentally friendly measures of intensification of technological/chemical processes, including those taking place in systems with natural aluminosilicates. Physical chemical properties and behavior of aluminosilicates and their dispersions can be significantly changed depending on duration and power of ultrasound, the nature of the solvent, an electrolyte present in dispersion and the type of aluminosilicate structure. The variety of processes carried out under sonication, the absence of a uniform procedure and equipment for ultrasound treatment brings difficulties in systematization and understanding of the effect of ultrasound on aluminosilicates properties.

The present research was aimed at studying the effect of ultrasound treatment of aqueous and H_2O_2, a “green oxidant, dispersions on physical-chemical properties of natural aluminosilicates. As objects of investigation were chosen natural aluminosilicates, having various structures: montmorillonite, 90% (Mt90); glauconite (Glt-Nat); attapulgite (Atp); zeolite/clinoptilolite (Zlt). 1wt.% dispersions of the clay samples in deionized water (W) or in 35% H_2O_2 (HP-dispersions) were exposed of ultrasound (US) for 60 and 120 min using the BRANSON Digital Sonifier (20kHz; 10% amplitude) at 19^{o}C. Physical chemical properties of natural and US-treated clay samples were studied by Dynamic Light Scattering (DLS); BET; TGA; FTIR; ICP-OES techniques.

The DLS-study confirmed that under no US both in water and H_2O_2 dispersions the particles size (PS) reduced in 3 times for Glt, Zlt; in 1,2-1,4 times for Mt90; whereas for Atp a strong agglomeration took place. The diameter of the agglomerates changed in the row: Atp > Mt90 > Zlt > Glt. Stronger decrease in PS was caused by sonication, i.e. 4-6 times for water, and 1.3-5 times for HP dispersions. The effect of US on dispersing of minerals varied in *water* as Mnt > Zlt > Glt; in H_2O_2-suspensions as Zlt > Glt > Mt90.

BET-specific surface area of aluminosilicates increased by 1.5-2.3 times after US-treatment of water dispersions, while that for HP-dispersions practically didn’t changed.

An increase in total pore volume (TPV) was found for Glt by 80% (UST-W) and 130% (UST-HP); by 10% for Zlt. For the rest samples TPV decreased after UST-W: by 80% for Mt90; by 50% for Zlt. The UST in W-dispersions enhanced volume of micropores, V_{micro}, by 40% (Glt) and in 7.7 times for Atp, whereas UST of HP-dispersions decreased V_{micro}. For Glt exposed of US significant increase in pore diameter (60%) was observed.

The TGA profiles and FTIR spectra observed slight changes. For Glt, Mt90, Atp temperature of dehydration T_{dhr} peak decreased in the order: Nat>UST+W>HP>UST+HP. The effect of HP and UST on T_{dhr} of the minerals changed in the row: Mt90>Glt>Atp>Zlt.

Hence, US-treatment of W- and HP-dispersions of aluminosilicates generally leads to reduction of agglomerates size, enhancing/changing of surface characteristics, and testifies at relative stability of the structure of investigated aluminosilicates within the specified time of US exposure.

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RECOVERY OF VALUABLE METALS FROM SPENT SCR CATALYSTS FOR DE-NOX BY USING HYDROMETALLURGICAL METHODS

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Recovery process is developed for the valuable metals such as vanadium and tungsten from spent SCR catalysts for de-NOx. The present study various hydrometallurgical techniques namely soda roasting, water leaching, precipitation and solvent extraction was performed successfully. The first part optimized is soda roasting at high temperature monitored by water leaching. Generated water based leach liquor is processed for the vanadium and tungsten recovery by precipitation and solvent extraction processing.

Soda roasting process carryout by using sodium carbonate at high temperature (850 oC), the roasted catalyst size reduced by the gridding then followed by water leaching (optimized the time, pulp density and temperature). The leach liquor further processed by precipitation using magnesium chloride; for separation of the vanadium and tungsten solvent extraction technique was applied and optimized the phase ratio, temperature, reaction time. Two nitrogen based extractants such as Alamine 336 and Aliquat 336 was used for valuable metals extraction process. The loaded organic (LO) processed for stripping of the two metals by most commonly used stripping reagents. But vanadium and tungsten were possible to selective stripping when NaCl and NH_4Cl used as the stripping reagents for Alamine 336 as an extractant system, whereas, in case of Aliquat 336 as an extractant system, NaOH was proved best selective stripping reagent for both title metal ions back recovery from LO.

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BULK PROPERTIES OF FINE CALCIUM CARBONATE POWDERS

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This paper deals with the bulk properties of fine calcium carbonate powders. As the measured material was used a number of surface treated and no-treated commercial fillers for plastics prepared on the basis of natural calcium carbonate raw materials. The bulk properties of the materials were measured on the standard Jenike box device, the Schulze shear tester, and the Johanson´s Hang-Up indicizer as well. The paper shows the changes of the bulk properties behavior of the materials as the function of grain-sizing and the surface treatment agents quality and the level of the particle products treatment. Obtained flow function curves are compared.

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PREPARATION, RHEOLOGY, AND NANOSTRUCTURE REVELATION OF Na-MONTMORILLONITE GEL

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Clay minerals as important layered materials are comprised of multiple layers of hydroxylated and coordinated tetrahedral and octahedral sheets [1]. As a representative of valuable 2:1 layered aluminosilicate clay minerals, montmorillonite (main constituent of smectite) has been applied extensively as stabilizing additives in engine oils, cosmetics, pharmaceutical and chemical industries due to its unusual colloidal behavior (thixotropy, viscoelasticity, and yield stress) [2]. Although many studies on the sol-gel transition of montmorillonite have been published, up to now the gelation mechanisms of swelling montmorillonite are still far from being clearly understood [2-3].

In this work, the effects of different electrolytes as a function of concentration on the rheological behaviour of Na-montmorillonite suspensions were studied. Furthermore, the viscosity and detailed image information about the nanostructure of prepared electrolyte-containing Na-montmorillonite gel was examined. First, the crude Ca-bentonite from a raw source (Inner Mongolia, China) was modified with sodium carbonate and purified through wet chemical processing, and then the as-prepared Na-montmorillonite suspension was gelled by adding a series of electrolytes such as MgO, $MgSO_4$, CaO, $CaCl_2$, $Ca(OH)_2$, $AlCl_3$, $Al_2(SO_4)_3$, and $BaCl_2$ with increasing concentration. The results showed that stable homogeneous gel could be formed when using MgO, CaO, and $CaCl_2$ as electrolytes respectively, while other electrolytes only led to the formation of flocculation. For MgO, CaO, and $CaCl_2$ as electrolytes, the rheological measurements reveal that the correlation between shear stress and shear rate exhibited Bingham plastic behavior. In addition, the shear rate-viscosity correlation study indicated that the viscosity of montmorillonite suspension with MgO as electrolyte is higher than that with CaO and $CaCl_2$. It is well-known the rheological properties of montmorillonite are controlled by its structural arrangement [4]. To further obtain much nanostructure information of swelling montmorillonite nanoplatelets, XRD, FTIR, and morphology investigations were conducted. The results reveal that the unique honeycomb structure with hole diameters on the nanometer scale only existed in freeze-dried Na-montmorillonite gel when using MgO as electrolyte.

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NANODIAMOND LAYERS/SPOTS FOR BIOSENSING

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Nanodiamond (ND) layers were produced by the pulsed spray technique on a heated silicon substrate. By varying the number of pulses it was possible to obtain a quasi-continuous layer on the substrate surface. The use of atomic force and confocal microscopies allowed evidencing the presence of self-assembled pillar structures.

The pillar formation was due to the evaporation of 1,2-dichlorethane solvent in which 250 nm nanodiamonds were dispersed and its mechanism was based on the *coffee stain* effect as described in detail in ref. 1.

Simple bio-chips on glass and silicon substrates can be fabricated spraying ND spots arranged in an array configuration (Figure 1a) through a mask, and can be suitable for bio-applications. Specifically, the presence of nitrogen vacancy (N-V) color centers in ND particles is promising as bio-markers[2]. An example of spot is illustrated in Figure 1b where pillars are present (zoomed area of Figure 1b). Additionally, the control of the pillar position represents an important challenge for micro-functionalised emitters arranged in a chip matrix suitable for bio-screening.

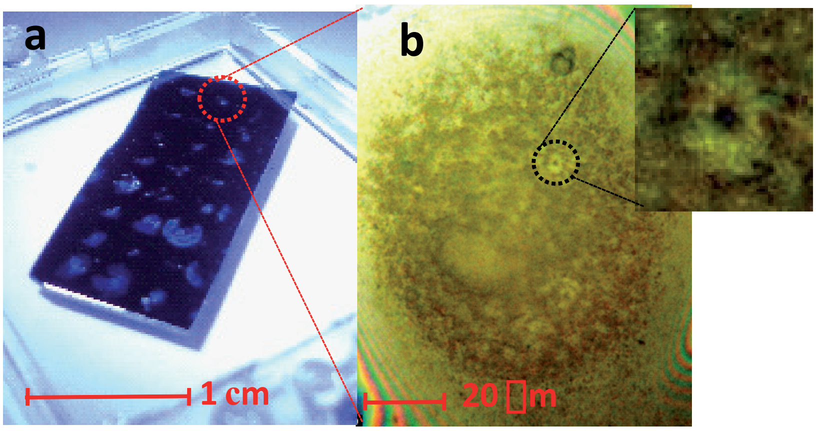

Figure 1: (a) Example of nanodiamond spots sprayed on a silicon substrate by a mask (b) single spot, related inset is referred to an isolated pillar.

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THE EFFECT OF FIRING TEMPERATURE ON MINERALOGY, MICROSTRUCTURES AND THERMAL CONDUCTIVITY OF CLAY-BASED CERAMICS

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Traditional ceramics are produced firing a clay mixture (made of a plastic and a aplastic components) at different temperatures. Firing temperature, firing environment and soaking time are the thermodynamic parameters which enable the formation of some phases instead of others. According to firing condition and raw materials different mineralogical phases and microstructures can develop in ceramic bodies. Consequently, physical properties of fired bodies, like thermal conductivity, can vary with firing temperature [1]. In the last decade a lot of attention has been paid to ceramics made of kaolinitic clays [2] and only some works deal with materials made of other kind of clay mixtures [1,3]. This work aims to study the effect of firing temperature on mineralogy, microstructures and thermal conductivity of ceramics produced with four different clays.

With this purpose, 18 ceramic disks are prepared using two kaolinitic clays (Switzerland), a kaolinite-illite clay (Ukraine) and one rich in micas (Greece) and hydrating them with 5 vol.% of water. Samples are produced by uniaxial pressing (25 MPa), have an height of 8 mm and a diameter of 30 mm. They are fired in the range from 950 to 1350 °C with steps of 100 °C, a heating rate of 150 °C/h and a soaking time of 1 h.

Mineralogy is studied via X-ray powder diffraction (XRPD) and quantitative phase analysis (QPA) is done using Rietveld method. The microstructure of the samples is investigated via scanning electron microscopy (SEM) while to study the ceramic thermal conductivity a modified Lee's disk apparatus is used. Finally, open porosity is estimated via water immersion.

Thermal conductivity increases with the amount of mullite, the vitrification of the samples and the decrease of porosity. The ceramics of micaceous clay fired at 1050 °C have a higher thermal conductivity (1.4 W/mK) than kaolite-based ceramics fired at higher temperatures (1.2 W/mK). The high vitrification of the ceramics produced with the Greek sediment enables this behaviour. Moreover, the higher content of coarse quartz grains in Swiss clay induces the formation of cracks in samples fired up to 1150 °C due to the α-β quartz phase transition.

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ONE-STEP MECHANOCHEMICAL SYNTHESIS AND PROPERTIES OF ORGANICALLY MODIFIED MAGNESIUM SILICATE

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Organically modified layered silicates are used in industrially as nanofillers in polymer-clay nanocomposites for improving of mechanical, thermal, and flame-retardant properties, as an effective thickening and gelling agents in paints, lubricants, ointments, and rheological control agents in drilling fluids [1, 2]. An important application area of organoclays is environmental protection. They are promising for water purification from phenol and its derivatives, oil and greasy substances, pesticides and herbicides, dyes, heavy metals (e.g. $Hg2^+$, $Pb2^+$, $Cd2^+$) and oxyanions (e.g. $CrO4^{2-}$, $NO3^-$) [1-3].

Generally, the organoclays are prepared in solutions by cation exchange reaction or by solid-state reaction. A mechanochemical reaction has obvious advantages, such as being a simple process, having a high capacity and relatively low cost. Moreover, this reaction is an environmentally benign process, using no solvents, or using them in very small quantities and is one of the most suitable techniques for industry. Typically, the mixture of clay and organic component is ground on the air at room temperature [4, 5].

Organically modified magnesium silicate was synthesized for the first time from silicon dioxide xerogel mechanochemically treated together with magnesium hydroxide, lithium fluoride, and hexadecyltrimethylammonium bromide. Synthesis was carried out in a colloid mill (CM-1) in the discrete and continuous modes.

According to the results of X-ray diffraction, scanning electron microscopy, differential scanning calorimetry and thermogravimetric analysis, it was found that the variation of the synthesis conditions allows to obtain products of different structural order and particle size.

The mechanochemical synthesis of organically modified (by hexadecyltrimethylammonium cations) magnesium silicate occurs in the presence of water only. That is confirmation for scheme of formation of the organically modified magnesium silicate structure proposed earlier [6].

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FROM PHASE DIAGRAMS TO THE SINTERING PROCESSES

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3D computer models of T-x-y diagrams for the ternary oxide systems help to analyze the space diagrams structure by means of projections and sections [1-3]. Additional information include visualization of mass balances calculation and 3-phase transformation type changing, competition of the crystals with different dispersity in uni- and invariant reactions. It is also possible to give an overview about perspective properties of these systems, the crystallization stages and micro-constituents for any phase in the process of the melt crystallization. By means of the vertical an horizontal mass balances (the latter coincides with an isopleth), a confirmation may be received about the concentration fields both with individual set of microstructure elements and those, at which the crystallization scheme and micro-constituents of phase's assemblage are the same as in the adjoining field.

T-x-y diagrams with silicon oxide systems are widely used in solving the problems related to obtaining information about the properties of ceramic materials (portland and aluminous cements, refractory and alkali-free glasses and so on).

Analyzing the concentration fields of the system CaO-SiO_2-Al_2O_3 (C-A-S) arranged under the C_2S liquidus by means of the T-x-y diagram computer model [1], it was shown, that the field of primary crystallization C_2S has the complex contour with 7 points and maximum point at liquidus monovariant line. It is divided at the projection into 13 two-, 24 one- and 11 zero-dimensional concentration fields. The analysis of crystallization schemas permits to identify 2 one- and 2 zero-dimensional fields with coinciding sets of phase reactions and micro-constituents. Else one- and two-dimensional fields coincide with the neighboring concentration fields by micro-constituents, but they differ by the schemas of phase reactions.

The sintering processes are decoding by means of the unstable phase diagrams with the labile eutectics [4].

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SIZE CONTROL OF AU NANOSTRUCTURE ARRAY FOR ZNO GROWTH USING NANOSPHE RE LITHOGRAPHY

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The influences of changing the pattern of Au nanostructure on the formation of ZnO nanorods are investigated by Nanosphere lithography (NSL). NSL is a low cost, simple to implement, nanofabrication technique capable of producing a large area of nanoparticle structures and well-ordered 2D nanoparticle arrays with relatively short preparation time. Polystyrene arrays was achieved through Langmuir-Blodgett process and the deposition of gold layer was performed in an ion sputter. Subsequently, the polystyrene were removed beads by pyrrolidone. We used two methods to fabricate monolayer of Au nanostucture, one was using 7nm in diameter of the Au nanoparticle with LB trough, and another one was using 412 nm and 762nm in diameter of the PS particle with LB trough. It was observed that in first method couldn't get the regular pattern, and most of samples didn't change morphology after after treatment except the solvent of Au nanoparticle with chloroform. From second method, periodic Au particle arrays with uniform particle size of 762 nm were deposited on the silicon substrates via NSL process. The results indicate that the periodic arrays of Au nanostructure with a size height of 10-70 nm were deposited on the substrate by NSL technique. We analyzed the thickness and formation on silicon (100) substrate by atomic force microscopy (AFM) and scanning electron microscope (SEM). Synthesized ZnO nanorods could be modified effectively by controlling the morphology of Au nanostructure and the optical and electrical properties of the resulting ZnO nanorods are expected to display improvement.

ENVIRONMENT & TECHNOLOGY

ET2

MATERIALS' BIO AND CHEMICAL DETERIORATION IN ARTEFACTS AND MONUMENTS OF CULTURAL HERITAGE

ET4

CLAY MINERALS FOR HEALTH, EARTH AND ENVIRONMENT

ET5

FLY ASH AND OTHER HAZARDOUS MATERIALS STABILIZATION AND REUSE. WASTES AS RESOURCE

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MICROBIALLY INDUCED CEMENTATION PROTOCOLS

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Microbially Induced Calcite Precipitation (MICP) is a biomineralization process applied to improve the engineering properties of granular structures. MICP uses populations of non-harmful bacteria, such as *Sporosarcina pasteuri* or *Myxococcus xanthus,* in order to cement sand, loam, calcarenite or clay, in a growth medium amended with urea and dissolved calcium source.
This research focuses on finding out the best conditions to cultivate populations of cementing bacteria and the suitable proportions of the mixing of urea, sand-like granular structures, bacteria and calcium chloride; to come out with customized solutions to improve soil stability, to heal concrete cracks, to build roads and paths, to restore monuments, to transform sand into sandstone, etc. It weaves together biotechnology and mineralogy to achieve sustainable and eco-friendly operational strategies and materials, which take advantage of living forms of intelligence to generate outcomes that meet our needs without consuming energy and harming the environment.

In order to complete the laboratory work that was carried out for this researching, several samples of clay, sand, loam and calcarenite were milled, using a planetary mill, to get the same grain size for all the samples. Then the same weight of every kind of milled sample was put inside Petri dishes, so that it would be easier to compare the results in relation to the same concentration of bacterial growth medium amended with urea and calcium chloride.
We tried several samples that weighted the same, with different liquid solutions that contained different proportions of water, urea, calcium chloride and populations of cementing bacteria. In general terms, we could say that the samples that showed the most consistent cementation features were the ones made of calcarenite, which makes sense because their content on calcium carbonate allows the chemical precipitation process to take place.

Keywords: Microbially Induced Calcite Precipitation (MICP), Sporosarcina pasteurii, Myxococcus xanthus, urea, calcium chloride, granular structures.

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PORTUGUESE TIN-GLAZED EARTHENWARE FROM THE 16TH CENTURY PRODUCED IN THE REGION OF LISBON: A SPECTROSCOPIC CHARACTERIZATION OF BODIES, GLAZES AND PIGMENTS

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Tin-glazed earthenware is known to be an old production in Portugal, namely at Mata da Machada kiln, active from about 1480 to 1530, although tin-glaze ware production is associated to 16th century contexts. From Santo António da Charneca kiln (also late 15th century to early 16th century) archaeological evidence exists for the production of tin-glaze tiles and also simple lead-glazed earthenware [1-3]. Both kilns were located South of Lisbon near Barreiro. There is also archaeological and documental evidence that tin-glazed productions started in the city of Lisbon at least in the middle of the 16th century.

In this work we performed archaeometric analyses on the ceramics of these production centres (Lisbon area), trying to identify the possible different clays used by the potters working in this region. Selected sherds representative of these Portuguese faience production centres of the 16th century in the region of Lisbon were studied with the use of non-invasive spectroscopies, namely: Ground State Diffuse Reflectance Absorption (GSDR), micro-Raman, Fourier-Transform Infrared (FT-IR) and Proton Induced X-Ray (PIXE) or X-Ray Fluorescence Emission (XRF). X-Ray Diffraction (XRD) experiments were also performed.

The obtained results evidence a clear similarity in the pastes of the pottery produced at Mata da Machada and Santo António da Charneca kilns, namely in the use of clays of Pliocene origin, characteristic of the area where these ceramics were produced. The main mineralogical components were Quartz, Kaolinite, Illite and Muscovite. Lisbon clays were quite different, namely of Miocene origin. In this case Quartz and Gehlenite were the main mineralogical components detected, although Andradite, Diopside and Anorthite could also be identified. The results obtained for the Lisbon's pastes, point to the use of several clay sources, where the relative amounts of these components exhibit a significant variation. It should also be mentioned for the Mata da Machada faience sherds that a second clay source was used, Miocene origin. It could be clays from the Lisbon clay sources easily available by boat transportation, but its origin can also be attributed to clay sources in the south bench of the river Tagus, which have a composition very close to the Lisbon clays.

The blue glaze from all the Lisbon samples is due to Co^{2+} ions that exist in the silicate glassy matrix. No clear micro-Raman signature was detected for all green and amber glazes, in spite of the clear evidence from GSDR and XRF experiments that copper and iron ions are responsible for these two coloured glazes. White glazes were obtained with the use of tin oxide. In particular tiles produced at Santo António da Charneca, most probably in the beginning of the 16th century, the first kiln for tile production reported in Portugal, exhibit excellent quality glazes, namely white, green, blue, amber, black and red coloured. A comparison with coeval tiles or sherds from Spanish production centres was also made, namely Seville, Valencia and Toledo pastes, glazes and pigments, and significant differences were observed.

All these findings will be described in detail in this presentation, and a comparison of the clays used for the faience productions with ceramic bodies after being fired in the kilns will also be made.

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PORTUGUESE CERAMICS FROM THE 17TH CENTURY: ARCHAEOMETRIC ANALYSES OF PASTES, PIGMENTS AND GLAZES

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In early 16th century, the Portuguese navigators arrived East establishing regular trade with China [1]. Many goods, namely Chinese blue and white colour porcelains, started arriving in Lisbon and being re-exported to the main European countries [2, 3]. Lisbon became a very important trading port and a new Portuguese ceramic production, in the form of faience, started in Lisbon's workshops [4, 5]. These ceramics reproduced, among other motifs Chinese patterns that arrived in large quantities in Lisbon in mid-16th Century [2, 3, 6, 7]. Afterwards, these ceramics' production spread to Coimbra and Vila Nova, where they were well settled in the early 17th century.

Glazes and pastes are different between the three centres, though a visual distinction may be made based on decoration. Lisbon was the biggest production centre and its ceramics famous within and outside the country due to their high quality and the craft specialization. Vila Nova's production quite similar to Lisbon workshops in terms of pastes and glazes, although tends to present a lower quality in decoration. Lower quality objects were manufactured in Coimbra's workshops, being quite distinguishable from the other two production centres presenting less delicate decorations.

In this communication, we will present the results on archaeometrical analyses of pastes, glazes and pigments for 17th century Portuguese faience. Representative sherds were studied with the use of non-invasive techniques, namely: GSDR (Ground State Diffuse Reflectance Absorption), micro-Raman, PIXE (Proton Induced X-Ray) or XRF (X-Ray Fluorescence Emission) and XRD (X-Ray Diffraction). The obtained results evidenced a clear similarity in the pastes of pottery produced at Vila Nova and some of the ceramic pastes from Lisbon, while compared to Coimbra's production. The Lisbon pastes contain Quartz, Gehlenite, Andradite and in some cases Calcite, and Anorthite, while Coimbra pastes evidenced Quartz, Diopside and Anorthite as main components.

In what regards glazed phases (white or coloured), tin oxide was used as whitening agent of the lead-alkali glazes in all cases. In all kilns cobalt blue is responsible for the coloration of the blue glazes, although differences were detected in the Raman spectra from Lisbon's production, due to the identification of cobalt silicate. Purple glazes (wine colour "vinoso") were obtained with the of manganese and iron oxides dissolved in the glaze. Hausmannite was the main manganese containing mineral detected by micro-Raman in Lisbon's purple glazes.

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SAMPLES FROM ARPI: A PECULIAR CASE INSIDE THE APULIAN RED FIGURED POTTERY PROJECT

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Our research group has been studying since several years Apulian red figured pottery.

So far, all 5th cent. objects analyzed show the same features: fine texture of the ceramic body, red figures saved from the ceramic paste and black gloss painted directly on the ceramic body. Some 4th cent. objects show features similar to the 5th cent. ones, whereas others are characterized by a ceramic body with a coarser texture and a layer of red slip to obtain red decorations, with a black gloss painted on it. This technology seems to represent a distinctive characteristic of Late Apulian production.

Here, our interest is focused on Late Apulian red-figured pottery from Arpi (Northern Apulia).

The finds were characterized from physical-chemical, and minero-petrographical points of view. We investigated the ceramic body, the red area, the black gloss and the over-painted pigments by SEM, XRD and ICP-MS. The chemical data, handled by a multivariate statistical treatment, discriminated Arpi's production from that one of other Apulian sites so far studied, allowing to hypothesize for Arpi a local production during the 4th cent. BC. Compositional differences in ceramic bodies of Arpi's samples, stylistically attributed to different painters, were highlighted. About the technological features, the results show for Arpi's samples, unlike from the sites of Peucetia and Messapia, the use of a single production technology - the traditional Attic one- also during the 4th cent. BC.

These results, together with those obtained for the sites already studied, provide objective evidences for replying to the archaeological questions still unsolved (Was one or more workshops active in Southern Italy? Were artisans local or from Greece? Was a painter present in each Apulian production site or few painters worked in the area, moving by demand? Were productions differentiated, depending on the area of destination and/or on the target of the client? etc.).

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AN OVERALL SCIENTIFIC INVESTIGATION ON PRE AND POST ANTONINIAN COINS FROM EGNATIA (SOUTHERN ITALY)

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We analyzed a collection of Antoninian coins, dated back from the second half of the third cent. bC. and coming from the archaeological site of Egnatia (Southern Italy).

Antoninianus was initially in silver, but was slowly debased to bronze. Each new coin had a lower amount of silver than the previous one, and each contributed to increasing inflation.

In 274 AD a partial solution to the crisis experienced by the Roman state came thanks to a series of measures taken by Aurelian: acting on the nominal values, closing provincial mints and activating those under the direct control of the emperor. Also, a new coin was introduced, heavier but still lighter compared to the first Antoninian coins, and with a content of Ag -presumably- higher than those produced in the recent past.

We analyzed thirteen coins: six pre-reform, six post-reform and a non-ascribable one (it is illegible) with the principal aims of:

- estimating the degree of devaluation, i.e. the progressive reduction of the silver content in the alloy for pre-reform coins;
- providing information on the actual effects of the monetary reform of Aurelian, i.e. the presumed increase in the amount of silver in the reformed coins.

The investigations were carried out by portable X Ray Fluorescence, Laser-Induced Breakdown Spectroscopy (LIBS), Raman Spectroscopy, Optical and Electron Scanning Microscopy with Energy Dispersive Spectroscopy.

The results revealed for all coins a Cu/Ag/Sn/Pb quaternary alloy, in which copper is the main alloying element. The Cu and Ag contents are more than 80% (>90% in the illegible coin) and about 1.5-2%, respectively. The Sn content is variable (0-12%) and the Pb content is <5%, consistent with the literature data on Antoninians [1,2], even if some coins showed an unexpected high surface lead content (close to 30%).

It was not observed a substantial difference in the amount of Ag in pre and post-reform coins.

The metallographic analysis of the microstructures highlighted a Cu/Ag biphasic structure in all the coins, as well as information on the techniques used to the manufacturing (structure with flattened and oriented parallel to the surface grains, lines of stress hardening and sometimes geminates of annealing, or residues of dendritic structure), implying a process of cold hammering of the dowels obtained by melting, in some cases followed by warming up.

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PRIMARY BIO RECEPTIVITY UNDER LABORATORY-CONDITION ON DIFFERENT LIMESTONE WIDELY USED IN THE CONSTRUCTION OF HISTORIC MONUMENTS IN SOUTH ITALY

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Weathering of natural stones exposed to the atmosphere is caused by a combination of physical, chemical, and biological processes. Several investigations during the last 10-15 years have made it apparent that, in addition to chemical weathering, microbiologically induced weathering contributes to the deterioration of building stones. All types of building material are colonisable by microorganisms, because it is virtually impossible to protect rocks or buildings from bacteria, fungi and microalgae in the natural environments. In particular, the fungal growth on stone surfaces is responsible not only of aesthetic deterioration due to the production of pigments and organic acids that can stain or damage the stone, but it is also responsible of the subsequent structural deterioration because of the hyphal growth through the rock material that increases the porosity of stone, favouring in the long time the settlement also of higher plants.

Guillitte in 1995 has introduced the concept of “Bio-receptivity” explaining it as «the aptitude of a material to be colonised by one or several groups of living organisms».

“Bio-receptivity” can also be defined as the totality of material properties such as roughness, porosity, moisture and the chemical composition of the surface layer that, exposed in particular environmental conditions, allows the establishment, anchorage and development of microorganisms.

The aim of this work is to test the receptivity to the fungal colonization of three different building stones (Lecce, Canosa and Grottaglie).

All sterile materials were inoculated under controlled environmental conditions with several species of fungi isolated previously from historical deteriorated surfaces in order to reproduce the natural colonization. Samples were successively exposed to natural solar light in aseptic conditions to avoid unwanted contaminations and to understand the time of degradation exclusively due to inoculated fungi.

Petrographic investigation, and Scanning Electron Microscopy (SEM) showed an elevated bio- receptivity of Grottaglie and Canosa stones more porous than Lecce stones that have different physical and chemical properties.

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MORTAR CHARACTERIZATION OF TEATRO NACIONAL DE SÃO JOÃO (PORTO, PORTUGAL)

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Teatro Nacional de São João (TNSJ) is the main theatre located in Batalha Square, in the historical centre of Porto city, NW Portugal. TNSJ was built in 1918 after the first São João Theatre was destroyed by a fire in 1908. Presently it is classified as a national monument, being one of the most important Porto monuments.

The facades of TNSJ are richly decorated with a variety of elements such simple patterns, floral elements and faces of a considerable size. These elements were built around a steel frame, using mortars that possibly incorporate a cement binder. However, TNSJ facades presented a high level of degradation, although they have been frequently intervened in the past. Mortars from decorative elements started to detach and fall, leading to the protection of the street below and determining the need for further intervention.

For that reason, mortar samples were taken from each facade in order to characterize constituents and proportions to identify variances in materials and determine the level and causes of degradation. Techniques such as acid dissolution, X-ray Diffraction and optical microscopy for the determination of mortar composition and capillary water absorption and mechanical strength for the determination of mortar properties were used.

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MINERALOGICAL AND CHEMICAL CHARACTERIZATION OF CERAMIC AND CONSTRUCTION MATERIALS FROM SANTA OLAIA SETTLEMENT (FIGUEIRA DA FOZ, PORTUGAL)

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Santa Olaia archaeological settlement is located close to Figueira da Foz town, in the central coast of Portugal, westwards of Coimbra. The settlement stands on a limestone hill, and is flanked to the North, West and South by alluvial lands [1]. The village occupation backs to the Neolithic continuing through Bronze, Iron, Roman and Medieval periods. Iron one being the most important archaeological period on the station [2]. The purpose of this study is the mineralogical and chemical characterization of the ceramic and construction materials found in the Santa Olaia station, in order to understand the used techniques and trying to establish relationships between them and contemporary materials. The studied materials were found during the construction of the Coimbra-Figueira da Foz Highway and they are pieces of furnaces, supposed to be from the Iron Age. Qualitative and semi-quantitative mineralogical analyses were carried out by X- ray diffraction (XRD) using a Philips®/PanalyticalX'Pert-Pro MPD, Kα Cu (λ = 1,5405 Å) radiation, with 0.02º 2θ s^{-1} steps in goniometer speed. The chemical composition of materials was assessed by X-ray fluorescence (XRF) using a XRF-Panalytical AXIOS116 PW4400/40.Results show 4 sample groups: silica-rich, carbonate-rich, iron-rich and a fourth group composed by a minority of samples not included in the groups mentioned before. In terms of mineralogy the silicate samples have a high quartz percentage followed by feldspars, opal, anhydrite, hematite, calcite, dolomite and phyllosilicates. In the carbonated samples the major mineral is calcite followed by feldspars, quartz andphyllosilicates. The iron rich samples have a high percentage of hematite, wustite, magnetite and maghemite, ferrihydrite, and iron silicates (fayalite). The fourth group comprises, among others, samples rich in copper (cuprite) and others rich in Sn (cassiterite). In this preliminary study, the characterization of a large group of different materials allowed us to understand their composition and to correlate them with different "industries" as components of ceramic and metallurgical (Cu - Sn ores) furnaces.

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HYDROCALUMITE OBTAINED BY A SIMPLE AND ENVIRONMENTALLY-FRIENDLY METHOD

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Hydrocalumite (HC) and hydrocalumite-like (HC-lc) compounds denote a branch of the anionic clay family which has been scarcely reported in the bibliography in comparison to other members of the anionic clay family such as the hydrotalcite. Recently, HC and HC-lc have been used as catalyst in aldol and transesterification reactions with good results. In this sense, their synthesis is conventionally carried out by the coprecipitation method [1]. However, this procedure involves environmental and technical drawbacks [2]

In this work, hydrocalumite-like compounds' synthesis was performed following the method described by Valente et al. [2], since this method is environmentally friendly and economically feasible. The optimal reaction conditions were determined considering the pH, type of water (deionized and decarbonated) and aging time effects.

Hydrated lime (HL), $Ca(OH)_2$, (A) and boehmite (B) were employed as precursors. The amount of A and B was calculated in order to obtain a nominal Ca/Al molar ratio of two. First, A and B were dispersed by separate at 5000 rpm for 30 min. Then, A was added to B and dispersed at 8000 rpm for 30 minutes. Afterwards, the slurry was pH adjusted and aged at 80ºC. Finally, the sample was filtered and dried. The materials were analyzed by X-ray powder diffraction (XRD) and the crystalline phases were identified by the JCPDS files.

According to the XRPD analysis, when HL and bohemite were dispersed and reacted without any pH adjustment employing deionized or decarbonated water the HC-lc phase was observed as the main crystalline phase together with hydrogarnet, calcium hydroxide and calcite as secondary crystalline phases, respectively. On the other hand, when HC was synthesized adjusting the pH at 12.5 with HNO_3 (employing decarbonated water and a nitrogen flow within the reactor), the nitrate HC-lc crystalline phase was achieved in 60 minutes with traces of calcite. Calcite presence was due to the fact that it was identified in the pristine hydrated lime. Pure nitrate HC-lc was only obtained with a calcite-free hydrated lime.

In this work, hydrocalumite-like compounds were obtained employing cheap and available raw materials and the optimal reaction conditions were determined. The results demonstrated the feasibility of producing these compounds by a simple, economic and environmentally-friendly method.

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INDUCING THE PRECIPITATION OF LDH TO REMOVE METALS FROM MINE-WASTE DRAINAGES

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The removal of toxic metals from waste waters is an important issue in mining environments. Layered double hydroxides (LDH) are a series of lamellar compounds with general formula $[M^{2+}_{1-x} M^{3+}_x (OH)_2] (A^{n-})_{x/n} \cdot mH_2O$, where M^{2+} are divalent metals (Mg^{2+}, Zn^{2+}, Fe^{2+}, Cu^{2+}, Ni^{2+}, etc.), M^{3+} are trivalent metals (Al^{3+}, Fe^{3+}, Cr^{3+}, etc.) and A^{n-} are anions such as CO_3^{2-}, SO_4^{2-}, Cl^-, NO_3^-. These compounds are widely studied for the removal of anionic pollutants from water thanks to their high anion exchange capacity [1-4].

Since LDH precipitation presupposes the presence of a divalent metal and a trivalent metal in adequate ratios, our idea was to use M^{3+}-poor drainages from the impoundment of "Red Muds" (metallurgical wastes from an electrolytic plant used in processing oxidized Zn-ores) in the Monteponi mine area (Iglesias, Sardinia, Italy) as a reagent for the precipitation of LDH and the consequent removal of metals. In fact, the "Red Muds" drainages are characterised by neutral pH and high levels of SO_4 (~ 4000 mg/L), Mg (~ 600 mg/L), Zn (~ 200 mg/L) and other metals (Pb, Mn, Cd), but very low concentrations of trivalent metals such as Fe^{3+} and Al^{3+}. The precipitation of LDH was tested through different batch experiments by adding to the drainage an adequate amount of a salt of Al $[Al_2(SO_4)_3 \cdot 18H_2O]$, in order to induce the LDH precipitation, and NaOH to maintain a neutral pH. The main parameter controlling the removal of metals and the type of precipitate seemed to be the pH. As a function of pH variations during the batch experiments, XRD analyses showed either the formation of poor crystalline LDH combined with removal of dissolved total Zn (98%) and significant amounts of Mn, Cd, Pb and Ni, or the formation of well crystalline LDH combined with significantly lower removal of Zn (63%), as well as of Mn, Cd, Pb and Ni. In all experiments, Al added to the drainage was not detected in solution, indicating a complete precipitation. The precipitates will be better characterized by HRTEM-EDS. These preliminary results encourage further investigations on the removal of divalent metals from M^{3+}-poor waste waters by inducing LDH precipitation at different pH conditions.

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SPECTRAL ANALYSIS BASED ON CLAY PERCENTAGE WITHIN THE SEDIMENTARY FILLING OF ENNOUAL CLAY PAN, SOUTHEASTERN TUNISIA

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The cyclostratigraphy of the Holocene series is currently well developed due to the high resolution sampling and the mathematical modelling [1]. The Holocene filling of Tunisian clay pans is candidate to record the climatic variability through a slight change of the clayey fraction [2,3]. Sedimentologically, the saline system of Ennoual is a clay pan because silt and clay are the dominant fractions [4]. This work aims to study the cyclostratigraphy based on clay percentage along a 150 cm core carried out in the sedimentary filling of Ennoual clay pan. Sampling was carried out each 0.5 cm to ensure the high resolution. Samples underwent grain size measurement by FRITSCH Laser Particle Sizer ANALYSETTE 22. From each grain size curve, we found out the clay percentage. The spectral analysis of values of the clay percentage shows the setting of dual spatial cyclostratigraphy. On the one hand, the low frequency cyclostratigraphy, which is found out by the naked eye, stretches along 2 cycles. On the other hand, high frequency cyclostratigraphy is detected only through the mathematical analysis. The spatial cyclostratigraphy expresses a temporal cyclicity caused by a change of the climatic conditions and/or the depositional environment.

Keywords: clay percentage, cyclostratigraphy, Ennoual clay pan, southeast Tunisia

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ANTIMONATE SORPTION BY Zn-Al SULPHATE LAYERED DOUBLE HYDROXIDE

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This study focuses on the efficiency of a specific Layered Double Hydroxide (LDH) in removing Sb(V) from aqueous solution. LDHs are a group of lamellar compounds with general formula $[M^{2+}_{1-x} M^{3+}_{x} (OH)_2] (A^{n-})_{x/n} \cdot mH_2O$, where M^{2+} are divalent metals (Mg^{2+}, Zn^{2+}, Fe^{2+}, Cu^{2+}, Ni^{2+}, etc.), M^{3+} are trivalent metals (Al^{3+}, Fe^{3+}, Cr^{3+}, etc.) and A^{n-} are anions such as CO_3^{2-}, SO_4^{2-}, Cl^-, NO_3^-. Thanks to their high anion exchange capacity, LDHs are widely studied for the removal of anionic pollutants from water [1]. Among the possible LDH compositions, in this study we used Zn-Al sulphate LDH, successfully tested in arsenate and molybdate sorption [2-5]. Antimony is listed as a priority pollutant by the World Health Organization, which established a guideline value of 20 µg/L for drinking water. Due to its various industrial uses, global fluxes of Sb have increased at least tenfold in the last decades, resulting in an increase of environmental Sb contamination. There are not many developed methods for the removal of Sb from contaminated waters. In oxic conditions $Sb(OH)_6^-$ is the dominant Sb(V) species over a wide pH range. The removal of Sb(V) from solution was carried out in a batch system by using variable Sb(V) concentrations and LDH amounts. Dosages were chosen assuming that the main Sb(V) removal mechanism was an interlayer anion exchange, and that for maintaining the electroneutrality of LDH the entrance of 1 mole of $Sb(OH)_6^-$ should be compensated by the exit of 0.5 mole of SO_4^{2-} present in the interlayer. Effectively, the removal of antimonate from aqueous solution was accompanied by a concomitant release of sulphate from LDH to solution. Sulphate release increased with time proportionally to antimonate removal with a molar ratio close to 2. XRD analyses showed a complex LDH structural rearrangement during the exchange process. This study confirms the huge capacity of Zn-Al sulphate LDH to adapt its original structure in order to host different-sized/charged anions, supporting its potential key role in water treatment.

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RIVER WATER DISCOLORATION WITH ACID ACTIVATED KAOLINITE - RICH CLAYS

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Nyong waters are naturally dark brown to light brown in colour because of humic substances. In the present report, Nyong waters treatment with kaolinite rich clays has been investigated. In raw state, 8 to 9 % of the best clay materials were necessary to eliminate all humic substances from Nyong waters. The best acid activation parameters were found with a solution/mass of clay ratio equal to 5: 0.48 N H_2SO_4, 60 min activation time at 97 °C. After acid treatment, the clay content necessary for total Nyong waters discoloration was consequently reduced from 8 to 1 %. The analysis of acidic sites developed during acid activation revealed the predominance of Lewis acid sites. Very low contents (< 0.7 %) of acid-activated clay could not be employed for Nyb discoloration because of sedimentation problems. Recycling of the best acid-activated clay was based on humic substances oxidation with hydrogen peroxide in an acid medium. After 15 cycles, the acid-activated clay still discoloured Nyong waters in spite of particles erosion.

Keywords: kaolinite, acid activation, humic substances, Nyong waters, recycling.

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NEW FRIENDLY ENVIRONMENT NANO-GOLD / PILLARED CLAYS COMPOSITES - CATALYTIC ACTIVITY

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The clay minerals are abundant natural materials, clean and inexpensive, which can be used in catalysis. These materials have a high adsorption capacity that is particularly interesting for the deposition of catalytic noble metal particles, in the interlamellar space of clay [1].

Furthermore, gold, which is the most noble metal, has long been regarded as catalytically inactive. In 1987 the group of Dr Haruta [2] discovered the catalytic properties quite remarkable of gold at low temperature. These catalytic properties are intimately related to the size of gold particles which have to be less than 5 nm.

The aim of our work was to deposit gold particles of nanometer size, catalytically active, on Fe and Al pillared montmorillonite - Na^+ (support effect), by deposition - precipitation. The objective was to study the reactivity and selectivity in the hydrogenation reaction of crotonaldehyde (synthesis of commodities in the cosmetic industry). A series of three catalysts 1% Au / bentonite (Au / B), Au / B-Fe and Au / B-Al were prepared from the precursor anionic $HAuCl_4.3H_2O$.

The characterization by XRD showed the expansion of the interlamellar distance of clay after intercalation by Fe or Al (calculated on the basis of (001) planes). Characterization by UV-Vis showed that the position of absorption bands corresponding to the resonance of the gold metal (plasmons) is influenced by particle size and the nature of the support. We have shown that most particles are smaller; the maximum absorbance band is shifted to smaller wavelengths. Indeed, the band located at 568nm (AU^0) (average size estimated by SEM is 10 nm) in the catalyst Au / B is shifted to 548nm in Au / Al-B (5nm). This confirms the interest of the intercalation of clay by species such as Fe or Al in order to obtain even smaller particles and therefore catalytically active. In the case of solid Au / Fe-B, bands corresponding to the absorbance of oxidized species of iron mask those of gold. We also showed the existence of other Au^{n+} species.

The reaction of hydrogenation of crotonaldehyde catalyzed by the prepared solids is selective. The Yield and the selectivity will be discussed.

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EFFICIENCY OF NATURAL CALCINED AND ACID-ACTIVATED BENTONITE FOR REMOVAL OF ATRAZINE

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One of the most imported herbicides for Thai agricultural industry is atrazine whose toxic contamination damages both human and environment. Therefore, the main purpose of this study was to investigate the adsorption of atrazine onto modified and unmodified bentonite in aqueous solution with a batch system. These adsorbents were characterized by X-Ray Diffraction, FT-IR, XRF and specific surface area. Also, their adsorption efficiencies for removal of atrazine in aqueous solution were performed with various conditions including contact time, pH and atrazine concentration. The findings revealed that bentonite modified by these two steps i.e. calcination at 500°C and then HCl-activation at 0.5M ($BC_{500}A_{0.5}$) yield the optimum adsorption efficiency compared to those modified with a single step either only by calcination or acid-activation. Moreover, the sequence of modification of bentonite with two treatments by calcination and acid-activation affects the adsorption capability. That is the maximum adsorption of 14.26 $mg.g^{-1}$ resulted from the sample of $BC_{500}A_{0.5}$ at ambient temperature with atrazine concentration of 50 ppm while the adsorption capability of unmodified bentonite was just 0.28 $mg.g^{-1}$. Thus, the adsorption efficiency of atrazine can be explained in relation to a higher specific surface area and porosity of the sample.

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STUDY OF BENTONITE / POLY (4-VINYLPYRIDINE) COMPOSITES - CALCINATION EFFECT ON THE ADSORPTION APPLICATION TO THE RETENTION OF HEXAVALENT CHROMIUM IONS

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New inorganic / organic materials such as calcined Bentonite / poly (4-vinylpyridine) were prepared and characterized.

The effect of Bentonite calcination on the adsorption of the polymer was studied by infrared spectroscopy and thermogravimetric analysis.

These composites were tested in the retention of hexavalent chromium ions. They showed a great affinity for these ions.

The influence of different parameters on the adsorption rate, such as: the equilibrium time, the concentration of chromium ions, pH effect and temperature effect, was studied.

Keywords: inorganic / organic materials, Bentonite, poly (4-vinylpyridine), hexavalent chromium ions

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BENTONITE CLAY PROPERTIES OF AKZHAR DEPOSIT IN ALMATY'S REGION OF KAZAKHSTAN

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Bentonite clays of Akzhar deposit contained montmorillonite from 70 to 86%, the rest was represented by hydromica, calcite, chlorite, quartz, dolomite, feldspar, analcime and zeolite. The radioactivity of rocks is low, in the range of 8-15 mR/h, no harmful for the body.

By the prevalence of exchangeable cations calcium and magnesium, bentonite clays of Akzhar field are alkaline earth. Clay are fine, oily to the touch, highly plastic, with strong adsorption and catalytic properties.

The genesis of these clays is sedimentary-diagenetic. The main clay mineral, montmorillonite, has a crystal structure with a layered arrangement of the anions and cations, wherein the crystalline lattice of silicon consists of two tetrahedral and octahedral intermediate grids. Feature of the package of the crystal lattice of montmorillonite is such that water can easily penetrate between the blocks and push them. The result is a huge adsorption surface, allowing the clay to adsorb a very large number of foreign substances introduced into the body - both soluble and insoluble.

Elements contained in the bentonite clay (Mg^{2+}, Ca^{2+}, Al^{3+}, Fe^{2+}, Fe^{3+}, $Si^{4+,}$ K^{+}, Na^{+}, almost the entire periodic table in microdoses), when applied topically can penetrate into the tissue to a considerable depth, pulling themselves pathological material and feed not only the skin, but also the muscles, ligaments, bones . Potential consumers of these products are:

- Pharmacy networks
- Public and private health institutions
- Supplements in forages, poultry farming
- Soil fertilizer
- Food-processing industry (winemaking and vegetable oils)
- Cosmetic clinics and salons
- Oil producing and oil refining branch (drill solutions)
- Manufacturing of construction materials

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TRPM8 CHANNEL-FUNCTIONALIZED HALLOYSITE NANOTUBES TO TARGET TUMOR VASCULARIZATION

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Cancer growth and metastasis are strictly dependent on tumor angiogenesis, which is promoted by tumour cells upon secretion of a number of growth factors. Vessel formation is a complex multistep process during which 'activated' endothelial cells (ECs), the first mechanical and functional interface between blood and tissues, proliferate, migrate, differentiate and are stabilized in a new circulatory network. Being involved in nearly all of the 'hallmarks of cancer', there is an increasing consensus on the idea that ion channels play a significant role in driving cancer progression at all stages. Accumulating evidence tends to demonstrate that the development of some cancers could also involve such ion channel aberrations. In this context ion channels may be seen as potential novel therapeutic, diagnostic, and prognostic targets for anti-cancer therapies. The discovery of Transient Receptor Potential (TRP) superfamily of channels provided putative candidates for non-voltage-gated Ca2+ entry mechanisms. Notably, several TRP proteins are up regulated in cancer cells and have been suggested as valuable markers in predicting cancer progress and as potential targets for pharmaceutical therapy. In particular, the cold/menthol-sensitive TRPM8 (belonging to the 'melastatin' TRP subfamily) has emerged as an important factor in cell migration and prostate cancer (PCa) progression [1]. TRPM8 channel activation by menthol could be used to induce apoptosis of TRPM8-expressing prostate cancer cells and to inhibit angiogenesis. A great advancement in anti-angiogenic therapy has come from the use of nanotechnology since several nanovectors have been used as drug delivery systems (DDS) to efficiently target and kill tumor-associated vasculature. In this project we pursue a strategy of drug delivery using Halloysite nanotubes (HNTs) functionalized to target tumor angiogenesis in PCa, conjugating these nanomaterials with a selective TRPM8 activator such as menthol. We evaluated the cytotoxic effect of functionalized HNTs on Human Endothelial Microvascular Cells (HMECs) through cellular toxicity in vitro assay. HNTs were then functionalized with fluoresceine isotiocyanate (FITC) to study their cellular localization and finally we decided to non-covalently functionalize HNTs with menthol through vacuum cycles to selectively activate TRPM8 in HMECs. [2] Consequently, menthol-functionalized HNTs' antiangiogenic role compared to free menthol was tested on HMEC through ECs migration and tubulogenesis in vitro assays. Menthol release was studied by GC-MS and the functionalized nanomaterials were characterized by TGA, SEM and TEM.

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STUDY ON THE COMPATIBILITY OF A NATURAL ZEOLITE IN THE FORMULATION OF PREPARATIONS TO BE ADMINISTERED ORALLY

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Clay minerals are widely employed in pharmaceutical applications [1], and the specifications required are reported in monographs of different international pharmacopoeias, e.g. *Eur Ph.*, JP, USP. On the contrary, in spite of the growing interest that natural zeolites are obtaining in pharmaceutical field [2], the aforementioned pharmacopoeias do not contain any monographs concerning these minerals. Furthermore, in several researches on possible biomedical applications of natural zeolites, their characterization is inadequate, when not even absent. This work presents the characterization, performed according to the *Eur Ph.* (7 ed.), of a clinoptilolite-based material. This study is the first step of a research aimed to develop systems based on natural zeolites as drug carriers to be used in gastric infections. A Sardinian clinoptilolite-rich rock was subjected to beneficiation, then conducted in Na-form by ion-exchange. Particle size distribution was determined by laser diffraction. Mineralogical and chemical compositions were determined by XRD (Rietveld method) and ICP (OES and MS) analyses, respectively. Release of major and minor elements in simulated gastrointestinal environment was checked by ICP. The following technological properties of powder were also measured: cation exchange capacity, surface area, porosity, true and apparent density, flowability, compactability, water uptake, pH of a given suspension. Finally, the microbiological quality of the material before and after the sterilization process was tested. The prepared powder (0.4-80 μm; unimodal distribution), contains ≈90 wt.% of Na-clinoptilolite, quartz (<0.5 wt.%), residual amounts of feldspars, opal-CT, glass and biotite. Trace metals are below the more restrictive limits established in the international pharmacopoeias for “bentonite”, taken as reference due to the similarities between smectites and zeolites, and releases during digestive simulation tests are negligible (highest value: Pb=3.8 ppb). The microbiological quality is according to the limits established by *Eur Ph.* No microbial growth was found after sterilization. From a mineralogical, chemical, microbiological and technological point of view, the prepared material is compatible with oral administration.

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THE ANTI-INFLAMMATORY ACTIVITY OF NATURAL ALLOPHANE

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This paper presents evidence of the novel anti-inflammatory properties natural allophane collected from New Zealand, Japan, and Ecuador. Allophanes were assessed by (i) the mouse-ear edema method using 12-O-tetradecanoylphorbol-13-acetate (TPA) as inflammatory agent; and (ii) the myeloperoxidase (MPO) enzymatic-activity method. After 4 h, applying 1 mg ear^{-1} allophane conveyed edema inhibition (EI; p £ 0.01) in up to 39%, while MPO content inhibition (CI) values surpassed 60%. Pearson´s correlation analysis between EI and MPO data showed that edema was mediated by the migration of neutrophils at $t = 4$ h ($p < 0.05$), but not at $t = 24$ h. The lack of variation in cellular migration with time was explained because a reaction of zero-order kinetics. EPR spectra for allophanes showing higher anti-inflammatory activity denoted a broad signal centered at $g = 2$, and an intense spin-spin interaction, typical of a low-spin, octahedral Fe^{3+} environment ($S = ½$); and overlapping signals typical for Ni, with octahedral coordination, explained either by oxidation states +1 (Ni^{1+}), +3 (Ni^{3+}), or bulk Ni^{2+} ions.

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ASSESEMENT OF CRYSTALLINITY AND CHEMICAL FORMULA OF PRISTINE SMECTITES FOR MEDICAL APPLICATIONS

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The development of new drugs, (modified) drug delivery systems and composites for medical devices are research areas that are devoting special interest to clays and clay minerals namely due to their versatility, biocompatibility, and added value in the improvement of mechanical properties. These are raw pharmaceutical materials that after submission to general and specific pharmaceutical operations may be suitable for incorporation in medicinal products [1]. Clay minerals can be used as excipients and active agents in pharmaceutical products. Smectites are used, as biologically active substances, mainly as antidiarrhoeal, gastrointestinal protector, antipruritic and antiacid [2]. These geomaterials are also used in drug delivery systems (DDS) or integrated in modified DDS. Additionally, the incorporation of a small weight percentage of clay, with emphasis on smectite type, into polymer matrix in the formation of polymer clay micro/nano-composites improves mechanical and material properties of the polymer without losing the inherent processability of the matrix [3].

In the present study we analysed five portuguese smectitic samples with the aim to evaluate the crystallinity and characterize chemically their clay minerals for medical purposes. Wet sieving was performed in order to separate fraction < 63μm of samples, which was further used for clay fraction extraction. Clay fraction obtained using sedimentation according to Stokes law was then characterized by XRD and FTIR. Sedigraph results revealed that samples had an amount of < 2 μm fraction above 29% and main clay mineral assemblages were composed by smectite, illite and/or kaolinite/chlorite. Smectite Biscaye's index which was estimated by the ratio between valley and peak heights of 001 reflection revealed medium to high degree of smectites' crystallinity.

From SEM observations, coupled with Energy dispersive X-ray spectroscopy, the chemical composition of clay particles was obtained. The main interlayer cation ranges from sodium (Na) to calcium/magnesium (Ca/Mg) types.

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PREPARATION OF MODIFIED CLAY FOR DRUG RELEASE SYSTEM

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The need for safe, therapeutically effective and patient-compliant drug delivery systems continuously leads researchers to design novel tools and strategies.

In recent years, clay minerals have been proposed as very useful materials for modulating drug delivery, delaying and/or targeting drug release or even improving drug dissolution [1].

In the present work a montmorillonite-type clay, commonly used as excipient in pharmaceutical industries, was used as controlled release system for a polar and non ionic drug such as Ibuprofene (IBU).

Particularly, a commercial clay (Veegum-Kâ supplied by R.T. Vanderbilt Company, Inc,) was used as matrix for intercalation.

Two different systems were prepared: the first one was obtained by mixing the clay with the Ibuprofen, while in the second one the clay and a solution of polyethylene-glycol (PEG) and IBU were used. The preparation procedure was conducted in a jacketed reactor, equipped with a cooler, where 1.25 g of clay were suspended in a ibuprofen acidified ethanol solution (or ibuprofen in a solution of ethanol and PEG), at 30°C, under stirring at 600 rpm for 24 h.

Successively, the suspension was centrifuged to separate the solid from the liquid. The so obtained clay was dried at r.t. grinded in a mortar and analyzed by means of XRD, TG and FT-IR, while the solutions (before and after reaction) were analyzed by UV measurements.

To evaluate the effectiveness of these systems a release test was conducted using a dissolution apparatus, according to USP method II (paddle) and consisted of vessels, containing 400 mL of phosphate buffer solution (pH 6.8)/glycerol 9:1, placed in a water bath thermostated at 37° ± 1 °C and stirred at 50 rpm. Sink conditions were maintained throughout the analysis. At prefixed time intervals, aliquots were withdrawn and the drug was determined spectrophotometrically.

The two systems showed a different behavior. The best results were obtained by the system without PEG, which showed the typical profile of a time-controlled release mechanism showing a progressive release of the drug in 6 hours while for the system containing PEG, the release ended in 8 hours.

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ZNO/MCM-41 COMPOSITE FROM HYDROTHERMALLY TREATED MONTMORILLONITE FOR ENERGY AND ENVIRONMENTAL APPLICATIONS

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Pollution of water, air and soil are becoming increasingly serious problems. In addition, chemical pollution in the urban environment is strongly connected with thermal pollution, or the “heat island effect”, where temperatures increase within cities. Treating existing contaminants with the prevention of new pollution and cooling the surfaces of buildings or the pavements of outdoor areas are among the challenges. In recent work, we have seen that by supporting semiconducting catalysts on hydrophilic porous materials, different parts of the solar spectrum could be utilized for simultaneous multifunctional purposes (like UV-VIS for photodegradation and IR for providing the thermal energy for phase changes) and nanocomposites could be applied for combined processes like solar cooling in addition to pollutants photodegradation.

In this work, we have extended our research in the synthesis of new supported catalyst matrixes with wide spectral response. This was followed by the enhancement of adsorption abilities, satisfaction of efficient charge separation and transportation in the final composite structures. A low cost clay mineral, montmorillonite, was hydrothermally treated in an alkaline solution and the silica was used as the raw source for the preparation of the composite. Under neutral pH, a well ordered MCM-41 material was prepared and characterized by XRD, SEM,UV/VIS/NIR spectrophotometry and nitrogen and water vapor adsorption-desorption isotherms. A high surface area and adsorption volume in the mesopores of the prepared material was measured. Furthermore, ZnO nanoparticles were in situ synthesized on the matrix (ZnO-FA) characterized and tested for the degradation of model pollutants and water vapor adsorption towards evaporative cooling of hydrophilic surfaces. In dark adsorption experiments, drastic decrements in the pollutant concentration in aqueous solutions were acquired by the implication of the ZnO/MCM-41 catalyst. This action was further enhanced under UV illumination. Thus, the preparation of a mesoporous adsorber from montmorillonite silica with photocatalysis widens the energy and environmental application prospects of clay minerals.

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WATER VAPOUR ADSORPTION ON POROUS MATERIALS FOR SOLAR COOLING APPLICATIONS

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A large number of microporous (< 2 nm), mesoporous (2-50 nm) and macroporous materials are currently under investigation as water vapor sorbents. In the last few years, these materials have attracted much attention for solar cooling applications either passive or adsorption heat pumps and chillers. In passive designs, we have recently shown that porous materials have the ability to adsorb water and thus, they interact with solar irradiation and heat in order to cool the inner space of buildings through the water vapor adsorption-desorption cycle. The purpose of this work was to investigate in detail how pore' size affects the water adsorption capacity and the thermal properties of the materials at the three pores' size range (micro (< 2 nm), meso (2-50 nm) and macro (>50 nm).

Representative and innovative hydrophilic micro-, meso- and macroporous materials have been purchased or prepared, characterized by several techniques and tested. Water adsorption capacity of the produced materials was examined as a function of relative humidity. Samples were placed in an array of sealed desiccators with saturated salt solutions for controlling humidity. Prior to measurements, samples were dried to constant mass in an air-circulated oven at 200°C. Then, they were periodically weighed while the moisture content was calculated as the difference of mass measurements in different time periods and the initial dry state. The materials showed high rates of water adsorption and the more suitable for surface cooling applications were determined. Additionally, phenomenological models were also applied to describe both kinetics and equilibria experimental data.

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APPLICATION OF ACID-BASE TREATED VERMICULITE FOR REMEDIATION OF WASTEWATERS LADEN WITH HEAVY METALS AND DYESTUFFS

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Dyes are extensively used in many fields of technologies such as the textile industry which is the largest consumer. It is estimated that globally 280 000 tons of textile dyes are discharged in textile industrial effluent every year. Some of these wastewaters contain also heavy metals used throughout the dyeing process [1]. Dyes may show acute toxicity, mutagenic or carcinogenic potential on organisms, and upset aqueous ecosystems by changing water transparency. They were designed to resist to harsh conditions and microbial attack therefore they are difficult to remove by conventional methods [1,2]. Metals are unique as toxicants because they cannot be degraded, they interact with enzymes, disrupt the structure and function of a number of organelles and are carcinogenic for humans and animals [3,4]. Vermiculite is a clay mineral with structure based on phyllosilicate sheets that carry a charge balanced with inter-layer ions that can be exchanged, which results in good sorption capacity [5]. Modifications of clays, such as common acid treatment [6], enhance their properties producing a good and inexpensive sorbent for the removal of pollutants from wastewaters [7]. It was found however, that sorption capacity rises even more when acid activation is followed by washing with citric acid and finished by treatment with NaOH. Optimal conditions for the removal of two cationic dyestuffs (methylene blue, C.I. 52015, and astrazon red, C.I. 110825) and heavy metals (Pb, Cu, Zn) were established by batch experiments. Series of adsorption and desorption cycles in a constant flow column system revealed that the material can be recycled and reused with no significant deterioration in sorption capacity. The material prepared in such a manner showed great colour and metals removal ability due to structural changes and extensive leaching of metals from the sheets and from the interlayer space. The results might open a new path to further modifications of clays and can help to obtain economically and environmentally sustainable sorbents in wastewater treatment.

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EQUILIBRIUM AND KINETIC ADSORPTION STUDY OF A ANIONIC DYE BY ACTIVATED CLAYS

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Textile and tannery effluents are two of the most polluting industrial wastes, and the problems of treatment and disposal of such wastes require much attention. The presence of dyes in aqueous effluent such as in river stream can be noticed easily because dyes are colored and highly visible. Certain amounts of dyes are lost in the manufacturing processes and their effluents have to be treated carefully before discharge.

This research involved the efficient adsorption of anionic dye Derma Blue R67 used in tanning industry on local natural and treated clays; DD3 and KT2, a low-cost material abundant which Algeria possesses estimated at millions of tons, in the East, and that need to be valorized. The kaolins before and after treatment were characterized by chemical analyses (XRF), X-ray diffraction, Scanning Electron Microscopy (SEM) to obtain information about their structure and surface texture. The adsorption kinetics was investigated using the parameters such as contact time, amount of clay, pH, initial dye concentration and effect of temperature. The adsorption amount of Derma Blue R67 dye on local kaolinite clays exceeds 1.8 mg/g observed after 40 to 80 min.

The adsorption of Blue Derma R67 on DD3 kaolin can be explained by the pseudo second- order kinetic model and on KT2 can be expalined by the pseudo second- order and pseudo first order kinetic model.

Keywords: Kaolin, DD3, KT2, acid activation, anionic dye, adsorption kinetics.

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EFFICIENCY OF A NEW FILTRATION PILOT BASED ON CLAY-COMPOSITE MATERIAL

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The presence of organic contaminants in the environment, especially in water, have become a major concern due to the toxicity of many of them. This is a growing problem because the organic compounds include pesticides, crude oil and substances called ‘emerging pollutants’, which comprise a large number of pharmaceuticals.

Most of pharmaceutical compounds found in the aqueous environments come either from domestic sewage or from hospitals, or industrial discharges. They are generally excreted from humans and animals after being partially or completely converted to metabolites with enhanced solubility in water, even if a significant quantity of the parent drug may also be excreted unchanged.

To remediate this pollution problem, various chemical, physical and biological processes have been developed, such as microbial degradation, filtration, adsorption, coagulation and membrane separation. However, all of these remediation methods have suffered from certain limitations and disadvantages such as high cost, poor removal efficiency and possibility of desorption and redistribution.

All of these compounds along with their metabolites, which can be sometimes more harmful than the original compounds, enter the municipal treatment plants (MTPs) in which they often cannot be destroyed or removed. Normally, MTPs are affected by a low efficiency of removal, ranging from 60% to 90% for a variety of polar compounds.

In this work a new filtration pilot system based on clay-composite material is described. This new tool has been validated to remove many organic contaminants (pesticide and pharmaceutical residues) generally present in real MTPs effluents. It has been also tested successfully to reduce the COD load of an industrial wastewater, whose organic content has been concentrated more than 10 times in the filtration material.

The Pilot equipment was designed and realised in the framework of the Project “Diffusion of nanotechnology based devices for water treatment and recycling - NANOWAT (1-B/2.1/049, Grant No.7/1997)”, with the financial assistance of European Union under the ENPl-CBC-MED Programme.

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PT DISPERSED ON SULFATED-ZIRCONIUM PILLARED SAPONITE AS CATALYST IN CITRONELLAL CONVERSION

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Metal modified clay materials have been found to be active and demonstrated their contribution to environmental friendly processes in some organic reactions for some advantages such as recovery, regenerability and reusability. The catalytic activity can be generated by modifying the silica-alumina framework by means of elements having Lewis acidity such as Ti and Zr. On the other side, menthol is an important chemical in cosmetics and toiletries industry. One of the scheme to obtain menthol is hydrogenation of isopulegol while isopulegol itself can be converted from citronellal. In previous work we have demonstrated the high conversion of citronellal to isopulegol with Ti and Zr pillared clays from montmorillonite clay as a raw material. In the present work we extend the applicability of pillared clay materials, as support of bifunctional heterogeneous catalysts, to produce futher intermediates and also menthol in a one pot conversion system so called as a tandem cyclization-hydrogenation. A bifunctional catalyst from Pt immobilized Zr-pillared clay derived from saponite as raw clays were prepared. Furthermore, the relation between the physicochemical characters and the catalytic activity in citronellal conversion was studied. Reaction conversion, catalyst activity, selectivity to a certain product, reusability and kinetic study of the reaction were evaluated based on the term of green conversion principles.

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UTILISATION OF REFINED COAL FLY ASH IN THE MANUFACTURE OF USEFUL MATERIALS

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Disposal of coal fly ash in can be a financial burden, as much is destined for landfill [1]. It is an abundant waste product which can be refined to produce a fine material suitable for use as a substitute for pozzolanic materials in cement, and a coarse material currently of use as an aggregate [2].

The coal fly ash processing company RockTron Ltd separates low density cenospheres, reduces the unburnt carbon content and magnetic component, leaving a product rich in silica and alumina, the finer portion of which satisfied EN450-1 and is apt for use in cement [2]. The coarse refined component of the coal fly ash is being investigated as a feedstock for the production of high purity synthetic zeolites Na-P1, Na-A, X and others.

Zeolite synthesis parameters were optimised with a view to providing profitability calculations for a full-scale plant. Si extraction methods investigated include hydrothermal treatment, pre-treatment fusion with NaOH and microwave-assisted extraction. Crystallisation parameters have been optimised to produce a variety of synthetic zeolites from coal fly ash leachates. Parameters investigated include process duration, temperature, alumina addition, halide salt addition, seeding with zeolites and recycling of leachates.

Synthetic zeolites, refined ash and leached refined ash have been tested for cation exchange capacity using synthetic acid mine drainage and sampled acid mine drainage from British mines.

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IMMOBILIZATION OF HAZARDOUS ELEMENTS IN MATERIALS CONTAINING FLY ASHES

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Major part of electrical and thermal energy is in the Czech Republic comes from combustion of subbituminous coal. Fly ashes produced by conventional as well as fluidized bed combustion of this coal often contain above-limit concentrations of As, Cd, Ni, V,As, Cd, Cr, Hg, Mo, and Se in batch test leachates.

In order to ensure the compliance of the ash-containing building materials with regulatory limits, extensive research of representative CCR from all Czech coal power plants and a choice of domestic heating plants was performed. It involved the study of the ash mineralogy, chemistry, leaching properties and speciation of hazardous elements with methods like ICP-MS, SEM, EMPA, HR-TEM, and XPS.

The binders used in concrete-type materials involved ordinary Portland cement (OPC), calcium-aluminate cement (CAC), special cement made of phosphorus-substituted clinker silicates, and their mixes, with further additives (diatomaceous earth, ashed meat-and-bone meal (MBM), zeolitic tuff, chemical additives).

The results of a series of 50 batch tests with various combinations of cements and additives have shown that cationic metals (Pb, Zn, Ni, Cd) were best immobilized by a mixture of 75% CAC, 20% of calcined diatomaceous earth, and 5% of ashed MBM. The same binder type is also most efficient in fixation of Cr, the leachability of which is less than 0.4 % of Cr leachability with reference CEM I 52.5N. Leachable amount of Zn is 9-10% of leachable Zn from reference OPC. Zinc and Cd are even better immobilized by a mixture of 80% CAC, 10% of ashed MBM, and 10% of clinoptilolite.

The oxoanions-forming elements are generally more difficult to immobilize. Nevertheless, chromium is highly fixed by both above described binder types as well as by special phosphorus-doped clinker [1]. Cr immobilization can be supported by addition of ferrous sulfate as a reducing agent. The long-term stability of their fixation was studied by monolithic test NEN 7345. The tests have shown that the thickness of the leached zone after a 64 days period of contact with leaching medium (distilled water) does not exceed tenths of millimeter. Practically only As has shown increase in leachability after 2 months of leaching.

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THE COSMOS-RICE TECHNOLOGY FOR FLY ASH STABILIZATION

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In this presentation a new stabilization process for municipal solid waste incineration (MSWI) fly ash is shown and discussed. The process originates from a well established technology for treating metallic contaminants MSWI rich fly ashes, based on the use of colloidal silica. The new present proposed technology shows several advantages in respect to the precedent process mainly in terms of cost of stabilizing agents. In addition no chemicals are involved in the the process, but all the reagents are waste materials. In particular, the COSMOS-RICE technology is based on the employ of rice husk ash (RHA), that is a by-product of rice cultivation. As a consequence RHA is much more sustainable than colloidal silica.

It was found that not only silica contained in RHA promotes the metallic contaminants stabilization, but also carbonation plays an important role in the final material stabilization. Carbonation reaction, which implies CO_2 sequestration, is expected to produces a strong impact of the new technology in terms of carbon footprint reduction.

Applying the new stabilization process, a new inert material is obtained. It can be employed as a filler in several applications. The applications that were already tested for this filler will be presented in this work.

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RECYCLING WASTES FROM HOT DIP GALVANIZING STEEL SHEET

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Hot dip galvanizing steel sheet is still the most applied method of corrosion protection with the best quality / price. Thus it is important to analyze the waste resulting from galvanizing process for assessing the environmental impact, consumption of raw materials and established possibilities of recovery. The biggest of zinc losses resulting from the formation in the galvanizing bath of a product called hard zinc or dross [1] and this paper show the possibilities of reduction and recovery of this waste.

The utilisation of additional elements in the zinc bath like lead, aluminium, bismuth, tin for minimise the dross forming has been presented in other paper [2,3]. The complex composition of dross makes it difficult to recycle. Wastes were analyzed for determination of chemical composition (EDX) and structure (macrostructure, microstructure and XRD).

Developing an effective technology for recycling the dross, recovering zinc from it, and returning that zinc in the production cycle would significantly reduce the cost of obtaining galvanized rolled products and environmental impact. Zinc and its compounds can be obtained from dross by pyrometallurgical techniques. But due to high fuel consumption to achieve high temperatures (over 1000 ^{0}C for reduction or distillation processes) [4], the hydro- and electrometallurgical technologies are preferred [5]. In experiments the dross has been dissolved in sulphuric acid solution 25% with intensive stirring. Recovery of zinc from the purified solution was made by two methods: by electrolysis solution and with ion exchange resins. Zinc extraction by electrolysis is recommended for solution with high content of zinc. The average output of the recovery was in this case 92.7 %. Recovery of zinc by ion-exchanging resins is recommended for solution with law content of zinc. This procedure implies zinc retention from solutions on the ion-exchanging resins (IER).

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RECYCLING OF INTEGRATED STEEL PLANT WASTES FOR RECOVERY OF THE VALUABLE ELEMENTS

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The iron and steel integrated plant is one source of large amounts of waste with valuable iron units. These are landfilled while most of iron concentrates used in iron and steel production are derived from relatively low grade ores. Many of the waste generated can be internal recycled as input in own stream of steel plants with sintering facilities [1-4]. Recovery of iron in the iron- or steelmaking process is an attractive option only if the zinc content is below 0.4 % (wt-%) [5]. The internal recycling of these materials is very important for Romania with environmental and economic advantages particularly in lack of own resources of iron ores. This solution reduces the volume of waste that must be stockpiled given that Romanian integrated metallurgical plant already face with the problem of an nonconforming old waste dump that was closed and very soon the exploiting of landfilled materials will be prohibited [6, 7]. The maximum economic benefit of utilizing of the iron rich waste is determined by knowledge of chemical and physical properties for dusts and sludges from blast furnaces and from basic oxygen furnaces, and also for rolling mill scale that come into consideration especially for their iron content.

The aim of this study is to obtain a detailed and comparative characterization of material samples collected from iron and steel company. These has been made in order to identify the recyclability issues or barriers. A complete chemical and physical characterization program was developed. The mineralogy and chemical composition, magnetic fraction, free CaO content, particle size and morphology, density, intergranular porosity, moisture content, water absorption, ignition losses, the conductivity and pH were determined and analysed.

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TRACE ELEMENT MOBILIZATION FROM FLY ASHES. IMPLICATION FOR THEIR REUSE

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Fly ash is a waste resulted during the incineration of municipal solid wastes. This waste usually has a fine grain size and high contents of elements in trace. To avoid its dispersion, disposal methods include irrigation or mixing with brine. Environmental risks associated with fly ash can be derived from air pollution, erosion, dispersion and water contamination due to leaching of potentially toxic elements. In this work we study the geochemistry and mineralogy of fly ash and the hazard derived from trace element leaching and mobility. Two samples of fly ash were studied. The chemical analysis was carried out by X-ray fluorescence (XRF) and the mineralogy by X-ray diffraction XRD). A sequential extraction procedure was carried out to assess the water soluble elements and the labile fraction after dissolution by acetic acid. The pH of the samples was measured after the water extraction step. Extractable elements were analysed by inductively coupled plasma absorption emission spectroscopy (ICP-AES). After each extraction step, an aliquot from the residual sample was separated for controlling the mineralogical dissolution associated. The fly ash is mainly composed of Cl^-, SO_4^{2-}, Ca, K and Na and contains high concentration of As, Cd, Cu, Hg, Pb, Sn, Tl and Zn. The mineralogy is composed of halite and sylvite (about 40 %), anhydrite (25%), calcite (5-10 %) and tertiary Na, Ca, Al oxides, hydroxides and carbonates; other minor components such as quartz and mullite are present. The pH of the fly ash samples is 10 and 12, respectively. After water extractions halite and sylvite are dissolved and it is expected that adsorbed As could be leach due to the high pH of the waste. On the other hand Cd, Pb and Zn can be leached after dissolution of carbonates. Due to the environmental risk associated to this waste other ways of consolidation/cementation could be possible applying microbially induced calcite precipitation using populations of bacteria (Bacillus pasteurii) that cement sand, loam or clay in a growth medium amended with urea and dissolved calcium source. By applying biomineralization methodologies could be reduce the environmental impact of this waste.

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FORMULATIONS AND STUDY OF SULFOBELITIC CLINKER OBTAINED FROM Zn-Pb MINING TAILING

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The aim of this study is recycling mine tailings resulting from processing of lead and zinc. Currently thousands tons of waste containing important levels of Pb, Zn, Cd are occupying large dumbing areas without taking any special precaution from their harmful effects. In a sedimentary context, as case of Tunisia, the main risk of mining activities is the dispersion of tailings particles by prevalent winds and tailing erosion by the means of streams during heavy raining seasons.

This work focuses on the study the environmental mobility of tailing leached metals in two sites; Fej Lahdoum and Lakhouat mines (Northern Tunisia). The mineralogical and geochemistry analyses, particle size, pH, calcimetry, X-Ray, optical microscopy were carried in samples collected vertically from the tailings of Fej Lahdoum and Lakhouat. The X-Ray patterns showed the existence of calcite, dolomite, quartz, gypsum, illite kaolinite and pyrite, also found in chemical analysis and SEM. Also, the accurate examination of this tailings showed high PTE (Potentially Toxic Elements) values; up to 42700 mg/Kg, 15700 mg/Kg, 24300 mg/Kg and 23700 mg/Kg for Zn, Pb, Ba and Sr, respectively.

To neutralize the negative impact of these discharges, sulfobelitic cements were produced using Zn-Pb mining tailings. From the diffractograms it is it is possible to identify the presence of the main crystalline phases: trialuminate sulfate (C4A3Š), belite (C2S), and ferrite (C4AF). The compressive strength of mortars cured for 28 days is 11.9 N/mm^2 for RFH clinker and 11 N/mm^2 for LKH clinker.

Keywords: Tunisia, lead-zinc, mine tailings, dispersion, Potentially Toxic Elements, Sulfobelite clinkers

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SYNTHESIS OF ZEOLITES IN WASTE MATERIAL-KAOLINITE MIXTURES

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Zeolites are hydrated aluminosilicate minerals that can be synthesized using several source materials, such as fly ash and kaolinite. In a previous study, we documented that the use of almost pure kaolinite is mainly conducive to zeolite A and to traces of zeolite X, but if minor amounts of other silicate minerals (e.g., illite and quartz) are associated with kaolinite, the quantity of zeolite X significantly increases. We also synthesised zeolite from fly ash and we ascertained that the presence of Mg and Ca in the contact solution plays a determinant role in the formation of zeolite X [1].

To provide more information about the parameters controlling the hydrothermal synthesis of zeolites after fusion with NaOH, we performed new experiments by fixing the temperature at 45 °C and ageing a coal fly ash, a pure kaolinite, and four derived mixtures in deionised water for 1 to 216 hours.

The results indicate that zeolite-X was the prevailing phase synthesized using pure fly ash, zeolite-A formed in higher amounts from kaolinite, and comparable amounts of A- and X- type zeolites crystallized, thereby adding 20 and 40 % kaolinite to the fly ash, respectively. Zeolite-A as main phase was synthesized already adding 60 % or even up to 80% kaolinite to the fly ash. Geopolymers also formed.

In addition to the Si/Al ratio of the starting materials, the synthesis of zeolites was driven by incubation times and supernatant solution chemistry. The variation in the zeolites concentrations during incubation is explained by their amorphization since there is no chemical evidence of their dissolution. This mechanism, together with ionic exchanges between gels and solutions, may be the cause of variation in the polymerization state of the alumino-silicate network over time.

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THE USE OF BIOMASS PELLET ASH FOR FLY ASH STABILIZATION

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This work proposes for the first time the integrated management of waste materials, coming from industrial process (fly ash from municipal solid waste incineration, coal fly ash, and flue gas desulfurization residue), agriculture (rice husk ash), and domestic activities (ash from stoves). The process originates from a well established technology for treating metallic contaminants MSWI rich fly ashes, based on the use of colloidal silica. As stabilizing agents rice husk ash (RHA), that is a by-product of rice cultivation, and biomass pellet ash are employed.

This paper shows that the opportune mixing of these wastes, without the addition of any commercial chemical, promote some stabilization reactions that allow to obtain a new material that can be reused as a filler in various applications. The reaction mechanism involves carbonation, that happens at room temperature promoting carbon dioxide permanent sequestration.

In view of these results it is possible to conclude that the environmental benefits of the proposed technology are several.

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DESIGN OF EXPERIMENTS FOR THE OPTIMIZATION OF A NEW PROCESS FOR THE STABILIZATION OF AIR POLLUTION CONTROL RESIDUES

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This work is part of the Cosmos-rice project (http://www.cosmos-rice.csmt.eu/), which was funded by the European Union under the Life+ program (LIFE11/ENV/IT000256). The aim of the Cosmos-rice project is to develop and optimize a new process, named Cosmos-rice process, for the stabilization of air pollution control residues coming from Municipal Solid Waste Incineration (MSWI) using rice husk ash as stabilizing agent [1].

The objective of this work is to present and discuss the optimization of the Cosmos-rice process parameters by means of the statistical Design of Experiments (DoE) methodology.

The DoE refers to the process of planning the experiments so that appropriate data that can be analysed by statistical methods can be collected, resulting in valid and objective conclusions (Montgomery, 2001). In particular, DoE is a statistical technique developed to test simultaneously the effects of several variables (called input factors) on a certain response (characterized by output factors) using only a limited number of experiments [2].

In the first part of this work, the selection of the appropriate input and output factors for the case of the Cosmos-rice process is discussed. In particular, the input factors include the percentage of rice husk ash, the mixing temperature, the environmental conditions (air temperature and humidity) and the mixing time, while the output factors include the concentrations of S, Cl, K, Ca, Br, Ga, Sr, Ba, Pb and Zn in the leachate and the pH of leachate.

In the second part, the plan of experiments set up for the optimization of the Cosmos-rice process is presented. In particular, after showing the levels adopted for each of the input parameters, the resulting plan of 64 experiments is shown.

Finally, the results obtained from the experiments, carried out by the Chem4Tech laboratory of the University of Brescia (Italy), are analysed by means of the Multivariate Analysis of Variance (MANOVA). The MANOVA represents the extension of univariate analysis of variance to the case of multiple dependent variables and allows for a direct test of the null hypothesis with respect to all the dependent variables in an experiment. Thanks to the statistical analysis, the relationship between input and output parameters is identified, along with the best combination of the input factors levels.

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INNOVATIONS IN INDUSTRIAL SOLID WASTE MANAGEMENT TOWARDS A MORE CIRCULAR ECONOMY

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Turning waste into a resource is one key to a circular economy. The objectives and targets set in legislation of many countries over the last years have been key drivers to improve waste management, stimulate innovation in recycling, limit the use of landfilling, and create incentives to change consumer behaviour. If wastes are re-manufactured, reused and recycled, and if one industry's waste becomes another's raw material, then all world regions can move to a more circular economy where waste is eliminated and resources are used in a more efficient and sustainable way. Furthermore, it has to be underlined that achieving the new waste targets would create thousand new jobs, while making world economy more competitive and reducing demand for costly scarce resources.

Improved waste management also contributes to elimination of health and environmental problems, reduction of greenhouse gas emissions (directly by eliminating emissions from landfills and indirectly by recycling materials which would otherwise be extracted and processed), and minimization of negative impacts including landscape deterioration due to landfilling and industrial hazardous waste disposal, surface, groundwater and air pollution.

The present paper aims to highlight and discuss innovative industrial solid waste management practices towards a world circular economy. Innovative research efforts involving selected solid wastes streams, such as slag, fly ash, red mud, construction and demolition waste and solid agricultural waste that are produced in huge quantities and if improperly disposed of may cause severe environmental impacts, are highlighted. Furthermore, the first calls in the frame of H2020 work programme are briefly mentioned to underline priorities set by the European Commission towards a near-zero waste society.

Finally, emphasis is also given to the estimation of the environmental footprint of industrial solid waste management technologies in order to assess their environmental benefits.

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ENHANCED CATALYTIC PERFORMANCE OF IRIDIUM CATALYSTS FOR THE SCR REACTION OF NO USING MIXTURES OF C_3H_6 AND H_2

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Catalysts for the SCR reaction of NO using hydrocarbons in the presence of O_2 include mainly non-noble metal oxides, molecular sieves and noble metals. Among these catalytic systems, noble metal catalysts have drawn interest of numerous research groups, due to their catalytic efficiency at low temperature ranges and their strong resistance to poisoning by SO_2 and H_2O. Recently, more and more research work has focused on the performance of iridium catalysts, as they display high catalytic activity and N_2 selectivity. In the present work, the H_2-assisted SCR of NO by C_3H_6 reaction was investigated over iridium (Ir) catalysts supported on pure or modified alumina.

The modified alumina samples were prepared using the co-precipitation technique [80% Al_2O_3-20 wt% CeO_2 (AlCe), 80% Al_2O_3-20 wt% La_2O_3 (AlLa) and 80% wt Al_2O_3-20 wt% $Ce_{0.8}La_{0.2}O_{1.9}$ (AlCeLa)], while incorporation of iridium (0.5 wt%) was realized using the incipient wetness impregnation method leading to a series of catalysts labeled as Ir/AlCe, Ir/AlLa, Ir/AlCeLa, respectively. The catalysts were characterized by means of the H_2-TPR, XRD and N_2 physisorption techniques. Their catalytic performance for the SCR of NO with propylene or mixtures of H_2 and propylene was evaluated in a fixed bed reactor, at temperatures ranging from 150 to 400°C. The total flow rate used was 500 ml min^{-1}, consisting of a mixture of NO (1000 ppm), C_3H_6 (1000 ppm), O_2 (2% v/v), H_2 (0 or 0.5% v/v) diluted with Ar, corresponding to a GHSV of 40.000 h^{-1}. The outlet of the reactor was analyzed by a gas Fourier Transformed IR (FTIR) Gasmet Analyzer and Buhler (NO_x, SO_2, O_2) analysers.

The co-presence of H_2 (0.5 wt% v/v) in the feed led to a significant enhancement of the selective catalytic reduction (SCR) of NO of the iridium catalysts, in comparison with the case of using only C_3H_6 as a reducing agent. Specifically, NO conversion (X_{NO}) was increased about twice for all of the catalysts (46-65%), while selectivity to N_2 (S_{N2}) was also increased reaching 95%, for reaction temperature ranging between 280-320 °C, with a simultaneous broadening of the active window.

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NITROUS OXIDE DECOMPOSITION OVER CUO-CEO$_2$ MIXED OXIDES: EFFECT OF PREPARATION PROCEDURE

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Nitrous oxide (N_2O) is one of the worse greenhouse gases, due to its high global potential (~300 times higher as compared to CO_2). It has a very long lifetime (about 150 years), having a prolonged effect in the depletion of the stratospheric ozone layer [1]. In this regard, considerable efforts have been devoted on the N_2O emissions control from anthropogenic sources, with the catalytic decomposition to be considered as one of the most efficient and cost-effective technologies[1].

In spite of the excellent catalytic performance of noble metals (NMs)-based catalysts, their high cost and sensitivity to oxygen poisoning limits the widespread industrial application. Therefore, the development of NMs-free catalysts of low cost and adequate de-N_2O performance is of paramount importance. Recently, it has been reported that mixed oxides could be possible candidates for N_2O degradation, with CeO_2 to be a key component due to its unique redox properties. Furthermore, Cu-based catalysts have received considerable attention in heterogeneous catalysis due to their adequate performance and low cost. Thus, it has been shown that CuO-CeO_2 mixed oxides confer a synergistic interaction effect toward enhanced reducibility and catalytic performance[2].

In the present work, the effect of preparation procedure on the N_2O decomposition is investigated by employing three different catalysts types, i.e., i) bare CeO_2, ii) Cu supported on CeO_2 and iii) Cu-Ce mixed oxides. In all cases, impregnation, precipitation and exotemplating methods were employed, whereas commercial samples were also used for comparison. All materials were characterized by BET, XRD, H_2-TPR, SEM and XPS. The results obtained clearly showed that single oxides demonstrated low N_2O conversion, never exceeding 40% at 600°C. The optimum performance is observed by Cu-Ce mixed oxides prepared by co-precipitation, which achieves full N_2O conversion at 550^{o}C. The superiority of Cu-Ce mixed oxides prepared by precipitation compared to all other composites is ascribed to its excellent redox properties linked to Ce^{4+}/Ce^{3+} and Cu^{2+}/Cu^{+} redox couples.

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EFFECT OF SO_2 ON N_2O DECOMPOSITION OVER IRIDIUM CATALYSTS SUPPORTED ON CERIA MODIFIED ALUMINA

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Nitrous oxide (N_2O) has recently attracted great attention, due to its deleterious environmental impact. It is a powerful greenhouse gas with a global warming potential (GWP) about 300 times higher than that of CO_2, while at the same time it notably contributes to stratospheric ozone depletion. Therefore, the abatement of N_2O emissions from combustion and chemical processes is of significant importance. Among the different remediation methods, the catalytic decomposition of N_2O to N_2, represent the most promising approach. Up to date several catalytic systems have been evaluated for N_2O decomposition. Among them, noble metal-based catalysts exhibit satisfactory activity at low temperatures. Additionally, the use of structural and/or surface modifiers seems to enhance further their intrinsic reactivity [1-2].

However, the coexistence of other gases, inevitably present in the flue gas stream, such as SO_2, significantly suppresses the catalytic performance thus limiting the catalyst's applicability [2]. In this regard, the present study aims to investigate the effect of SO_2 on the de-N_2O performance of Ir catalysts supported either on Al_2O_3 (Ir/Al sample) or Ce-promoted Al_2O_3 (Ir/AlCe sample). The catalysts were characterized *via* N_2 physisorption (BET method), H_2-TPR, XRD and TEM techniques and tested for N_2O decomposition in the absence and presence of O_2 and/or SO_2 in a bench-scale, fixed bed reactor. Selected catalytic samples were also characterized after reaction to explore the impact of reactions conditions on catalyst's characteristics.

N_2O conversion values as high as 99% and 97% are obtained over Ir/AlCe sample, during the N_2O decomposition in the absence or in the presence of O_2, respectively, compared to 98% and 66% over Ir/Al sample. In the presence of SO_2 under oxygen deficient conditions (N_2O+SO_2 reaction) the N_2O conversion is decreased to 82% over Ir/Al catalyst, whereas the de-N_2O performance of Ir/AlCe sample remained almost unaffected (~94%). On the contrary, in the presence of oxygen (N_2O+O_2+SO_2), Ir/Al catalyst retains most of its de-N_2O efficiency (61%), in contrast to the Ir/AlCe, which presents a more significant decrease (39%). The latter could be ascribed to the presence of cerium oxide, which favours SO_x uptake [3]. Most interestingly, N_2O conversion increases from 66% over the fresh Ir/Al sample to 78% over the sulfated, during the N_2O+O_2 reaction. The obtained results are interpreted on the basis of characterization studies, which revealed significant modifications on the surface and redox properties of Ir-based catalysts upon the sulfitation pretreatment.

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BTX SORPTION ON NA-P1 ORGANO-ZEOLITES AS A PROCESS CONTROLLED BY THE TYPE OF SURFACTANT

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The main objective of the study was to prepare synthetic Na-P1 zeolite by hydrothermal reaction of fly ash with sodium hydroxide [1]. The obtained Na-P1 zeolite has been modified with a surfactants:

- DDTMA (dodecyltrimethylammonium bromide),
- DDDDMA (didodecyldimethylammonium bromide),
- TDTMA (tetradecyltrimethylammonium bromide),
- DTDDMA (ditetradecyldimethylammonium bromide),
- HDTMA (hexadecyltrimethylammonium bromide),
- DHDDMA (diheksadecyldimethylammonium bromide),
- ODTMA (octadecyltrimethylammonium bromide)
- and DODDMA (dioctadecyldimethylammonium bromide)

in amount of 1.0 of external cation exchange capacity (ECEC) of the Na-P1 zeolite. The process reported hereunder was designed at 60°C and a high solid/solution ratio (1:40). The determination of CHN was used for verification of the quantity of the adsorbed surfactant on the crystallites' surface. The sorption properties of eight organo-zeolites derived from benzene, toluene, p-xylene (BTX) were evaluated.

Zeolite Na-P1 and organo-zeolites after modification show a significant ability to remove BTX contamination from the aqueous solution. The results showed that the modification of the Na-P1 zeolite by surfactants with double carbon chains (DDDDMA, DTDDMA,DHDDMA and DODDMA) improves the sorption properties in terms of benzene and toluene. Based on experimental data the removal efficiencies for a single-solute system follows the order: p-xylene > toluene > benzene. Xylene was adsorbed in the greatest quantity, however, sorption efficiency from aqueous solutions does not depend upon the type of the surfactant used. The length of the carbon chain in the surfactant does not significantly affect the sorption efficiency. Sorption efficiency depends on the chemical properties of the various organic compounds, their concentrations and the time of the sorption process.

The results of this research can be used in environmental protection and for further study into the properties of surfactant modified synthetic zeolites and their potential industrial applications.

We gratefully acknowledge the support of NCBiR having provided Grant No. PBS1/A2/7/2012.

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BIOMINERALIZATION TO REDUCE SEEPAGE IN TUNNELS

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Low cost, sustainable, and environmentally friendly microbially-induced crystallyzation of calcium, magnesium, and iron compounds can be used in geotechnical engineering for [1,2]:

- bioaggregation of soil particles that is diminishing wind and water erosion of soil;
- bioclogging of soil and sedimentation rocks that is sealing water seepage in tunnels, levies, ponds, and channels;
- biocementation of construction ground and materials to increase their strength.

Construction-related biomineralization is performed by different physiological groups of microorganisms: urease-producing, halophilic, alkaliphilic, denitrifying, iron- and sulphate-reducing bacteria, cyanobacteria, microscopic fungi and algae [3].

Most popular microbially-induced calcium carbonate precipitation (MICP) is formation of calcium carbonate minerals (calcite, vaterite, or aragonite) due to: 1) adhesion of cells of urease-producing bacteria on the surface of particle; 2) creating a microgradient of concentration of carbonate and pH in the site of cell attachment due to hydrolysis of urea by urease of UPB; and 3) with formation of the calcite, vaterite, or aragonite crystals. The biogeochemical reaction of this process catalized by urease-producing bacteria is as follows:

$(NH_2)_2CO + 2\ H_2O + CaCl_2 \rightarrow CaCO_3\downarrow + 2\ NH_4Cl$ (1).

The shares of calcite, vaterite, or aragonite crystals in biocemented material are controlled by the rate of enzymatic reaction and concentration of magnesium. The biocementation of sand with the formation of mainly aragonite crystals at the content of precipitated Ca and Mg 6% (w/w) gave highest unconfined compressive strength of 12.4 MPa.

Very important for construction industry can be calcium-phosphate biocementation mediated by phytase, phosphatase, or urease activity of microorganisms producing monetite ($CaHPO_4$), whitlockite [$Ca_9(Mg,Fe^{2+})(PO_4)6HPO_4$], or hydroxyapatite [$Ca_5(PO_4)_3OH$]. However, the biotechnologies for practical applications are not developed yet and could be too expensive for large-scale construction applications.

Iron-based biocementation could be suitable for numerous geotechnical applications if to combine acidogenic fermentation of cellulose-containing agricultural or food-processing residuals with bioreduction of iron ore, hydrolysis and precipitation of produced soluble Fe^{2+} using urease-producing bacteria:

$Fe^{2+} + 1.5\ (NH_2)_2CO + 0.25\ O_2 + 5.5\ H_2O + UPB \rightarrow Fe(OH)_3\downarrow + 1.5\ (NH_4)_2CO_3 + 2H^+$(5).

Ferric hydroxide is stable biomaterial to reduce seepage in tunnels.

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NOVEL CO_2 SORBENT SYNTHESIZED BY IMPREGNATION OF CAO ON NANOSILICA

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The Ca-looping process consists of the carbonation reaction of CaO at high temperature followed by the calcination of natural limestone ($CaCO_3$) to regenerate the sorbent. Capture efficiencies of 90% have been attained in carbon fired pilot-scale plants of up to 1.7 MWht. In the practical application, CaO particles react in a fluidized bed reactor with CO_2 at low concentration (around 15 vol%) with flue gases for short residence times and temperatures around 650ºC. The partially carbonated particles circulate to a second reactor in which they are regenerated by calcination at about 900ºC producing pure CO_2, ready for storage. A major focus of studies oriented towards further improving the efficiency of the technology is how to prevent the gradual loss of CO_2 capture capacity of limestone derived CaO as the number of carbonation/calcination cycles is increased. Moreover, calcined limestone is a fragile material, producing intense attrition and sorbent losses by elutration.

In our work, Calcium nitrate tetrahydrate and nanosilica have been used as raw materials. Samples of dried nanosilica were impregnated with a saturated aqueous solution of calcium nitrate tetrahydrate, heated for dehydration and decomposition of calcium nitrate and calcined at 900ºC. Samples were subjected to further reimpregnations obtaining different proportions of CaO (10%, 23%, 30 % and 40%) in a layer uniformly covering the nanostructured calcium silicate matrix. CO_2 capture capacity has been subjected to carbonation/calcinations cycles in a thermogravimetric analyzer. Multicylic TGA results show that the CaO conversion of impregnated samples reach stable values ranging from 15% (40% wt CaO) to 60% (10% wt CaO), compared with only 7-8% for natural limestone. The results suggest that a nanostructured Ca_2SiO_4 matrix formed during preparation prevents sintering of the impregnated CaO layer. To test the mechanical resistance of the samples, they have been ultrasonicated and the resulting size distribution measured by means of laser diffractometry. The results show that synthetic sorbents are more resistant to attrition than natural limestone.

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DOLOMITE AND LIMESTONE: NATURALLY OCURRING SORBENT PRECURSORS FOR CO_2 CAPTURE

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The low cost and wide availability of natural limestone ($CaCO_3$) is at the basis of the industrial competitiveness of the Ca-looping (CaL) technology for postcombustion CO_2 capture from fossil fired plants. In this process, CO_2 is chemisorbed on the surface of CaO particles fluidized in a gas-solid reactor (carbonator) by the postcombustion gas stream at atmospheric pressure and temperatures about 650ºC. The solids partially carbonated after typically short residence times (of a few minutes) are circulated into a second gas-solid reactor (calciner) where CaO is regenerated by calcination at atmospheric pressure and a gas stream of highly concentrated CO_2 is retrieved for compression and storage. A major focus of studies oriented towards further improving the efficiency of the CaL technology is how to prevent the gradual loss of capture capacity of limestone derived CaO as the number of carbonation/calcination cycles is increased. Natural dolomite ($MgCa(CO_3)_2$) has been proposed as an alternative sorbent precursor to limestone. Yet, carbonation of MgO is not thermodynamically favorable at CaL conditions, which may hinder the capture performance of dolomite. In the work described in this paper we carried out a thermogravimetric analysis on the multicyclic capture performance of natural dolomite under realistic regeneration conditions necessarily implying high calcination temperature (around 950ºC), high CO_2 concentration and fast transitions between the carbonation and calcination stages. Our study demonstrates that the sorbent derived from dolomite has a greater capture capacity as compared to limestone. SEM analysis shows that MgO grains in the decomposed dolomite are resistant to sintering under severe calcination conditions and segregate from CaO acting as a thermally stable support which mitigates the multicyclic loss of CaO conversion. Moreover, full decomposition of dolomite is achieved at significantly lower calcination temperatures as compared to limestone, which would help improving further the industrial competitiveness of the technology.

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REMOVAL OF VANADIUM(VI) FROM AQUEOUS SOLUTION BY HDTMA-MODIFIED CLINOPTILOLITE

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The objective of this research work was to investigate the possibility of using an organically modified natural clinoptilolite from Ukraine as a sorbent for the removal of vanadium(V) from aqueous solutions. Clinoptilolite has been modified using hexadecyltrimethyl ammonium bromide (HDTMA-Br) in an amount of single external cationic exchange capacity (1.0 ECEC). This alteration makes it possible to use organo-zeolite as a sorbent to remove anionic forms of metals [1,2]. Batch experiments were carried out to define the impact of HDTMA surfactant, its amount and organo-zeolites' properties order on the sorption capacity, the sorption mechanism, sorption kinetics, the pH effect and the immobilization durability. The effect of HDTMA surfactants loading (1.0 of ECEC of the zeolite) on the adsorption of vanadium(V) was measured at initial concentrations of the V(V) in the range 0.05 - 20.00 mmol/L. Langmuir and Freundlich isotherms have been studied.

Surface modification of the clinoptilolite using HDTMA-Br led to the formation of a material with improved sorption properties in terms of its removal of vanadium(V) from aqueous solutions. The maximum adsorption capacity was observed in the pH range 4.0−6.0. The mechanism of adsorption suggests that the surface adsorption was the main process and that the adsorption mechanism was predominantly an ion exchange.

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SYNTHESIS AND SPECTROSCOPIC CHARACTERIZATION OF Pt(II), Pd (II), Ni(II), Co(III) AND Cu(II) COMPLEXES OF N-ALLYL-N'-(4'-METHYLTHIAZOL)-2YLTHIOUREA

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Metal complexes of Co^{III}, Ni^{II}, Cu_{II}, Pd^{II} and Pt^{II} with N-allyl-N'-(4'-methylthiazol)-2ylthiourea (HL) were prepared and characterized by elemental analyses, magnetic susceptibilities, and by i.r., n.m.r., electronic and mass spectral measurements. The i.r. spectra indicate that HL acts as bidentate ligand coordinating via the endocyclic imine-nitrogen and thione- or thiol-sulfur atoms. The ^{1}H- and ^{13}C-n.m.r. chemical shifts reveal coordination of endocyclic-imine-N and thiourea-S atoms to the metals. The magnetic moments and electronic spectral data suggest an octahedral geometry for $CoL_3.H_2O$, $[Cu(HL)Cl_2]0.5H_2O$ and $[Cu(HL)Cl_2]$ a square-planar for ML_2 (M = Ni_{II}, Pd_{II} and Pt_{II}), $[PdL(OAc)(H_2O)]$ and $[Pd(HL)Cl_2]$. The EI mass spectra of Pd_{II} and Pt_{II} complexes showed some isotope peaks Pd_{II} and Pt_{II} of $[M]^+$ and fragments containing metals; assignments of fragments containing metal ions were supported by the appearance of their peaks among isotope clusters.

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CRYSTAL STRUCTURES AND HIGH-TEMPERATURE PHASE TRANSITIONS OF THE NEW ORDERED DOUBLE PEROVSKITES $SrCaCoTeO_6$ AND $SrCaNiTeO_6$

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In the present work we report X-ray powder di_raction measurements of $SrCaCoTeO_6$ and $SrCaNiTeO_6$, at di_erent temperatures. The crystal structures at room tem- perature of both compounds are determined; and results showing the existence of high-temperature phase transitions in them are presented. Both compounds have double perovskite structure with 1:1 ordered arrangement of the B site cations. At room temperature their symmetries are described with the $P2_1/n$ space group, that correspond to the $(a^+b^-b^-)$ tilt system. The evolution with temperature of the structure of both compounds shows the presence of three phase transitions: a continuous one, at 450 and 500 K, a discontinuous one, at 700 and 775 K, and a continuous one at 900 and 950 K for SrCaCoTeO6 and SrCaNiTeO6, respectively with the following phase-transition sequence: $P2_1/n \rightarrow I2/m \rightarrow I4/m \rightarrow Fm\bar{3}\bar{3}m$.

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MITIGATION OF GREENHOUSE GAS EMISSION BY ENHANCEMENT OF MINERAL CARBONATION OF ULTRAMAFIC MINE TAILINGS

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The increasing concentration of greenhouse gases in the atmosphere has led to the development of several mitigation strategies to reduce anthropogenic impact on climate. Mineral carbonation is a process where CO_2 reacts with a divalent cation to form a carbonate mineral that is stable over geological periods. This process offers an opportunity for permanent storage of atmospheric CO_2 emitted from small and diffuse sources. Due to their high content in Ca and Mg, mafic and ultramafic rocks are the most reactive rocks for CO_2 capture and storage. Magnesium silicates, such as olivine and pyroxene, contain a high weight percent MgO (35-40 wt %). Some of these ultramafic rock sequences have been hydrated and the olivine or pyroxene has been replaced by various serpentine minerals ($Mg_3Si_2O_5(OH)_4$) that can react with CO_2. The magnesium carbonate formed in this reaction is stable at Earth surface conditions. Moreover, mineral carbonation occurs naturally in some ultramafic mining waste forming cemented crusts at surface. Finely ground ultramafic mine tailings are a promising material for mineral carbonation.

The purpose of this research is to kinetically enhance the mineral carbonation of different ultramafic mine tailings. Real time monitoring of CO_2 uptake at atmospheric conditions was performed using the Laval eudiometers, a device containing a known volume of gas and able of measuring changes in real time. Tests were conducted by varying the concentration of CO_2 in the gas phase, the tailing water content, the material porosity and the addition of different organic salts such as sodium EDTA, sodium oxalate and sodium citrate to determine the optimal carbonation conditions. Experimental conditions were optimized in order to reach a compromise between solubility of magnesium ions and carbonate precipitation. Carbonate minerals precipitated were investigated by X-ray diffraction, scanning electron microscopy and electron probe microanalysis.

Results indicate that CO_2 reacts with the total mass of the sample and not only with the layer in contact with the gas phase. The water content for optimal carbonation reaction ranged from 20% and 60% according to the type of tailing investigated. Interstitial water is necessary as solvent for dissolution of Mg ions, but saturated pores reduce diffusion of CO_2. A linear relationship was obtained between the CO_2 concentration in the gas mixture and the CO_2 absorption rate of the mine tailings. By replacing the water by chelate solutions, CO_2 uptake was increased by 24% with a saturated sodium EDTA solution (0.2M) of pH 8.35. However, the best CO_2 uptake conditions vary from mine tailings to another. According to the O/Mg ratio, the carbonate minerals formed are probably hydromagnesite or dypingite. These data show that it is possible to significantly enhance the natural mineral carbonation reaction of various ultramafic mine tailings by adequate porosity, water content, increased CO_2 concentration in air, and by adding chelating agents.

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TITANOSILICATES WITH A FRAMEWORK STRUCTURE, SYNTHESIS AND SORPTION PROPERTIES

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Nowadays much attention has been paid to the synthesis of novel zeotype materials such as ETS- 4 and ETS-10, which possess improved catalytic and sorption properties in comparison with the classical zeolites. A number of attempts have been known to optimize the synthesis of ETS materials, which consisted in studying the effect of molar ratio, reagents, pH, synthesis time, and temperature as well as purity and costs. There is also a certain interest to finding a new titanium sources to replace the relatively expensive $TiCl_3$ currently in use. The reagents such as $TiCl_4$, TiO_2, $TiOSO_4$, $Ti(SO_4)_2$ and Na_2TiF_6 were tested to produce the titanosilicates. In this paper the ammonium oxotitanium sulphate $(NH_4)_2TiO(SO_4)_2 \cdot H_2O$ was chosen as a new titanium source. The synthesis of porous alkaline titanosilicates with a framework structure was studied in details. It was shown that pure phases of ETS type titanosilicates (ETS-4, ETS-10) were obtained by hydrothermal synthesis from gels of molar composition TiO_2: 3.8-5.5SiO_2: 4.4-4.8Na_2O :0.2-0.3KF: 200-250H_2O in absence of seeds and organic template agents. Using of the new titanium precursor allows to reduce both the consumption of alkali component for synthesis and crystallization time. This phenomenon is due to the effect of NH_4^+ ion as a structure-breaking agent. Ammonium ion compensates an outer-sphere negative charge, which is caused by sulphate groups bonded to titanium (IV) through oxygen atoms. As a result the bonds became weaker, providing an increase in the rate of sulfate groups substitution for structure-forming agents. IR, XRD, BET, SEM and NMR techniques were used to characterize the final materials. It has been established that NH_4^+ ion as an extraframework cation increases the porosity and sorption properties of titanosilicates. It has been demonstrated that final materials have a good affinity for mono- and polyvalent cations. High ion-exchange capacity and chemical stability of synthesized titanosilicates provide for their effective use for liquid wastes treatment containing radioactive and hazardous metals.

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MINERALOGY OF PLACER IRON DEPOSITS IN SANGAN AND SIRJAN (IRAN)

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INNOVATIVE METHODOLOGIES IN NANOTECHNOLOGY FOR THE PREVENTION OF BACTERIAL DISEASES

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In the last decades, research has been devoted to the development of new products for enhancing the quality of human life. The antimicrobial agents, generally used to avoid the production of unpleasant odor or the increase of potential health risks, are one of these products. Therefore, various antibacterial finishing and disinfection techniques are being developed to be applied from hospital environment (medical clothes, protective garments, etc.) to everyday household and clothing. Almost every class of chemical products, ranged from the very simple substances such as halogen ions to very complex compounds, has been tested to confer the antibacterial activity to one material. But the use of many of these antimicrobial agents without a tight control over their bioactivity has been stopped because of their possible undesired harmful or toxic effects.

Recently, the market for natural products from plant extracts, dry extracts and essential oils [1,2], and their use as "Green Advanced Materials", is undergoing a rapid expansion following the now recognized antimicrobial action spectra extremely large of these substances. The properties of the natural products resulting from the presence of bioactive molecules capable of performing various pharmacological activities, antimicrobial, antioxidant and flavoring.

This work presents the study on the development of new materials for sanitizing processes of environments and work ambient. Investigation on antimicrobial activity of essential oils and on the synergies created by their combined use with zinc oxide or other nano- or micro- phases having known antibacterial properties will be presented and discussed. Finally, a short description will be provided on the preparation and deposition methods, this last based on Spray technique [3], which are being used in the authors' labs for the development of new class of devices starting from powders composed of nano- and micro- particles of the material of interest [4].

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REDUCTION OF CO_2 EMISSION FROM CARBONATE CERAMIC MATERIALS BY THE ADDITION OF AL-SHALE

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The fabrication of ceramics can produce emission of several gases, the denominated exhaust gases and the vapors produced during firing processes, which usually contain metals and toxic substances that can affect to environment and also the workers themselves. Especially harmful are the emissions of CO_2, fluorine, chlorine and sulfur from ceramic industry, mainly in areas with high number of industries, due to the accumulative effect of emissions.

Presently there are some studies on the emissions of the gases produced from the raw material processing, which account for the main factors that influence such emissions and define threshold values. Concerning CO_2, one of the gases with a higher contribution to the ‘‘green-house effect’’, the factories that use carbonate-rich raw materials (> 30% carbonates) can emit high concentrations of CO_2 into the atmosphere [1,2]. Therefore a carbonate reduction, or substitution for other appropriate component, of the ceramic raw material would reduce the CO_2 emissions. Recently Del Aguila D. [3] has proposed a CO_2 emission reduction adding wollastonite to the fabrication process, but this theoretically possible solution presents the problem of the market price of the mineral.

In this contribution we propose to add aluminous shale to the carbonate ceramic materials for CO_2 emission reduction and improve the quality as building materials This shale is an inexpensive materials of large reserves in SW Spain. Nevertheless, attention must be paid for the material selection, because shale can contain a high proportion of micas, and, in some cases, undesirable minor alunite that could produce fluorine and sulfur emissions.

We present here the study of ceramic bodies prepared with the addition to marls of variable proportions of selected Al-shale samples, poor in the problematic mineral phases above mentioned. The results indicated that the CO_2 emission of new ceramic materials decreased around 30%, and the properties of products obtained were improved. This research underlines the adequacy of the use of a low-price raw material to reduce CO_2 emission, which can contribute also to obtaining products with higher added value.

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SYNTHESIS AND CRYSTAL STRUCTURE ANALYSIS OF THE LACUNAR APATITE NAPB2CA2(PO4)3

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The apatite structure present o lot of characteristics, One of the main characteristics is to allow large and various substitutions for both cations and anions. Beside their biological importance in hard tissue (bone and teeth), apatites have been extensively studied for their potential use as fluorescent lamp phosphors or laser host materials. The apatite have interesting possible application fields such as in medicine as materials of bone filling, coating of dental implants, agrochemicals as artificial fertilizers.

Polycristaline sample of the lacunar apatite NaPb2Ca2(PO4)3 was obtained by the solid state reaction. The structure of NaPb2Ca2(PO4)3, isostructural with Fluoroapatite was determined by the use of X-ray powder diffraction method. The Rietveld refinement results revealed that it crystallizes in the hexagonal system with the space group P63/m (a = 9.6075(2) Å, c = 7.0167(1) Å). The existence of the lacunar structure is stabilized and conditioned by the presence of the lone pair cations Pb2+. An XRD analysis at non-ambient conditions has shown that no temperature induced phase transition is observed in NaPb2Ca2(PO4)3 in the studied temperature-range (300-850K).

Keywords: apatite; Lacunar; crystal structure; Rietveld method ; NaPb2Ca2(PO4)3,Phase transition.

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“MICRO X-RAY LAB”: A NEW APPROACH FOR HEAVY METAL SPECIATION IN POLLUTED SOILS AND ENVIRONMENTAL MATERIALS

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Heavy metals (HM) in soils can be toxic for cultivated plants and living organisms and can pose a serious risk for human health, especially if they can reach underground waters or enter the food chain. Determining HM total concentration in soil is only the starting point of a risk assessment, but nowadays information about HM speciation is crucial to understand the real impact of HM pollutants on the environment. In addition, soil is an extremely heterogeneous matrix where different organic and inorganic components are mixed down to the micrometer or nanometer scale. Therefore analytical instruments capable of resolving such a complexity at the nanometer/micrometer scale are also needed. To this purpose, a proper combination of X-ray analyses can provide both information about HM total concentration and speciation also at the nanometer/micrometer level.

At the University of Bari a new laboratory called “Micro X-ray Lab” has been created. In this lab, the potentialities of different X-ray based analytical techniques are combined to solve problems related to soil HM pollution and remediation. To this purpose the following instrumentation is available: a portable X-ray fluorescence spectrometer (pXRF) (for quick semiquantitative in situ analyses), a wavelength dispersive X-ray fluorescence spectrometer (WD-XRF) (for more precise determinations of HM in solid and liquid samples), a total reflection X-ray fluorescence spectrometer (TXRF) (for the determination of HM at ppb levels), a micro X-ray fluorescence spectrometer (**μ-XRF**) and a Variable Pressure Field Emission Scanning Electron Microscope (for the identification of HM pollutants at the micro/nanoscale). In addition, HM-containing mineral phases of soil samples are investigated by X-ray powder diffraction (XRPD) and thermogravimetrical and differential thermal analyses (TGA/DTA). Finally, X-ray microtomography (μ-CT) is used to characterize the soil structure, its porosity as well as the internal structure of microscopic soil minerals.

The same methodological approach can be applied to the study of HM in other environmental materials such as plant and biological matrices and to assess the efficacy of technologies developed for the remediation of HM polluted soils.

In this work, preliminary results on HM speciation and biaccessibility studies in polluted soils are presented and discussed with a focus on As-polluted soils. The aim of these studies are to identify the source and the fate of pollution as well as to develop suitable physical-chemical procedures to remediate the contaminated sites.

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RARE EARTHS RECOVERY BY SOLID-LIQUID EXTRACTION WITH NATURAL AND MODIFIED CLAYS

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Nowadays there is an increasing need for Rare Earths (REs) due to their usage in numerous high-technology applications, so their recycling from Waste Electrical and Electronic Equipment (WEEE) can only be considered a valuable opportunity: this perspective is known as "urban mining" [1]. Among others, the use of solid-liquid extraction is obtaining more and more attention because of many advantages such as high recovery, short extraction time, high enrichment factor, low cost and no consumption of organic solvents [2]. The critical step in such a recovery process is the metal ions removal from the aqueous solutions. Recently, clays have been proposed as solid-phase being characterized by low cost, good mechanical properties, good acid tolerance, convenient solid-liquid separation and excellent reusability. Furthermore, clays show a natural adsorption behaviour towards REs [3]. On these bases, the aim of the present work is the study of REs recovery from WEEE via solid- liquid extraction. For this purpose different solid sorbents were considered, namely two natural smectite mineral clays (STx-1 and SWy-2) and four modified organo-clays. Their effectiveness towards adsorption and release of lanthanum ions (selected as representing element of the REs family) model solutions was tested. Modified clays were synthesized by intercalating two different polymers having chelating properties, N-(methoxy-polyethylene glycol) ethylene diamine and N-(methoxy-polyethylene glycol) ethylene diamine trimethylene phosphonic acid. All the solid materials were characterized by FT-IR, thermo gravimetric analyses (TGA), X-ray diffraction (XRD) and XPS analyses, while the amounts of the intercalated polymer were estimated by COD (Chemical Oxygen Demand) analysis. Also the intercalation mechanism was investigated, varying the operating parameters, such as polymer concentration and pH in order to select the optimal intercalation conditions.

The best organo-clay system was produced using 90 mM of initial polymer concentration and an intercalation pH of about 11, corresponding to a not-protonated condition of the chelating amino-groups. The adsorbed and released lanthanum ions were estimated by ICP-OES. A global efficiency (uptake and release) of lanthanum recovery around 30-35% was found for both pristine clays, while an improvement of the efficiency up to 43% was measured upon intercalation. Also the mechanisms and the kinetics of these reactions were evaluated and the results were mainly related to the amount and the nature of the intercalated polymer present in the clay.

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ELECTRIC DISCHARGE ASSISTED MECHANICAL MILLING - BLUE SKY TECHNOLOGY FOR SYNTHESIS AND PROCESSING OF MATERIALS

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Advanced materials manufacturing methods require clean non-polution process, high speed and precise process, mechano-chemically integrated process, and highly reliable final products. Conventional oxide reduction and synthesis of functional materials are traditionally slow processes that are energy and time consuming. In the present world there is strong demand on development of modern materials and materials processing methods that could offer rapid reaction rates, high energy efficiency and be environmentally safe.

Electric discharge assisted mechanical milling (EDAMM) [1] is a new and exciting materials processing technique which combines the attributes of conventional mechanical milling with all effects generated by electric discharges. It is demonstrated that EDAMM can be used to reduce oxides and synthesize a range of functional materials in a matter of minutes, rather than days.

This presentation provides an overview of recent development of Electric Discharge Assisted Mechanical Milling and its application in rapid materials processing and synthesis of functional materials and their applications.

In particular: i) detailed analysis of the method will be presented, ii) the effect of AC and DC discharges on phase transformations in solid will be discussed, iii) characteristic of power supplies and construction of reaction chambers will be presented, iv) example applications of this method for rapid reduction and replacement reactions

In typical pyrometallurgical processes that are employed to obtain metals from ores (such as oxides or sulphides), the solid raw material is transformed to the product by a liquid and/or gas phase reaction. These processes require high reaction temperatures and pressures and long processing time. The final products then require an additional processing step to separate the desired metal product from any by-products, remnant starting materials and/or solvent. Several types of reduction reactions have been demonstrated using our EDAMM device which at present is powered by 2 kW pulsed power supply. We will show that both Fe and Mg can successfully be used to fully reduce PbS and Sb2S. In the reduction of copper sulphide (Cu2S) with elemental Fe and Mg EDAMM replacement reactions were generated on a laboratory scale. The outcome of the reaction was 98% pure Cu. In both above cases the reaction time was 5 min. Conducting EDAMM experiments on natural ilmenite concentrates over a range of durations demonstrated that during EDAMM, the pseudorutile component is decomposed in less than 10 s, whilst the ilmenite component is completely oxidised in less than 2 min. - in conventional processing similar reactions can be achieved after several hours of furnace annealing at 1400ºC.

This is the fastest known reduction technique, and has the added advantage of not requiring any external heating of the reactants during processing.

- rapid synthesis of complex oxides
- synthesis of ultrahard materials

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VALORIZATION OF PHOSPHATE FROM AQUEOUS SOLUTION AS CALCIUM PHOSPHATE-ZEOLITE (CAP1-) BY MODIFICATION OF FLY ASH

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In this work the use of zeolites (NaP1:NA) synthesized from flying ashes origin and their Ca form after proper chemical modification (CaP1:NaP1) as potential materials for recovery and valorization of phosphate from aqueous effluents has been studied.

Equilibrium and kinetic experiments were performed to study the effects of operating conditions such as, solution pH, coexisting ions, and initial concentration on either the capacity or the rate of phosphate uptake by the zeolites. The phosphate sorption capacity, described properly by the Langmuir isotherms, increases with increasing the initial phosphate concentration and sorption processes are influenced by solution pH. To evaluate the chemical stability of phosphate in the phosphate-adsorbed CaP1 zeolite, phosphate fractionation was performed. The effect of anions such as,,and on phosphate adsorption were also investigated. The obtained materials were analyzed by infrared spectroscopy (IR), scanning electron microscopy (SEM/EDS) and X-ray diffraction (XRD). The main process responsible for the removal of phosphate was the formation of brushite (precursors of Hydroxyapatite) by the reaction between the calcium zeolite and high P(V) concentration in solution converted into a novel slow-release inorganic fertilizer consisting of zeolite CaP1/Brushite.

The overall adsorption process with CaP1 was assumed to be controlled by intra-particle diffusion. The adsorbed phosphate can be partially desorbed by a mixture of 0,1M $NaHCO_3$ and Na_2CO_3 for CaP1 and more efficiently desorbed (above 90%) with NaP1. CaP1, with large capacity and high selectivity, is therefore a very promising adsorbent for phosphate recovery from aqueous solution.

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UV AND OZONATION TREATABILITY OF AMOXICILLIN: PROCESS OPTIMIZATION, BYPRODUCT PROFILE AND TOXICITY

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Trace amounts of pharmaceutical compounds have been detected in drinking waters and wastewaters as a result of improved technological development. They have been suspected to cause endocrine-related disorders in human and wildlife [1]. Recently, World Health Organization and European Union projects have been proved that advanced oxidation techniques (ozonation, activated carbon adsorption, membrane processes) totally (100%) removed most of the pharmaceuticals compared to secondary treatment options (activated sludge, biofiltration) which were only resulted with 20-90% removal [2].

UV and Ozonation processes are the mostly applied advanced oxidation technique in large scale treatment facility therefore; investigation of their performance to eliminate pharmaceutical compounds is an important issue. In this study, a model antibiotic compound *amoxicillin* was used between 25 mg.L^{-1} and 100 mg.L^{-1} aqueous concentrations and they were subjected to UV irradiation and ozonation process. UV photon flux was calculated by chemical actinometry and found as 2.3 W.m^{-2}. UV processes were carried out in a flow reactor and various pump rates have been tested to find optimum removal. Ozonation experiments were conducted in a batch reactor. Aqueous and gaseous ozone concentrations were measured by standard procedures [3] and calculated for various pH conditions (pH 3 $O_{3(aq)}$=0.24 mg.L^{-1}; pH 7 $O_{3(aq)}$=0.18 mg.L^{-1}; pH 10 $O_{3(aq)}$=0.13 mg.L^{-1}; $O_{3(g)}$=25.6 mg.L^{-1}).

Optimum residence time for UV irradiation was found at 25.6 minutes and ozonation process was conducted for 30 minutes. 23% amoxicillin removal and 14% COD removal was achieved for 25 mg.L^{-1} amoxicillin solution whereas; ozonation process was more powerful causing 100% elimination of 100 mg.L^{-1} within 1 minute for optimum pH (pH 10) and COD mineralization after 30 minutes were found as 22 %. Under neutral conditions total removal occurred after 5 minutes and 11.2 % COD elimination was calculated. UV and ozonation degradation products were identified by GCMS WILEY 7 Library. According to the results sixteen byproducts were observed after UV treatment and four products were identified after O_3 treatment. Treated effluents has shown a toxic nature (EC_{50}%<20) whereas; synergetic effect was tested to reduce the toxicity of treated effluents.

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HYBRID PVA-FULLERENOL MEMBRANES FOR THE SEPARATION OF AZEOTROPIC WATER MIXTURES

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It is well known that the separation of azeotropic mixtures, a thermodynamic bottleneck, is a very difficult and energy intensive industrial task conventionally solved by vacuum distillation. This work concerns the separation of azeotropic mixtures by an alternative membrane process -pervaporation. Pervaporation is a method of the separation well suited for low molecular liquid components that allows to separating azeotropic, temperature sensitive and close-boiling point component mixtures. In contrary to other separation methods pervaporation is energy effective and ecological process that does not require additional chemicals and complicated equipment to carry out the mixture separation. To achieve a high efficiency by pervaporation, polymeric membrane materials with good transport properties should be used and the preparation of mixed matrix membranes is recognized to be a good strategy to get enhanced separation properties.

One of the ways to get the materials with the tailored properties is modification of well-known selective polymers by adding carbon nanoparticles [1,2]. This research demonstrates the methods of preparations and physico-chemical properties of novel membrane materials based on PVA-fullerenol composites. The morphology of composite films was visualized using SEM. The interaction between polymer and carbon particle was studied by FTIR and NMR. The effect of carbon inclusion in the polymer matrix on physical properties was characterized by sorption tests and contact angle measurements. Transport properties of composite membranes were studied in pervaporation of binary azeotropic ethanol-water and tetrahydrofuran -water mixtures. The improved results obtained with these new membranes will be presented and discussed comparatively to pristine PVA membranes.

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T-x-y DIAGRAMS OF Pd-Cu-{Ag, Ni, Pt} SYSTEMS FOR MEMBRANE MATERIALS

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In order to obtain the best properties of ternary mixtures, the space (3D) computer models of T-x-y diagrams are used.

Real 3D computer model permits to visualize the T-x-y diagram by any section, to compare the model sections with experimental ones, to calculate and to design so called mass balances diagrams, which demonstrate crystallizations of any initial composition, beginning from the liquid up to the final sets of microstructure elements.

Properties of the metal alloys, applied for membranes, are inconsistent. The Pd-Cu-based membranes have the most appropriate characteristics. The quality of 2-component alloys may be improved by addition of third component (Pt, Ni, In, or rare earth metal). In this case 3-dimentional (3D) computer models of T-x-y diagrams become very convenient tool for selection of materials characteristics.

T-x-y diagrams of ternary systems Pd-Cu-{Ag, Ni, Pt} have similar geometric structure. Liquidus and solidus surfaces in the systems with Ni and Pt are the borders of 2-phase region with the continuous solid solution crystallization.

Liquidus of the analogous system with Ag includes the invariant curve, which is given by eutectic solubility gap in the binary system Ag-Cu.

Solubility gap in solid state has a place in the systems Pd-Cu and Cu-Pt. Appropriate order and disorder curves form in the ternary systems the pairs of individual surfaces and continuous surfaces extending from one binary system to another. The same type of surfaces exist in the systems with Ag.

As for the system with Ni, it differs by the continuous ternary solid solutions. Computer models are specifically needed in cases of discrepant information about binary systems. For instance, the system Pd-Cu has one region of solid solution ordering in some papers or two regions - in others, and different 3D computer models make possible to simulate and to analyze both variants.

Space models of ternary systems are able to show the dynamics of material microstructure forming by observing the stages of crystallization at cooling of initial melt by means of so-called mass balance diagrams.

Computer model of PD helps to design the miscrostructure of heterogeneous material and to decipher its genotype.

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T-x-y DIAGRAMS OF CERAMIC SYSTEMS FOR MEMBRANE MATERIALS

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Increased interest to ceramic membranes is connected not only with a possibility of their application at high temperatures, but also thanks to a low power inputs. One of ceramic membranes disadvantages is the sophisticated obtaining of membrane layer with the homogeneous porous structure.

The computer models of phase diagrams for oxide systems permit to reduce the quantity of experimental work and to examine the different sets of microconstituents of phase assemblages with the purpose to optimize the microstructure [1].

We have considered four ternary systems Al_2O_3-SiO_2-TiO_2, Al_2O_3-SiO_2-ZrO_2, Al_2O_3-TiO_2-ZrO_2, TiO_2-SiO_2-ZrO_2, bounding the quaternary system Al_2O_3-TiO_2-SiO_2-ZrO_2 (for its future simulation), as commonly used materials in the membrane techniques has been consisted of.

The phase diagram of system Al_2O_3-SiO_2-TiO_2 is formed by five surfaces of primary crystallization, the region of immiscibility of two liquid phases, three horizontal planes and one triangulating vertical plane.

The phase diagram of system Al_2O_3-SiO_2-ZrO_2 includes four surfaces of primary crystallization, the region of immiscibility of two liquid phases, two horizontal and one vertical planes. The monovariant curve of liquidus between two ternary eutectic points has a maximum.

T-x-y diagram Al_2O_3-TiO_2-ZrO_2 has five surfaces of primary crystallization, three horizontal and one vertical planes, maximum point on one of the monovariant liquidus curve.

T-x-y diagram SiO_2-TiO_2-ZrO_2 involves four surfaces of primary crystallization, two regions of immiscibility of two liquid phases, two horizontal planes.

Binary incongruently and congruently melting compounds as well as the compounds decomposing in the solid phases are taken into account at phase diagrams simulation.

The spatial scheme of mono- and invariant equilibria for each model is formed on these data. Then the ruled surfaces and phase regions are formed.

The elaborated models give the possibility to identify phases and to obtain the set of microconstituents in any part of the phase diagram of oxide-ceramic system.

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STRUCTURAL EVIDENCES OF FUEL-BASED POLLUTANTS REMOVAL FROM WATER BY HIGH SILICA ZEOLITES

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Removal of fuel-based compounds from natural water is of considerable interest due to the harmful effects of these pollutants on the environment, even at very low concentration. Adsorption is a reliable alternative to eliminate these compounds from wastewaters because of the flexibility of the process, low energy and cheap operation costs [1-5].

This work is a part of a wider project whose purpose is to limit the water diffusion of fuel-based pollutants through their adsorption into zeolites pores. Organophilic synthetic zeolites, which are cheap and available on the market, with different topology, channel systems and free window apertures were tested for fuel-based-pollutants with different chemical properties and molecular dimensions. The selected adsorbents were commercial as-synthesized ZSM-5 and Y zeolites with high SiO_2/Al_2O_3 ratio. Among pollutants, toluene, chlorobenzene, 1,2-dichloroethane and methyl-*tert*-butyl-ether are of special relevance since they are toxic and commonly found in surface and ground water. In particular, structural evidences of adsorption from dilute solutions into the zeolites, as well as the competitive role of humic monomers, and the effect of the temperature in the adsorption processes will be discussed. Kinetics and adsorption isotherm batch data were obtained via Headspace Solid Phase Microextraction-GC. X-ray powders patterns were collected before and after adsorption on a Bruker D8 Advance diffractometer equipped with SOL-X detector. Thermal analyses (TG and DTA) were performed in air up to 900°C at 10°C/min. Variable pressure and temperature infrared spectra were collected on a Thermo Electron Corporation FT Nicolet 5700 Spectrometer. The simulation of the diffusion process was carried out by the numerical resolution of the Maxwell-Stefan. This combined diffractometric, thermogravimetric, chromatographic, computational and spectroscopic study allowed us to: 1) measure the sorption capacity of zeolite materials weighed against organic pollutants dissolved in water; 2) characterise the sorbent structure after pollutant adsorption; 3) localise the organic species in the zeolite channel systems; 4) highlight the role of humic monomers in the removal of pollutants from water; 5) probe the interaction between the adsorbate and zeolite framework. The very favorable adsorption kinetics of pollutants along with the effective and highly irreversible adsorption into zeolite pores make these cheap and environmental friendly materials applicable for the treatment of water contaminated with fuel-based pollutants.

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MICROPOROUS & MESOPOROUS MATERIALS

MM3
ADVANCED NOVEL FUNCTIONAL MAGNETIC MATERIALS

MM5
THE UNIVERSE OF MICROPOROUS & MESOPOROUS MATERIALS

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SYSTEMATIC MAGNETO-OPTICAL STUDY OF AMORPHOUS MICROWIRES FOR SENSORS AND ACTUATORS APPLICATION

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Taking into account the importance of surface magnetic properties for the optimal operation of magnetic sensors we have systematically studied the surface magnetization reversal and surface domain structure of magnetic microwires. The investigation was performed in wide series of glass covered microwire with the diameter range of 1 µm-100 µm. The main results of our last years investigation have been published in our book [1].

The investigations have been performed using the magneto-optical Kerr effect (MOKE) by means of polarizing microscopy at the temperature range 300-500 K and in the presence of the electric current of super high frequency (SHF). The tensile and torsion stresses have been applied during the experiments.

The existence of the bistability effect has been confirmed by MOKE technique for all studied diameters that confirms the potential sensors application. Application of different types of the external stresses permitted us to select the optimal magnetic properties of micriwires, in particular to determine the best value of surface helical structure of the highest value of giant magneto-impedance effect (GMI).

One of the observed essential effects is the sharply change of the direction of the magnetization in the existing domains in the presence of low SHF circular field. The contribution of such type of magnetization reversals is very essential to the circumferential permeability and in turn, to the GMI amplitude. Also we have found that the SHF circular magnetic field induces the existence of the meta-stable inclined helical state. The degree of the helicality and the sign of the meta-stable states depend on the frequency and the amplitude of the SHF field.

The temperature induced transformation of the magnetic structure also has been discovered in the frame of the providing of the stability of the GMI sensors operating. The experimentally observed coexistence of different domain structures with different values of the domain wall mobility has an ambivalent influence on GMI effect. Clear increase of the number of the inclined domain walls with the temperature leads to the increase of the GMI effect and in turn to the increase of the sensitivity of the sensor. From the other side, change of the number of the domain walls is the evident reason of the possible instability of the sensor operating.

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NEW TERNARY COMPOUNDS OF Tl_9LnTe_6 TYPE AND SOLID SOLUTIONS ON THEIR BASE

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Tl_9BiTe_6 substitution variant of mixed-valent Tl_5Te_3 (Sp.gr. I4/mcm) and exhibits a very small thermal conductivity compared to that of Tl_5Te_3. Thallium lanthanoid tellurides, Tl_9LnTe_6, might exhibit good thermoelectric properties like Tl_9BiTe_6 as they are equally isostructural to Tl_5Te_3. Furthermore, lanthanide elements are lighter than thallium or bismuth elements resulting in significant mass fluctuation between the Tl and Ln atoms, which may further lower the thermal conductivity. On the other hand, the magnetic properties are popular among the f-block metal compounds as all the Ln^{3+} ions contain unpaired electrons.

In our previous study we reported some new ternary compounds Tl_9LnTe_6 which crystallize in Tl_5Te_3 structure type [1,2].

In present report the crystal structure of Tl_9LnTe_6 compounds and phase equilibria in Tl_5Te_3-Tl_9LnTe_6-Tl_9BiTe_6 (Ln-Dy, Tm) systems for obtaining of solid solutions with Tl_5Te_3 structure are discussed.

The samples were prepared by heating the high purity elements into graphitized silica ampoules. The ampoules were heated to maximal temperature 1000 K and were kept at this temperature during 4 h. After that they were cooled slowly to 650K and annealed at this temperature during ~1000h.

Investigations were carried out by using differential thermal analyses and X-ray powder diffraction technique. X-ray powder diffraction study shows that Tl_9LnTe_6 compounds crystallize in Tl_5Te_3-type structure with the lattice parameters a=8.8875(7), c=12.902(1) Å (Tl_9DyTe_6) and a=8.9096(4), c=12.741(8) Å (Tl_9TmTe_6).

Based on experimental data a number of vertical sections and isothermal sections at 600 and 700 K of the phase diagrams, as well as projections of liquidus and solidus surfaces of above-stated systems were constructed. It was shown, that all investigated systems are characterized by formation of continuous fields of solid solutions with Tl_5Te_3-type structure (δ-phase).

Moreover, it was shown that obtained new phases possess thermoelectric and magnetic properties.

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SUPERCONDUCTIVITY AND PECULIAR MAGNETISM IN MINERALS

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The manifestations of quantum cooperative phenomena, i.e. superconductivity and peculiar forms of low dimensional and frustrated magnetism, can be found in both common and rare minerals. Even the discovery of superfluidity in liquid helium is obliged in a sense to mineralogy since the first terrestrial source of this noble gas was mineral cleveite UO_2 subject to a radioactive decay. The superconductivity was found and investigated in details for miassite $Rh_{17}S_{15}$ [1,2], palladseite $Pd_{17}Se_{15}$ [2,3] and calaverite $AuTe_2$ [4,5] minerals. The miassite demonstrates fascinating features of strongly correlated superconductivity as opposed to conventional superconductivity in palladseite, while calaverite exhibits superconductivity associated with breaking of Te_2 dimers. The most versatile are magnetic effects in minerals containing various transition metal ions. A fairly abundant ferromagnetic magnetite Fe_3O_4 is a host of important metal - insulator transition whose nature with regards to structural and electronic properties is still elusive [6]. Apart from strongly magnetic minerals, an interest is attracted recently by minerals whose properties are directly opposite to that of magnetite. Some Cu-based minerals realize at low temperatures the states of gapped or gapless spin liquids. These are the cases of valence bond crystal in clinoclase $Cu_3(AsO_4)(OH)_3$ [7] or spin singlet state in edwardsite $Cd_2Cu_3(OH)_6(SO_4)_2 4H_2O$ [8]. Another interesting class of magnetic materials is represented by minerals forming exotic long - range ordered magnetic structures, as are the cases of newly studied francisite $Cu_3BiSe_2O_8Cl$ and dugganite $Pb_3TeCo_3V_2O_{14}$. All in all, the investigations of basic properties of spin liquids and spin solids in minerals are quite instructive to get better insight into mechanisms of quantum ground state formation in matter.

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THE QUANTUM GROUND STATE IN SPIN GAP URUSOVITE

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Urusovite with chemical formula $CuAl(AsO_4)O$, is a new mineral found among products of volcanic exhalations of the great Tolbachik fissure eruption in 1975 at Kamchatka, Russia [1]. The temperature of the locality, where the sample was found, was 400^o C which explains absence of the hydroxyl groups or water molecules inevitably present in the crystal structure of numerous naturally occurring compounds with a spin gap behavior. A variety of mechanisms are found to be responsible for the spin gap formation with similar magnitudes, such as found in i) libethenite $Cu_2PO_4(OH)$ described by an isolated square-spin cluster model [2], ii) malachite $Cu_2(OH)_2CO_3$ representing weakly interacting alternating spin chains [3,4], iii) clinoclase $Cu_3(AsO_4)(OH)_3$ being a combination of two nonequivalent spin dimers [5], and iv) euchroite $Cu_2(AsO_4)(OH)x3H_2O$, a model compound for the frustrated delta chain composed of corner-sharing triangles [6]. Unlike listed compounds, chemical stability of $CuAl(AsO_4)O$ opens a perspective to study the physical properties of a large spin-gap compound in an exceptionally wide temperature range. Synthetic mineral urusovite $CuAl(AsO_4)O$ was prepared through the wet chemistry route and characterized in a wide temperature range in studies of magnetization, specific heat and X-band electron spin resonance. The basic structural units of the compound are distorted square pyramids CuO_5 assembled into corrugated honeycomb layers separated by AsO_4 and AlO_4 tetrahedra. Both thermodynamic and resonant measurements indicate that $CuAl(AsO_4)O$ is a spin-gap system with a gap D of about 350 K. The electronic structure calculations performed within the framework of density functional theory suggest a weakly interacting dimer model with antiferromagnetic signs for intradimer and interdimer superexchange interactions, establishing the valence bond solid as quantum ground state of the title compound.

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STUDIES OF HIGH FREQUENCY GIANT MAGNETOIMPEDANCE EFFECT OF AMORPHOUS MICROWIRES

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Amorphous glass coated ferromagnetic microwires (typically of 1-30 μm in diameter) have attracted growing attention in the last few years owing to excellent soft magnetic properties and Giant Magneto-impedance, GMI, effect [1,2]. The extremely high sensitivity of the GMI effect to even low magnetic field attracted great interest in the field of applied magnetism basically for applications for low magnetic field detection.

Recently major attention is focused on high frequencies (GHz range) GMI applications owing to the development of thin magnetically soft materials and recent tendency in miniaturization of magnetic field sensors [1,2]. Therefore, the purpose of this paper is to study the GMI effect in thin amorphous magnetically soft microwires suitable for miniaturized GMI based magnetic field sensors paying attention to the high frequency GMI effect.

We measured magnetic field, H, dependence of real part, Z_1 of the longitudinal wire impedance Z_{zz} ($Z_{zz} = Z_1+iZ_2$), up to 4 GHz in various Co-rich microwires. General features of these dependences is that the magnetic field of maximum shifts to the higher field region increasing the *f*. High enough magnetic field sensitivity, i.e. GMI effect till GHz- range frequencies has been observed. On the other hand, from the point of view of applications GMI ratio, $\Delta Z/Z$, defined as: $\Delta Z/Z = [Z(H) - Z(H_{max})] / Z(H_{max})$ is relevant. In most studied Co-rich microwires the optimum frequency for achievement of the highest GMI ratio is about 100- 300 MHz.

Features of high frequency GMI effect have been analyzed using FMR-like approximation as suggested in ref. (3). This approach allows to estimate the saturation magnetization. We performed high frequency GMI effect fitting using Kittel formula for studied Co-rich microwires. We got linear fit of the square of the resonance frequency on applied field, although some deviation can be appreciated in low-field region. The origin of this deviation is unclear and can be related to low magnetic field GMI hysteresis recently discussed elsewhere [4]. Consequently some features of high frequency GMI effect can be described using FMR-like approximation.

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BISTABLE GLASS-COATED MICROWIRES FOR SENSING APPLICATIONS

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Amorphous glass-coated microwires are composite materials that consist of metallic nucleus (1-50 μm in diameter) covered by glass-coating (thickness 2-20 μm). Having positive magnetostriction, they are characterized by monodomain structure, within which the magnetization process runs through the single Barkhausen jump of single closure domain along entire wire [1]. This domain wall is characterized by extremely high domain wall velocities sometimes higher than sound speed [2].

Based on the above described magnetization process, such wires are characterized by a magnetic bistability. Their magnetization can reach only two values (+ Ms or- Ms) and switching between the two values runs through the single Barkhausen jump when the external field approaches the value of switching field H_{sw}. The switching field of magnetic microwires is extremely sensitive to external parameters (like temperature, mechanical stress, frequency of applied magnetic field, etc…) the feature that can be successively employed in various sensors construction.

It has been shown earlier that the switching field in amorphous microwires has two contributions: magnetoelastic and another one arising from structural relaxation [2]. These two contributions have different sensitivity to the external parameters [3] which gives us opportunity to tailor the overall sensitivity of the switching field to stress, temperature, magnetic field according to desired conditions.

All the above mentioned properties allows application of the fast domain wall dynamics in bistable microwires for construction of different miniaturized sensors of magnetic field, temperature [4], mechanical stress [5], deformation [6] etc…

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MAGNETIC SHAPE MEMORY M$_N$ RICH M$_N$-N$_I$-S$_N$ ALLOYS

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Magnetic refrigeration is an alternative to conventional refrigeration. Ferromagnetic Heusler alloys based on Ni-Mn-Z (Z = In, Sn or in general an element of IIIA-VA group) have been presented as an important class of magnetocaloric materials for enhancing refrigeration capacity.

As increasing temperature, these alloys can undergo: a) a first-order martensitic transformation from a low symmetry phase (martensite) to a high symmetry phase (austenite) and b) a second-order magnetic transformation (ferromagnetic to paramagnetic). It is well known that the magnetic and martensitic transitions can be tuned markedly by the composition and processing conditions. In the literature, analyzed alloys usually are Ni rich, whereas in our work are Mn rich. We produce three compositions $Mn_{50}Ni_{50-x}Sn_x$ (x = 5, 7.5 and 10 at.%) by arc melting (bulk) and by melt spinning (ribbons). We built the phase diagram.

Structural transformation of alloys was analyzed by differential scanning calorimetry (DSC) and X-Ray diffraction (XRD). Thermodynamic parameters as enthalpy and entropy were calculated. Thermomagnetic measurements are performed by vibrating sample magnetometry (VSM).

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RECENT RESEARCH ON THE MAGNETOIMPEDANCE EFFECT IN Co-BASED AMORPHOUS RIBBONS

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The giant magnetoimpedance effect (GMI) discovered in 1994 by Mohri and Panina [1] and Berkowitz and Beach [2] in non-magnetostrictive soft magnetic amorphous wires has open new opportunities of research owing to the promising and, even, real technological applications. Such scientific research has dealt with several aspects concerning the intrinsic magnetotransport properties (i.e.: frequency range, intensity of the effect, magnetic field to observe possible maximum, noise…) as well as those related with microstructural (mainly amorphous or nanocrystalline) or geometrical character (as has been mentioned, initially wire, but GMI has been reported in glass-coated microwire [3], ribbon [4], multilayers [5]) and, therefore, GMI is actually opening a new branch of research combining the micromagnetics of soft magnets with the classical electrodynamics. Obviously, the different geometry together with the magnetic anisotropy lead to some differences in the GMI response like the range of frequency and the magnetic field dependence of the impedance curve with one or two peaks or even, it could be relevant the shape of the peak, etc.

In this work we report the recent results obtained on the magnetoimpedance (MI) response in several nearly-zero magnetostriction Co-based amorphous ribbons with different width, and different transverse magnetic anisotropy (developed during the fabrication process or processing after production by the current annealing technique) in the frequency range of 10 MHz - 3.5 GHz. The evolution of the maximum of MI with the axial magnetic field, ascribed to the anisotropy field, as a function of the frequency provides useful information on the soft magnetic character of the ribbons.

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FERROMAGNETIC SHAPE MEMORY THIN FILMS AND APPLICATIONS

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Ferromagnetic shape memory alloys (FSMA) such as off-stoichiometric Ni-Mn-Ga Heusler compounds display excellent actuation ability in external magnetic field, because of the extraordinary mobile martensitic microstructure and a strong coupling between elastic and magnetic properties. This is the so called “magnetic-field-induced strain” (MFIS) effect. Due to their high power density, these materials have a great potential to be used in magnetic MEMS.

In the present work we overview recent advances made in the FSMAs thin films in the submicron range of thickness. Particular emphasis is given to the experimental and theoretical studies of the magnetic anisotropy exhibited by a) films deposited onto cold substrates and subsequently annealed and b) epitaxial films grown onto hot substrates. The “cold-substrate” preparation method usually results in polycrystalline films with (220) out-of-plane fiber texture, while “hot-substrate” method leads to the single crystalline films. The symmetry and strength of the magnetic anisotropy (MA) of the films are important factors to be clarified in the relationship with the magnetic-field-induced strain (MFIS) and related phenomena. It has been studied by ferromagnetic resonance (FMR). Magnetic anisotropy is controlled by the film crystallography, the martensitic nanostructure, type of substrate and film thickness.

The effect of substrate nature on the FSMA film anisotropy is demonstrated by comparing the in plane magnetic anisotropy for a Ni-Mn-Ga/NaCl(001) film and out of plane oblique anisotropy in an identical film with the same texture deposited onto Si (001). Another important effect on MA is the influence of the film-substrate stresses on the transformation volume strain. A reduction of MA by one order of magnitude due to mesoscale twinning is found by FMR in a single crystalline Ni-Mn-Ga/MgO(100) film. These results are explained in the framework of magnetoelastic model of martensite. From which second- and forth-order magnetic anisotropy constants are evaluated. The estimated value of the magnetic domain wall width is comparable with the widths of mesoscale twins, indicating that the magnetic vectors of twin components are strongly coupled by the exchange interaction.

Applications of FSMA in MEMS are discussed in the case of single and double beam Si cantilevers with deposited submicron Ni-Mn-Ga films.

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DEVELOPMENT OF HIGHLY PRECISE MAGNETO-IMPEDANCE GRADIOMETER FOR BIOMAGNETIC FIELD MEASUREMENT

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Highly sensitive micro magnetic sensors, based on Magneto-Impedance (MI) element, have been developed [1]. The signal processing of this MI sensor is relies on CMOS IC electronic circuits of to provide a sharp-pulse excitations [1]. Mass product Magneto-Impedance IC sensors (MI IC) have been produced by Aichi Steel Corp.. The MI sensor that using pick-up coil for signal detection, have been investigated as off-diagonal MI sensor [2] . The off-diagonal impedance of GMI element has been utilized for highly sensitive magnetometer [3],[4].Utilizing both 30 um diameter amorphous wire and pick-up coil, the resolution of CMOS MI sensor have been estimated to be $1 \mathrm{pT/Hz}^{1/2}$[5].

In order to detect very weak magnetic field such as a biomagnetic field, we constructed MI gradiometer for the cancellation of background uniform noises such as the geomagnetic field. For this sensor head, the amorphous wire has two coils: a sensing coil and a reference coil. For a helical static magnetization, a pulse current passing the wire induces a coil voltage proportional to an external applied magnetic field in the coil around the wire. The distance between the two pick up coils is set to be 3 cm. The sensitivity of the system more than100kV/T achieved without amplification of the voltage. The difference in sensitivity between sensing element and reference element is within 1.5% by adjusting using variable resistance. The system noise of developed gradiometer under no shield environment is about $5 \mathrm{pT/Hz}^{1/2}$ at 10Hz.

We carried out biomagnetic field measurement from living cell tissue using developed precise gradiometer. We have detected magnetic field synchronized with electric potentials at the surface of stomach tissue isolated from guinea pig. The effect of ion channel blocking with applying TEA (Tetraethylammonium) have been repeatable observed by means of biomagnetic field measurement in ileum of guinea pig. In addition, magnetic field from mouse heart with rhythmical activity can be detected using developed gradiometer system.

We have also measured biomagnetic field from the heart and brain of the human. Cardiac magnetic field of premature ventricular contraction was identified. Evoked brain magnetic fields of such as P300 and N100 have been measured.

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MAGNETO-OPTICAL SENSOR BASED ON MAGNETOPLASMONIC CRYSTAL

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Continuous improvements in nanofabrication and nanocharacterization capabilities have changed predictions about the role that metals could play in the development of new optical devices. Using of noble metals in magneto-optics has shown a big potential for constructing sensors based on surface plasmon resonance phenomenon. Adding a possibility to control the magneto-optical (MO) properties of such structures by applying external magnetic field allows opening the door for designing of novel active plasmonic sensors. The technological drawback is that the magnetic fields that enable noticeable changes in noble-metal-based plasmonic structures in visible spectral range are of the order of several tesla and too large for applications. Using the ferromagnetic-metal-based structures is limited by high ohmic losses. It is possible to reduce these losses and to add the possibility to control the MO properties by using magnetoplasmonic crystals (MPlCs) - multilayer structures made of noble and ferromagnetic metals [1]. From the one side changes in magnetic properties of ferromagnetic layer will influence on the MO properties of MPlC. From the other it is possible to control the MO properties of MPlCs by applying external magnetic field [2].

Magnetic and MO properties of MPC structures, based on embossed substrates with different spatial profiles, and magnetic properties of structures on smooth Si/SiO_2 substrates which were created by ion beam sputtering were investigated. Spatial profiles of the MPlC were obtained by atomic-force microscopy (AFM). Magnetic properties were investigated by vibration sample magnetometer (VSM). MO response of the MPlC was measured by setup which consists of the halogen lamp with a monochromator as a light source, Glan-Taylor prism as polarizer and a photomultiplier tube with a lock-in amplifier as detector. The samples were fabricated by ion beam sputtering. Substrates were made of commercial digital discs. The polymer spiral gratings inside the Blu-ray disc and DVD have declared periods of 320, and 740 nm, respectively. First, protective layer of the digital disc's surface was mechanically removed. Then, metals (Ag and Ni) were sputtered on the polymer gratings with thicknesses from 80 to 100 nm and from 5 to 100 nm respectively. In the end structures were covered by SiO_2 layer to prevent oxidation.

The feasibility of creation of the alternating magnetic field sensor based on such structures was demonstrated. It was shown, that the alternating magnetic field sensor can measure the alternating fields with amplitude of 10^{-6} - 10^{-4} Oe with relative error smaller than 5%. It is necessary to investigate the properties of the different MPlCs to improve the mean free path of SPP, i.e. sensitivity and accuracy of the alternating magnetic field sensors.

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CHEMICAL FORMATION OF RUTHENIUM NANOPARTICLES SUPPORTED ON MICROPOROUS AND MESOPOROUS MATERIALS

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Ruthenium nanoparticles were synthesised by chemical formation and supported on mesoporous and microporous materials. ZSM-5 zeolite was synthesized according to the literature [1]. Under hydrothermal treatment at a temperature 130 °C for 3 days, after filtration and washing calcination at 550 °C for 12 h. The SBA-15 support was prepared according to previously published method [2]. The preparation of nanoparticles was carried out by anionic exchange followed by reduction using NaBH4. Several physicochemical methods such as XRD, MET, FTIR and UV-visible were used to determine the character of catalysts. The effect of metal loading and support nature were investigated. Other inert supports will be used as natural clays and modified clays.

Keywords: Ruthenium nanoparticles, SBA-15, ZSM-5, Chemical reduction.

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ELABORATION AND CHARACTERIZATION OF FE-ZSM5 ZEOLITES - APPLICATION IN CATALYTIC ELIMINATION OF PHENOL FROM INDUSTRIAL WASTEWATER

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Porous materials such as microporous solids (zeolites) have the advantage of developing pores of different sizes and shapes which gives them a large surface area necessary to disperse and “expose” the active phase, which will promote the approach of organic molecules to be transformed.

The objective of this work was to prepare a stable support, inert with high internal surface, in order to disperse the active phase (iron) and generate an efficient and stable catalyst. Two series of zeolites, ferrisilicates (based on salts of Fe3+) and ferrosilicates (based on salts of Fe2+) were prepared by hydrothermal synthesis involving direct mineralization by methylamine (MA) to introduce the iron in isomorphic position. The resulting solids were characterized by various physicochemical techniques (XRD, SEM, BET surface areas, as well as chemical analysis using the atomic absorption (AA), EDX).

To evaluate the efficiency of iron inserted in the framework of the zeolite we realized the catalytic oxidation of phenol in aqueous medium by H_2O_2 at room temperature and atmospheric pressure. This choice is based on the possibility of replacing the classical Fenton system (homogeneous catalysis), by a heterogeneous catalytic system which operates according the same principle. In fact, phenol and substituted phenols are toxic organic pollutants commonly found in industrial wastewater, including discharges of chemical and metallurgical industries. Such a system may also be relevant in terms of recovery, reuse and recycling of the catalyst.

The evaluation of catalytic performance of solids synthesized shows that the oxidizing properties are dependent on preparation protocols, the nature of the precursor and synthetic environments. The solids prepared by MA method exhibit very good stability in aqueous medium in the presence of H_2O_2 (eluted Fe <1%) and lead to a rapid transformation of phenol. Some parameters seem important and could be the cause of these properties: particle size, amount of iron in the structure, amount of iron out frame. The activation method also influences the interaction between iron and silicon, which govern the activity and stability of the catalyst.

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EFFECT OF HEPTANE CONCENTRATIONS INTO MICROEMULSION LYOTROPIC LIQUID CRYSTALLINE TEMPLATES FOR MESOPOROUS PTRU NANOPARTICLES

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Mesoporous PtRu bimetallic catalysts were used as anodic electrocatalysts for the methanol oxidation reaction (MOR) in direct methanol fuel cells (DMFC). We investigated the formation process of mesostructured PtRu nanoparticles electrochemically reduced on a microemulsion lyotropic liquid crystalline (MLLC) template of a 2D hexagonal packing by the addition of heptane with different concentrations. Microemulsion type of LLC templates containing small alkane molecules of the selected chain length and concentration exhibited a convenient control over the nanopore sizes of the mesostructures. The MLLC template was proved to be more stable than the corresponding LLC one without alkane. The structural evolution and atomic distribution of the MLLC-templated mesoporous PtRu nanoparticles during electrodeposition were revealed using in situ small-angle X-ray scattering (SAXS), in situ X-ray diffraction (XRD), complemented by X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) spectroscopy and field-emission transmission electron microscopy (FE-TEM). There were hexagonal to lamellar phase transition of MLLC templates for the duration of electroreduction when heptane concentrations were more than 8 wt%. With the increased with heptane concentrations, the alloying extent and the atomic distribution of PtRu nanoparticles would be improved. The complementary results provide insight into the effect of heptane concentrations for growth and structural evolution of mesostructured PtRu bimetallic nanoparticles from the use of the MLLC-type templates.

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LASER BASED COMBINATION OF MESOPOROUS SILICA AND SILVER NANOPARTICLES FOR NEW CATALYTIC MATERIALS

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Insertion of metal nanoparticles into porous structures, such as adsorbents and catalysts (*e.g.* zeolites, zeotypes, silica) has been pursuing as a goal to produce materials suitable for different applications in microelectronics, medical diagnosis among others [1] with finely tuned characteristics. The traditional methods of dispersing metals in these three-dimensional mesoporous structures are ion exchange, incipient wetness impregnation and subsequent *in situ* reduction to form metal particles inside the pores. Each method allows the introduction of large quantities of the metal inside and also outside the porous structure although of lacking in controlling the metal particle size and shape can be present. In order to circumvent this drawback, the insertion of metal nanoparticles generated by laser ablation into a porous material was first explored by Hashimoto *et al.* [2] obtaining Au NPs-doped zeolite L crystals with controlled dimension and shape distributions. The goal of dispersing Ag nanoparticles in the mesoporous SBA-15 silica structure has been pursued in the last few years [3-5] applying new synthesis and encapsulation techniques.

Loading silver nanoparticles in hexagonally ordered mesoporous silica materials (MCM-41 and SBA-15) by ultra-short pulsed laser ablation of silver in liquid has been employed in our work [6]. Catalytic properties of the samples have been tested. Experimental results show that nanostructured silica supporting metallic silver nanoparticles are suitable catalysts for oxidation reaction of toluene. The resulting generated Ag/SBA-15 catalyst displays a favorable Ag dispersity, better catalytic stability and higher activity than the conventional Ag/SBA-15 preparations [6].

Further experimental work is going to be presented for enhancing the catalytic activity of these systems in oxidizing different volatile organic compounds (VOCs).

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FAUJASITE ZEOLITE PREPARED FROM SHALE ROCK AS A CATALYST FOR BIODIESEL PRODUCTION

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Zeolites occur in nature and have been known for almost 250 years as aluminosilicate minerals. Examples are faujasite, mordenite, offretite, and ferrierite, Today, these and other zeolite structures are of great interest in catalysis, yet their naturally occurring forms are of limited value, because (i) they almost always contain undesired impurity phases, (ii) their chemical composition varies from one deposit to another and even from one stratum to another in the same deposit, and (iii) their properties are not naturally optimised for catalytic applications [1-3]. For these reasons we synthesis faujasite zeolite from inexpensive raw materials.

It is well known that fly ash may be used to successfully prepare Faujasite zeolite. Here we investigate the use of ash derived from a variety of fuel types (coal, timber and peat), following their combustion in a domestic solid fuel stove, as a reagent to prepare zeolite catalysts. The fuels used in this study originate from different geographical locations and the ash residing from their combustion is thus expected to exhibit distinct mineralogical properties. Experiments are also being conducted to prepare zeolite using naturally occurring shale as an aluminosilica source. Results will be presented showing the elemental composition and crystal structure (where relevant) of the ash and shale samples following varying degrees of thermal pre-treatment. The zeolites prepared will be fully characterised and their activity tested in the esterification of oleic acid (a simulated free fatty acid found in waste cooking oil). A full set of results showing catalytic testing of all prepared catalysts will be presented.

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NANOMATERIALS

NM2
FUNCTIONAL POLYMERIC COMPOSITES WITH NANOCLAYS

NM3
ADVANCED FUNCTIONAL MATERIALS

NM5
MAGNETIC NANOPARTICLES

NM6
THE UNIVERSE OF NANOMATERIALS

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PROPERTIES OF ACCELERATED DEGRADATION LINEAR LOW DENSITY POLYETHYLENE-STARCH-CLAY NANOCOMPOSITE FILM

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Blending starch with commercial plastics such as Linier Low Density Polyethylene (LLDPE) was the alternative material for disposable plastic packaging, which was one of the largest contributors of waste material and had the lowest recovered material compare to the other municipal solid waste [1]. Unfortunately this alternative material generally had poor mechanical properties and transparency [2]. In this work, clay was used to increased mechanical properties and transparency of packaging film product by well dispersed of layered clay on LLDPE-starch nanocomposite. Polymeric materials exposed to the weather will change due to mechanical, thermal, chemical and light. It could be an initiate factor to the process of degradation [3]. Accelerated photo degradation test with a Xenon Arc was conducted on LLDPE-starch-clay nanocomposite film. The process condition in light: Irradiant: 0.55 ± 0.01 W/m2 @ 340 nm, duration in one cycle: 4.8 hours. Nanocomposite compound was prepared by extrusion of LLDPE, masterbatch from previous work that consist of clay, compatibilizers and starch. Samples film was prepared from the compound using Blown film Rheomex Haake.

Ultra violet - visible spectrophotometer results shows that nanocomposite film with 10% starch had transmission higher than pure LLDPE, meanwhile nanocomposite film with 20% starch had transmission lower than pure LLDPE. The well dispersed of clay, functions as a nucleating agent on nanocomposite matrix.

Characterization after accelerated photo degradation was observed in tensile strength and strain at break using Universal Testing Machine. Sample with 10% starch was 55% decrease in tensile strength after 14 days and sample with 20% starch already brittle after 7 days, the sample cannot be used as tensile strength specimen. Meanwhile, pure LLDPE used as a control was decreased 30% in tensile strength after 14 days. Fourier Transform Infra Red spectrophotometer result for nanocomposite with 10% and 20% starch proved that degradation was occurred by increasing the intensity in the wave number at 1722 cm-1, corresponding to carbonyl bond [4]. The longer the degradation, the intensity of carbonyl bond was higher.

Keyword: LLDPE, starch, clay, photo degradation.

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FUNCTIONAL CLAY NANOTUBE-ENZYME COMPOSITES

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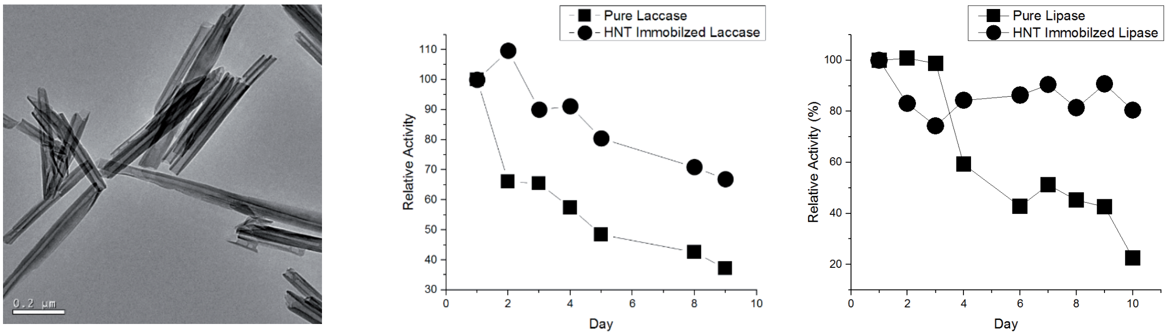
Halloysite nanotubes are aluminosilicate nanotubes formed by the rolling of sheets of kaolinite clay. They have a 15 nm lumen, 50 nm external diameters and length of ca. 1-1.5µm. Owing to these properties, they are currently being developed for loading, storage, and controlled release of active chemical agents (anticorrosion, flame-retardants, biocides, drugs and proteins) [1]. Proteins are a diverse group of biopolymers that serve as the backbone of functionality in nature. Enzymes are a particular class of proteins that cease to function in non-aqueous environments and are sensitive to both pH and temperature and have restrictions in their usage. Furthermore, enzymes are soluble and hence difficult to reuse. Enzymes were immobilized on solid surfaces to overcome these limitations [2-3]. In the current study, we have immobilized the enzymes laccase from *Trametes veriscolor* and lipase from *Candida rugosa* on clay nanotubes (HNT). The enzymes were immobilized using incubation in solution and vacuum treatment. Enzyme adsorption was studied using thermo gravimetric analysis (TGA) since enzymes showed decomposition generally within the temperature range of 200-400 C. Enzyme desorption (release) was studied at their specific absorption maxima using UV-vis spectroscopy. Enzyme assays were performed at various pH to assess the pH stability of the immobilized and free enzyme. Lipase when adsorbed onto HNTs can be described with a Langmuir adsorption isotherm whereas Laccase can be described with a linear adsorption. Both enzymes displayed enhanced pH stability at acidic pH when immobilized. Laccase shows greater temporal stability at acidic pH and no difference at basic pH. From the above results, we can conclude that HNT can be used as an immobilization tubule substrate that provides long term enzymatic stability especially in acidic pH.



(a) (b) (c)

Fig 1. (a) A TEM image of halloysite nanotubes. (b) Stability of laccase samples at pH 5. (c) Stability of lipase samples at pH 7.4

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CERAMIC NANOTUBES FOR POLYMER COMPOSITES WITH STABLE ANTICORROSION PROPERTIES

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Natural halloysite clay nanotubes were used as inexpensive minicontainers for encapsulation and slow release of organic corrosion inhibitors in coatings based on polymer paints. A longterm anticorrosive protection based on doping polyacryl and polyurethane paints with 5 wt% halloysite loaded with benzotriazole, mercaptobenzimidazole, and hydroxyquinoline, was proposed for steel, copper, and aluminum. These inhibitors were loaded into clay nanotubes in amounts of 10-25 wt % and released to coating defects for 10-20 h to suppress point corrosion in the initial stage. The anticorrosion activity of polymer composites doped with loaded halloysites was verified in highlycorrosion solutions (0.5 M NaCl) using microscanning corrosion currents. The corrosion development was controlled during 6 months by measuring the concentration of corrosion products, studying the adhesion of composite coating, and analyzing

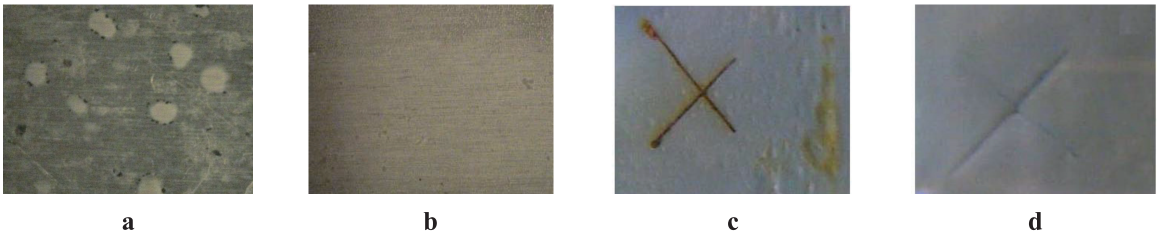

Fig. 1. Optical image of a corrosion process developed for 6 months in 0.5 M NaCl solution: on (a, b) aluminum coated by a 40 μm thick layer of (a) conventional polyurethane paint and (b) the same paint doped with 5 wt % halloysite loaded with hydroxyquinoline and (c, d) a steel plate coated by (c) polyurethane paint with artificial scratches and (d) the same paint doped with 5 wt % halloysite loaded with dodecylamine.

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NANOGOLD AND NANOSILVER IN CLAY MINERALS

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The most important ore-hosting rock of nanogold and nanosilver in many fields in Kazakhstan is the kaolinite group minerals (Al_2O_3 and SiO_2) - the clay. The investigation of gold ores has showed, that the main types of gold nanoparticle emissions are the single individuals and their aggregates of different shapes assigned to the deepening of microrelief and nanorelief of grains of bulk metal surface. Gold-silver mineralization is represented by ultra finely dispersed, finely dispersed and dust gold, silver and electrum. The size of the gold discovered Au varies within <0,5-1mk - 10x12 - 12x25mk^2, the size of electrum Au, Ag 0,5-3,5mk - 3x6,5mk^2. In rare cases, there is vein silver represented with noncontinuous micro-veinlets with crimps and nubbly fascicular puff-ups of overall size up to (0,5-10)x65mk^2. The major part of the finely dispersed and dust-like gold-silver ore grade mineralization (Figure 1). Nanogold and nanosilver are absorbed by clay, and this is a problem during the extraction of precious components. Technology requires fine grinding of ore and the use of high concentrations of sodium cyanide.

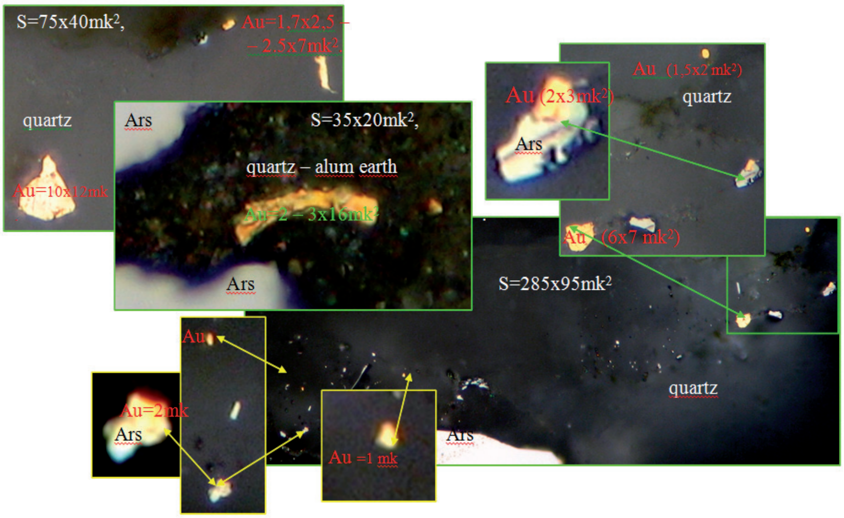

Fig. 1. Finely dispersed gold-silver ore grade mineralization of the tested samples

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IMPROVING GEOPOLYMER RHEOLOGY WITH CLAY NANOTUBES / POLYELECTROLYTE NANOCOATING ON FLY ASH

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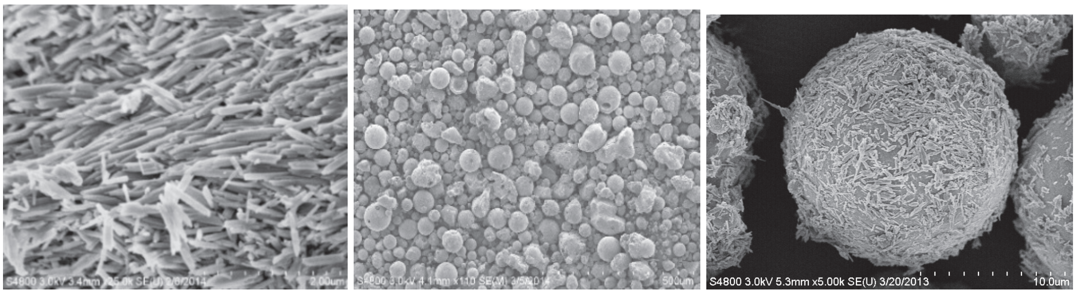
Geopolymer binders are aluminosilicate inorganic polymers with expanding applications as construction materials. For wider industrial use of these binders, limited controls of their rheological properties and short solidification time have to be improved. Naturally occurring nanoclays, such as halloysite nanotubes are cheap and abundantly available materials allowing encapsulating alumosilicate microcores with simple and scalable layer-by-layer (LbL) nanocoating technique. A dry mixing approach was followed for the coating of fly ash particles using polyelectrolytes and halloysite nanotubes. This approach allowed faster coating of the fly ash particles than the solution approach, where fly ash particles are mixed with the polyelectrolyte solutions. An electrostatic attraction drives coating of anionic nanoclays onto fly ash particles providing a potential to controllably adjust properties of geopolymer composites. LbL technique was used to modify geopolymer through nanoarchitectural formation of composite shells on ash microcores. We describe mechanical and rheological enhancement of geopolymers produced from ash microparticles coated with tubule or platy nanoclays sandwiched with polycations, and its advantages for better concrete materials.



(a) (b) (c)

Fig 1. SEM images of a) halloysite nanotubes, b) fly ash particles, and c) fly ash particles surface coated with polyelectrolytes followed by mixing with halloysite nanotubes.

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CLAY NANOBRICK WALL MULTILAYER THIN FILMS THAT SLOW GAS AND STOP FIRE

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Layer-by-layer (LbL) assembly is wide-reaching conformal coating "platform" technology capable of imparting a multiplicity of functionalities on nearly any type of surface in a relatively environmentally friendly way. At its core, LbL is a solution deposition technique in which layers of cationic and anionic materials (e.g. clay nanoplatelets, polymers and even biological molecules) are built up via electrostatic attractions in an alternating fashion. Here we are producing nanocomposite multilayers having 10 - 96 wt% clay that are completely transparent and exhibit oxygen transmission rates below 0.005 cm^3/m^2•day (at a film thickness below 100 nm). This exceptional oxygen barrier makes these layers interesting for food and flexible electronics packaging. These same 'nanobrick wall' assemblies are very conformal and able to impart flame resistance to highly flammable foam and fabric by uniformly coating the complex three-dimensional geometries. On foam, these coatings can simultaneously cut the heat release rate (HRR) in half, relative to uncoated foam, and eliminate melt dripping without adding halogenated flame retardants. Greater reductions in HRR and smoke release can be achieved with nanocoatings deposited using only inorganic platelets (i.e., anionic and cationic clay). I'll also describe how these films can also act as a barrier to hydrogen gas, reducing the permeability of a 51 μm polystyrene film 1000X with only a 122 nm thick coating containing five clay layers. All of the materials described are water-based and processing occurs under ambient conditions in most cases. Our work in these areas has been featured numerous times in C&EN and also highlighted in Nature, ScienceNews, Smithsonian Magazine and various other scientific news outlets.

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HALLOYSITE CLAY NANOTUBE BIOCOMPATIBILITY: A KEY POINT FOR BIOMEDICAL APPLICATION

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Halloysite is a naturally occurring aluminosilicate clay with hollow tubular structure. It was found to be a viable and inexpensive nanoscale container for the encapsulation of biologically active molecules like biocides and drugs [1], and useful biomaterial for other biological applications, such as gene delivery vehicles, ultrasound contrast agents, anticancer therapy and stem cells isolation [2,3]. Therefore, biocompatibility of halloysite is one of the main requisites for the employment of halloysite clay nanotubes (HNTs) for clinical purposes. [2].

In this work we coated HNTs surface with poly(ethylene glycol) (PEG) in order to increase biocompatibility, to prolong circulation time and to prevent protein adsorption and aggregation in biological environments. The dose- and time-dependent cytotoxicity of the PEG-HNTs obtained was evaluated *in vitro* on two different human cell lines, namely MCF-7 (breast cancer) and HeLa (cervical cancer) cells. Cell viability was assessed by MTT assay after 6-72 h exposure to increasing doses (from 0.05 to 0.5 mg/mL) of HNTs.

The results obtained showed that both HeLa and MCF-7 cell viability decreased at increasing concentration of HNTs, and the inhibition of cell growth was more pronounced at longer incubation time. After 24-h incubation, MCF-7 cells survival was around 70% (considered as threshold value for cell toxicity) at any concentration tested, whereas a significant decrement was observed at HNTs concentrations above 0.25 mg/mL at longer time exposure. On the other hand, HeLa cells exhibited a fairly higher sensitivity to HNTs exposure with respect to MCF-7; in fact, HeLa cells showed a significant mortality at HNTs concentrations above 0.25 mg/mL already after 24-h incubation. Moreover, for longer incubation time (48- and 72-h), HeLa cell viability was preserved (>70%) only for HNTs concentration up to 0.1 mg/mL.

Therefore, we can conclude that PEG-coated HNTs examined in this study exhibit good level of biocompatibility at concentration up to 0.1 mg/mL over 72 h incubation, and that the PEGylation process improves HNTs biocompatibility as compared to the effects of uncoated HNTs tested on the same cell lines reported in previous studies [4].

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HALLOYSITE CLAY NANOTUBES AS CARRIERS FOR DELIVERY OF CURCUMIN

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The increasing interest in nanoscience and nanotechnology has led to the development of advanced materials with unique chemical and physical properties, such as liposomes, nanocapsules or carbon nanotubes, and also to the investigation of nanostructured naturally present materials. Halloysite is a clay mineral, chemically similar to kaolin, which has a predominantly hollow tubular structure, in the submicron range [1]. Halloysite has found an important role as nanocarrier for encapsulation, delivery and controlled release of biologically active molecules and drugs [2,4]. Halloysite nanotubes (HNTs) sizes varies between 0.5 - 5 microns in length and their external diameter is of 50 ± 10 nm and their lumen is around 15 nm, when they are completely rolled [3]. The use of halloysite nanotubes offers significant advantages over other systems: they are naturally occurred, easily available and not expensive, and the loading procedure is quite simple. In this work, we characterize HNTs, in terms of both structure and biocompatibility, and use them for loading and controlled release of curcumin. Curcumin is a naturally occurring yellow compound, found as the main constituent in the rhizome of the plant Curcuma Longa, grown in tropical Southeast Asia. It exhibits anti-oxidative, anti-inflammatory and anti-cancer properties [5], but its therapeutic potential is hindered by its low water solubility and bioavailability, whence the need for suitable carriers.

The structure of HNTs has been analyzed with a combination of Transmission Electron Microscopy (TEM), Scanning Electron Microscopy (SEM) and Scanning Force microscopy (SFM) imaging. The loading efficiency of curcumin has been determined by TEM analysis and absorbance measurements, while the release kinetics has been studied photometrically. To provide an additional control over the drug release rate, HNTs have been coated with polyelectrolyte multilayers by the Layer-by-Layer (LbL) technique. The stability of naked and coated HNTs in solution has been evaluated by Dynamic Light Scattering measurements. MTT assay has also been used to investigate the biocompatibility of HNTs and the anti-cancer activity of naked curcumin and drug-loaded halloysite, at different concentrations and upon different time intervals against the breast cancer cell line MCF-7 whereas confocal fluorescence microscopy imaging has been used to monitor the intracellular localization of both HNTs and curcumin. Our results envisaged the use of Halloysite Nanotubes as efficient carriers for polyphenols delivery to tumoral cells.

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PERVAPORATION HYBRID PVC MEMBRANES FOR THE SEPARATION OF TOLUENE - N-HEPTANE MIXTURES

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The design and preparation of hybrid membranes based on polyvinylchloride (PVC) were studied for the separation of Toluene - n-Heptane mixtures by pervaporation. PVC was chosen as polymeric matrix because of its strong intrinsic affinity for aromatic compounds and its weak affinity for aliphatic compounds.

Indeed aromatic-aliphatic liquids found in industrial C6 cuts formed organic mixtures which are very difficult to fractionate by conventional processes at reasonable cost because of the close boiling points of the components and of their mutual physical chemical affinities. It is well known that, when distillation or liquid -liquid extraction are not enough efficient or too energy consuming, pervaporation can be an alternative technology to consider. However for this type of organophile separation, there is currently no commercial membrane with enough high separation properties which could be used. That is why the study hybrid polymeric membranes was considered in this work.

PVC was chosen as selective starting material because it gathers two key advantages: firstly it is a lost cost polymer which is readily available, contrarily to speciality polymers which often need to be developed for membrane application; secondly, PVC thanks to the presence of its chlorine atom gives rise to a polar macromolecular structure endowed with a good affinity for aromatic species. To improve the mass transfer this glassy structure, the incorporation of several inorganic micro and nanoparticles particles in PVC matrix was carried out to prepare mixed matrix membranes and to understand if it was possible to obtain enhanced separation properties from this simple, cheap polymer.

The results reported were obtained using several types of clay to get hybrid PVC membranes. Hence inorganic clays like Maghnite, Wyoming, Kaolin and Nanocor have been used as fillers to modify the PVC basic properties thanks to the formation of a hybrid network. Our results show that indeed the PVC transport properties can be drastically modified both by the type and by the amount particles used. According to the fillers incorporated in the polymer matrix, the transport properties of the hybrid PVC membranes could be tuned either as barrier materials or as toluene selective network with strongly enhanced flux compared to the initial PVC membranes.

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PREPARATION OF COMPOSITES DERIVED BENTONITE-P4VP APPLICATION TO THE RETENTION OF THE TEXTILE DYES

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Textile industries release large quantities of wastewater at risk of toxicity [1]. There are already treatments such as activated carbon adsorptions are an effective but expensive process that produces a sludge component itself an environmental threat [1].

Clays, poly (4-vinylpyridine) and its derivatives could be alternative adsorbent materials to the economic times and less polluting. Many authors have studied the adsorption of cationic dyes, but few have focused on anionic dyes hardly adsorbable on these media.

The aim of this work is to obtain new materials rigid and microporous structure is used clay and poly (4-vinylpyridine) quaternized [2] for the adsorption of anionic dyes (orange Telon) encountered in effluent dyes.

This study been monitored by the influence of the type of clay (bentonite, sodium bentonite), the degree of quaternization of poly (4-vinylpyridine) [2], pH of the medium [3], the effect of concentration and temperature.

The test results showed that the material based on the sodium bentonite and poly (4-vinylpyridine) with a low quaternization has the best adsorption capacity whereas bentonite compounds and poly (4-vinylpyridine) with high rates of quaternization play a minor role.

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CHEMICAL MODIFICATIONS OF HALLOYSITE NANOTUBES FOR THE DEVELOPMENT OF SMART NANOMATERIALS

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Halloysite nanoclays (HNTs) are promising nanomaterials because of their versatile properties, such as hollow tubular morphology and tunable surface chemistry. HNTs are biocompatible, no toxic and abundantly available at low cost. Due to these characteristics HNTs are suitable for development of hybrid sustainable materials, which are perspective for wastewater remediation, green packaging and drug delivery. HNTs are quite polydisperse in size with a length of ca. 1 μm, while the external diameter and the lumen range between 50-80 nm and 10-15 nm, respectively. Chemically, halloysite is composed of gibbsite octahedral sheet (Al-OH) groups on the inner surface and siloxane (Si−O−Si) groups on the external surface. This different chemistry allows the selective modification of HNTs surfaces. We performed several chemical functionalization of HNTs materials to confer properties valuable in specific applications.

The HNTs inner lumen was modified to generate an hydrophobic microenvironment for the solubilization of compounds sparingly soluble in water (aromatic and aliphatic oils). Oppositely, the outer surface hydrophobization was employed to create reverse inorganic micelles to be used as dispersant for hydrophilic compounds (such as $CuSO_4 \cdot 5H_2O$) in a confined environment within an organic solvent.

Grafting chemically modified cyclodextrin units onto the nanotube surface endowed to obtain a singular nanoparticle with double cavity (HNTs and cyclodextrin lumen). The obtained materials were characterized to investigate the structure and colloidal stability in aqueous dispersions. The grafted cyclodextrins were modified with thiosaccharide

pendants, to mimic the binding of sugars to proteins and the glyco-cluster effect for cellular recognition events. Drug-loading and delivery abilities were tested by using curcumin, a common naturally occurring anticancer agent.

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NEW TRENDS OF LDH PLATELETS TO FUNCTIONALIZE POLYMER

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Two-dimensional inorganic materials due to their structural anisotropy and possible chemical versatility are extensively studied for their application as filler for polymer, this in an attempt to fulfill the ever-growing topical needs in different nano-technologies regarding safe (flame retardant and thermal stabilizer), functionalities (pigments, biocide), as well as eco-friendly and environmental aspects (bio-source).

The contribution will emphasize the relevance of Layered Double Hydroxide-type (LDH) materials on the different forefront aspects in nanoscience and nanotechnology research.

Indeed, taking advantage of the versatility in terms of its chemical composition, its exchange ability, and its tunable layer charge and form factor, layered double hydroxide (LDH) type material is considered today as promising and adaptable filler for polymer. Aside the conventional organo-modification of the inorganic platelets by a surfactant to render the filler compatible with the polymer chains, another strategy consists in embarking functionalized tethered agent relevant for the whole and suitable for desired applications.

Examples taken from both academia and an industrial collaboration with BASF COATINGS will highlight the role of LDH in acting on the Newtonian rheological flow of polymers of great relevance such as polydimethylsiloxane (PDMS), polypropylene (PP) or as functionalized container with UV-absorbing properties, photoactive surfaces for biocide activity, as well as specific container inside a polymer coating to possibly release active species resulting in “self-healing” properties regarding corrosion inhibition.

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BIONANOCOMPOSITES BASED ON FIBROUS CLAYS AND NANOFIBRILLATED CELLULOSE

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Bionanocomposites are hybrid materials consisting of naturally occurring polymers associated with inorganic solids, such as clays, through nanometric scale interactions between the two components (Darder et al., 2007). Among other biopolymers, celluloses can be used in the preparation of clay-based bionanocomposites. Cellulose is a natural polymer consisting of β-D-glucose, which is mainly in higher plants as a structural component of the cell wall. The organization of individual polysaccharide chains in crystalline and amorphous regions originates elementary fibrils that assemble into cellulose fibres. Through processes of disaggregation of these larger fibres the elementary fibrils, also called "ground-wood pulp" can be prepared derivatives at different scales, giving rise to the so-called microcrystalline cellulose (fibres of 50-10 µm length and 10-50 µm diameter) and nanocelulloses. In this last group are included "microfibrillated cellulose" (fibres of 0.5-10 µm length and 10-100 nm diameter), "nanofibrillated cellulose" (fibres of 500-2000 nm length and 4-20 nm diameter) and "nanocrystalline cellulose" (50-500 nm length and 3-5 nm diameter) (Habibi, 2014). Micro- and nano-celluloses are being widely used in the development of new nanostructured materials have been used for example in the preparation of composites with laminar structure clays mainly montmorillonite and vermiculite (Liu et al, 2012).

In this communication we will introduce bionanocomposites resulting from the combination of fibrillated cellulose with sepiolite and palygorskite fibrous clays. The bionanocomposites are prepared by applying high energy homogenization, such as ultrasonic irradiation to aqueous dispersions of both types of organic and inorganic fibres (Ruiz-Hitzky et al., 2014). In this condition, it is achieved the simultaneous breakdown of agglomerates of both types of fibres favouring their inter-recombination, leading to the formation of highly stable and viscous hydrogels. The composite gels can be dried and processed into films, foams or monoliths. Like other fibrous clays based bionanocomposites (Ruiz-Hitzky et al., 2013), these materials have properties of interest for diverse applications such as adsorbents and nanoparticle scaffold.

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FABRICATION OF IRON(III) OXYHYDROXIDE-REDUCED GRAPHENE OXIDE COMPOSITE AND ITS PHOTOCATALYTIC APPLICATION FOR THE HYDROGEN EVOLUTION REACTION IN WATER

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Using iron(II) chloride and graphene oxide as reactants, *β*-FeOOH@reduced graphene oxide (rGO) nanocomposites were easily synthesized through a redox reaction at room temperature. The prepared *β*-FeOOH@rGO was characterized by X-ray powder diffraction spectroscopy, scanning electron microscopy, transmission electron microscopy, X-ray photoelectron spectroscopy and UV-vis diffuse reflectance spectroscopy. The FeOOH formed nanorods that were 50-100 nm long and 15-20 nm wide and they were uniformly distributed on the rGO sheets. The *β*-FeOOH@rGO nanocomposites exhibited good photocatalytic performance for the hydrogen evolution reaction in water using methanol as a sacrificial reagent under visible light ($\lambda > 420$ nm) irradiation compared to pure *β*-FeOOH. Possible mechanisms for the formation of the photocatalyst and the photocatalytic reaction are proposed. The rGO sheets have good conductivity and can enhance the charge transfer of the catalyst, thus, it can prevent the recombination of electron/hole pairs in the *β*-FeOOH.

Keywords: photocatalyst, graphene, composite, hydrogen generation, visible light.

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EFFECTS OF LI/MN MOLE RATIO ON THE SYNTHESIS OF $Li_{1+X}Mn_{2-X}O_4$ BY LOW TEMPERATURE SOLID-STATE REACTION FOR CATHODE MATERIAL

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Manganese dioxide (MnO_2) and its derivatives are used as a cathode material for both primary and rechargeable lithium batteries. $Li_{1+x}Mn_{2-x}O_4$, as one of the derivatives, can serve as one of the main candidates of cathode materials for lithium batteries thanks to their being abundant, low cost and environmentally friendly. This study aims to determine the effects of the mole ratio of precursor on the synthesis of $Li_{1+x}Mn_{2-x}O_4$ (x=0; 0.02; 0.04; 0.06; 0.08; 0.1**)** by low temperature solid-state reaction**.** The variable examined in this study was the mole ratio of Li/ Mn in $Li_{1+x}Mn_{2-x}O_4$. The compound was characterized by XRD, TEM and SEM while the analysis of $LiMn_2O_4$ microstructure was carried out by Direct Method using several programs including winPLOTR, DICVOL, Checkcell and Diamond using XRD data. It is found that the mole ratio of the precursor affects the size, crystallinity and structure of $Li_{1+x}Mn_{2-x}O_4$. The results shows that $Li_{1+x}Mn_{2-x}O_4$ has a cubic crystal structure with *Fd3m* phase and the increase in the mole precursor causes a change in the material structure of $Li_{1+x}Mn_{2-x}O_4$.

Keywords: *$Li_{1+x}Mn_{2-x}O_4$, mole ratio of Li/Mn, low temperature, solid-state reaction.*

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MAGNETICALLY STIMULATED CIPROFLOXACIN RELEASE FROM POLYMERIC MICROSPHERES ENTRAPPING IRON OXIDE NANOPARTICLES

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To extend the external control capability of drug release, iron oxide magnetic nanoparticles encapsulated into polymeric microspheres were used as magnetic media to stimulate drug release using an alternating magnetic field. Chemically synthesized magnetic nanoparticles, maghemite or hematite, and the antibiotic ciprofloxacin were encapsulated together within poly(ε-caprolactone) (PCL) microspheres. The PCL microspheres entrapping ciprofloxacin and magnetic nanoparticles could be triggered for immediate drug release by magnetic stimulation at a maximum value of 40%. Moreover, the microspheres were cytocompatible with fibroblasts *in vitro* with a cell viability percentage of more than 100% relative to a non-treated control after 24 h of culture. Macrophage cell cultures showed no signs of increased inflammatory responses after *in vitro* incubation for 56 h. Treatment of *Staphylococcus aureus* with the magnetic microspheres under an alternating (isolating) magnetic field increased bacterial inhibition further after 2 and 5 days in a broth inhibition assay. The findings of the present study indicate that magnetic nanoparticles, maghemite and hematite, can be used as media for stimulation by an external magnetic energy to activate immediate drug release.

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FLEXIBLE SYMMETRIC SUPERCAPACITOR OF NI(OH)$_2$/CARBON CLOTH

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As the novel trend of flexible devices such as wearable electronics, roll-up displays and smart shirt have brought a next-generation living convenience and high-tech surroundings. Supercapacitors, known as electrochemical capacitors, have great life cycles, high power density and eco-friendly properties. Flexible supercapacitors have nearly become a main theme in the past years. Herein, we demonstrate flexible symmetric supercapacitors with a facile electrochemical method, low-cost and environmental friendly process. Dense and entangled Ni(OH)$_2$ directly grown on the carbon cloth have been employed as hierarchical supercapacitor electrodes in aqueous solution (KOH, 1 M),X-ray Photoemission Spectroscopy (XPS) and X-ray Diffraction (XRD) identifying the characteristic of Ni(OH)$_2$ and Scanning Electronic Microscope(SEM) observing the morphology of Ni(OH)$_2$. The voltammograms and galvanostatic charge/discharge are performed to probe the capacitive characteristics of Ni(OH)$_2$/carbon cloth electrode. The pseudocapacitive characteristics of Ni(OH)$_2$/carbon cloth electrodes associated with variation of the Ni oxidation state during the charge and discharge cycles were elucidated using *in-situ* X-ray absorption near-edge structure (XANES) spectra.

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MICROWAVE DIELECTRIC PROPERTIES OF LI_2WO_4-DOPED $LA(MG_{0.5}SN_{0.5})O_3$ CERAMICS

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Excellent dielectric properties of complex perovskite ceramics $A(B'_{0.5}B''_{0.5})O_3$ ($A=Me^{2+}$, Me^{3+}; $B'=Me^{2+}$, Me^{3+}; $B''=Me^{4+}$, Me^{5+}, Me^{6+}) at microwave frequencies are reported. Several investigations of researches of $Ln(Mg_{0.5}Sn_{0.5})O_3$ (Ln=La, Nd) ceramics and related ceramic systems have examined their potential application in resonators, filters and antennas in the modern communication systems, including radar and global positioning systems (GPS), which are operated at microwave frequencies [1-2]. An apparent density of 6.29 g/cm^3, a dielectric constant of 15.6, and a $Q\times f$ of 30,600 GHz were obtained for $La(Mg_{0.5}Sn_{0.5})O_3$ ceramics, sintered at 1500 ^{O}C for 4 h [6]. In this investigation, the effects of extent of Li_2WO_4 additive and sintering temperature on the microwave dielectric properties of $La(Mg_{0.5}Sn_{0.5})O_3$ ceramics were studied. The microwave dielectric properties of $La(Mg_{0.5}Sn_{0.5})O_3$ ceramics were found to vary with the extent of Li_2WO_4 additive and sintering temperature. These different microwave dielectric properties of Li_2WO_4-doped $La(Mg_{0.5}Sn_{0.5})O_3$ ceramics, following sintering for 4 h at different temperatures, were analyzed by densification and X-ray diffraction (XRD) patterns. The correlations between the parameters, including density, porosities of open pores, amount of second phase, and the microwave dielectric properties were investigated.

The X-ray diffraction patterns of Li_2WO_4-doped $La(Mg_{0.5}Sn_{0.5})O_3$ ceramics exhibited no significant variation of phase with sintering temperature. The amount of the second phase sintering at optimum temperature increased from 7.83% to 15.67% as the amount of Li_2WO_4 additive increased from 0.25 to 0.75 wt.% and decreased from 15.67% to 10.96% as the extent of Li_2WO_4 additive increased from 0.75 to 1.00 wt.%. $La(Mg_{0.5}Sn_{0.5})O_3$ is the main crystalline phase, which is accompanied by small amount of $La_2Sn_2O_7$ as the second phase. Formation of second phase was attributed to the loss on ignition of MgO resulting in the Sn-rich phase $La_2Sn_2O_7$. The formation of second phase of $La_2Sn_2O_7$ affected the microwave dielectric properties of Li_2WO_4-doped $La(Mg_{0.5}Sn_{0.5})O_3$ ceramics. By adding 0.5 wt.% Li_2WO_4, a dielectric constant of 19.9, a quality factor ($Q\times f$) of 55,900 GHz, and a temperature coefficient of resonant frequency (-80 ppm/^{O}C) were obtained when $La(Mg_{0.5}Sn_{0.5})O_3$ ceramics were sintered at 1475 ^{O}C for 4h. The microwave dielectric properties of $La(Mg_{0.5}Sn_{0.5})O_3$ ceramics depended on the apparent density, the porosities of open pores, and second phase.

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FACILE SYNTHESIS OF NANO-ARCHITECTURED CuO ELECTRODES FOR HIGH-PERFORMANCE SUPERCAPACITOR

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In recent years, the depletion of fossil fuels and global warming issues require not only urgent development of clean alternative energies and emission control of global warming gases, but also more progressive energy storage, conversion and management systems. Supercapacitors (SCs) have received considerable attention as a key energy storage device because of their high power densities, fast recharge capability and long cycle life;[1,2] therefore, they have became increasingly attractive for use in hybrid electric vehicles, consumer electronics, medical devices, and military missile systems. Here, we report a simple electrochemical process to prepare nano-architectured CuO electrodes with 3D hierarchically porous structure and excellent supercapacitive performance. These nano-architectured CuO electrodes were included the co-deposition of a Ni-Cu layer on the Ni foam, selective etching of Cu from the Ni-Cu film (leaving tentacle-like nanoporous Ni), and anodic deposition of CuO nanoribbons (NR) on the tentacle-like nanoporous Ni/Ni foam substrate. Due to its unique nano-architecture, the prepared CuO nanoribbons-on-Ni nanoporous/Ni foam (CNRNP) electrode shows exceptional energy storage performance as compared to that of the conventional version of the electrode. The CNRNP electrode also had superior kinetic performance as compared to the CuO nanoflakes-on-Ni foam (CNFNF) and flake-like CuO (FLC) electrodes. Exceptionally high specific capacitance of 880 and 800 F g^{-1} (deducting substrates' capacitance from total), is obtained under scan rates of 10 and 200 mV s^{-1}, respectively, with excellent cyclic stability. The excellent pseudocapacitive characteristics of CNRNP electrodes associated with the great variation of Cu oxidation state during charge and discharge cycles were also elucidated using *in-situ* X-ray absorption near-edge structure (XANES).

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A NON-TRIVIAL WAY TO SYNTHESIS OF HIGH-TEMPERATURE MATERIALS

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Self-propagating high-temperature synthesis is a type of combustion that is the mode of occurrence of strong exothermic reaction (combustion reaction) in which the heat is localized in the layer and spread from one layer to another by conduction. The main purpose of SHS is the synthesis of substances and materials. There have been studies of SHS in layer systems of exothermic oxide mixture.

During SHS-process active metal oxides (WO_3, CuO, Co_3O_4) interacted with reducing agents (aluminum). As a result of exothermic reactions can be obtained metallic materials and complex inorganic compounds. It is difficult problem to obtain pure metallic and ceramic materials under normal conditions of synthesis without using of furnace. Phase separation does not occur due to rapid cooling, synthesis products are mixed in a single volume. So in order to separate them we apply additional acceleration. The centrifugal force contributes to effective phase separation in multicomponent molten combustion products, intensifies a flow of the melt, in addition, its action stabilizes combustion, prevents splashing mixture and products in the SH-synthesis.

The studies have been carried out using the unit specially designed to model the combustion process under the centrifugal force effect The device has three main units: an electric motor, shaft with traction and a steel cup (with a hole for the exit gas, temperature sensors and the rate of combustion). A narrow cut has been made both in one of the three rotating reactors and in the unit cover so as to observe advance of the combustion wave front. High speed video cameras used for supervision.

The initial mixture in a quartz tube (quartz tube is selected as the high temperature and a dielectric material) is placed in a steel cup, and then is rotated at a certain speed (which is selected depending on the condition). Then the initial mixture ignited by electrical coil with the power load on it. At this device magnitude, centrifugal acceleration varies at 1000 rpm from 60 to 150g; at 4000 rpm - from 900-2500g along the length of the sample. Different materials can be obtained by this method.

Actually the burning process in the three-layer system lasts 0.8 seconds. This time is sufficient for the formation of gradient material, for example. The material structure changes from metal (tungsten) to ceramics (aluminum oxide, corundum). The basic phases take 91.9 %. Other involved substances are boron-containing solid tungsten and boron compounds.

Mixture combustion of by non furnace SHS under the influence of centrifugal acceleration at temperatures above 2050 °C was obtained a new material composition $NiO_{16}Al_2O_3$, It has a bright blue colour. Its microstructure is characterized by high porosity and grain size ranging from 50 to 60. This suggests the possibility of using it as a high-pigment for decorating ceramic and porcelain. one thing worth to mention here SHS of this mixture was impossible in conditions of natural gravity.

An interesting material has been produced at combustion of the three-layer system based on tungsten and boron oxides - an extremely porous aluminum oxide crystallized in its three modifications such as α, δ and γ.

The developed methods allow to create wasteless production, to combine recovery of metals and production of various ceramic materials in one technological process. Realization of SHS under the action of centrifugal force allow, to control the kinetics of the combustion process, phase formation and properties of the final product of synthesis and to synthesize earlier unknown materials. SHS under the action of centrifugal force combines economy, organization a wasteless production and possibility of usage technogenic wastes.

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EFFECT OF CARRIER SCATTERING IN THERMOELECTRIC PROPERTIES BY MULTI-LAYERED Bi_2Te_3 THIN FILM

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Te-based chalcogenide material has been used in thermoelectric devices. Specially, Bi_2Te_3 have been one of the best n-type thermoelectric material characteristic at room temperature. Since electron and phonon plays a crucial role in determining the performances of the real devices, a better understanding between amorphous/crystal phases and the transition mechanism between them is necessary. Recent, optical pump THz probe spectroscopy (OPTP) is a powerful tool to study the ultrafast carrier dynamics of structural phase transition occurring on ultrafast timescale.

In this study, we fabricated the multi-layered films composed of alternately layers of Bi and Te ($\{Bi(3)Te(9)\}_n$) by controlling the layered thickness within atomic scale using thermal evaporation technique. After annealing treatment, $\{Bi(3)Te(9)\}_n$ alternately layered film is changed to high degree of crystallinity with single phase Bi_2Te_3 rhombohedral crystalline structure. Moreover, we investigated ultrafast carrier dynamics in multi-layered {Bi(3)Te(9)} thin film during the phase change from amorphous into crystalline states using THz-TDS spectra. The data showed the relationship between structural phase transition and optical properties transition in 2.6-0.2 THz range. OPTP spectroscopy was closely dependent on phase of the $\{Bi(3)Te(9)\}_n$ film, indicating that decay time is a crucial carrier dynamics mechanism to the thermoelectric properties.

In conclusion, carrier dynamics data of thermoelectric materials in $\{Bi(3)Te(9)\}_n$ thin film showed fast decay time within 5 ps caused by the carrier diffusion and electron-phonon coupling. On the other hand, the slow decay time is caused by recombination process of trapped carriers (native defect). The thermoelectrical properties and thermoelectric figure-of-merit (ZT) closely correlated with the structural characteristics, i.e., the superlattice-like structure with semiconductor-semimetal layers is contributed to both the electron and phonon scattering, resulting in an improvement in electrical conduction and increase in phonon scattering. In particular, phonon scattering was significantly increased to further reduce thermal conductivity in the self-ordered superlattice-like structure of the $\{Bi_2Te_3/Te\}_n$ sample. As a result, a thermoelectric figure of merit of ZT = 2.0 was obtained at 400K for $\{Bi_2Te_3/Te\}_n$ sample, indicating that the self-ordered superlattice-like structure holds great promise for thin film thermoelectric material.

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METAL-INSULATOR TRANSITION IN STRAINED GETE

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Chalcogenide based compound, especially GeTe and related compounds exhibit pronounced structural and optical contrast with rapid phase transition from amorphous and crystalline phase. And these compounds have possibility of multi-level capacitor by controlling the disordering. This makes them suitable candidates for rewritable optical storage media and universal memory device. Simultaneously, GeTe have the peierls instability showing difference in bond-length between long-bond (3.15Å) and short-bond (2.83Å). Since the resistivity affected by peierls instability play a crucial role in determining the performances of any real devices, it is important to understand the relation of peierls instability and electronic band structure. In this study we can find these relation and even observe the metal-insulator transition under the aggravated peierls distortion.

In this study, the GeTe film (200 nm thick) was deposited on a polyimide(500um thick) substrate at room temperature by an ion beam sputtering deposition using a single GeTe target. For acquiring the crystalline phase, the annealing process was conducted in a N2 ambient using a rapid thermal process (RTP), where isothermal duration was retained as 60minutes at 300'C exceeded crystallization temperature.

From the X-ray scattering (XRS), the bended crystalline GeTe on PI is under stress. The maximum tensile strain according to the diffraction peak of (111) and (200) is 0.5% which means that under bending geometry the GeTe film has the more distorted rhombohedral structure. The enhancement of A_{1g} mode compared with E_g mode is also observed from Raman spectroscopy. We also investigated ultrafast carrier dynamics and the temperature coefficient of the resistivity (TCR) in the GeTe film under bending geometry because the more strain can induce the decrease of conductivity and give rise to metal-insulator transition. We can find that the core-level binding energy to the unoccupied p-orbital decreases from XANES spectra and the band gap increase from FT-IR measurement. It induces the Fermi level shift toward the energy gap which triggers the metal-insulator transition.

In conclusion, using bending module, peierls distortion of crystalline GeTe can be aggravated. The change in electronic structure from this enhanced rhombohedral distortion can induced Metal-Insulator transition. Not only the disordering controlled metal-insulator transition, but also the strain induced metal-insulator transition can be used for multi-level capacitor.

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SOLVOTHERMAL SYNTHESIS OF ONE-DIMENSIONAL TRANSITION METAL DOPED ZnO NANOCRYSTALS AND THEIR APPLICATIONS IN SMART WINDOW DEVICES

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Oxide semiconductor nanowire (NW) suspension based devices haveattracted growing interest in smart window applications since these devices exhibit great controllability of light transmittance, long term stability and are simple. Recently, we demonstrated smart window device using the suspension of electrospun TiO_2 or solvothermally synthesized ZnO NWs in viscous polydimethylsiloxane (PDMS) matrix. The operating principle of the oxide semiconductor NW/ PDMS composite device is based on the alterable orientation, alignment or spatial distribution of the NWs in an electric field, thus changing light scattering cross-section and reversibly increasing or decreasing transmittance [1]. One-dimensional (1D) nanostructures such as NWs exhibit a good response to electric field due to the highly anisotropic shape.

Herein we report transition metal doped ZnO NW and PDMS based smart window devices. Doping ZnO NWs with metal ions, such as transition metals, may significantly alter the properties of the material. For instance, high quality ZnO nanocrystals doped with transition metal cations lead to enhanced optical absorption in visible range. The pristine ZnO NWs used in our previous work did not exhibit visible light absorption. Transmittance of ZnO NWs and PDMS-based smart window device was regulated by changing scattering cross-section. Visible light absorption could increase efficiency of smart window device, because during electrophoretic alignment of NWs towards direction of electric field will change not only scattering, but also visible light absorption cross-section.

One-dimensional ZnO nanostructures have been synthesized by wet chemical techniques including microemulsion hydrothermal synthesis, surfactant-assisted hydrothermal orientation growth and alcohol solution refluxing. However, synthesis of high quality transition metal doped ZnO NWs with small diameter and high aspect ratio is still a challenge. Most wet chemical methods fail to produce high aspect ratio doped ZnO NWs in large quantities. Here we are demonstrating large-scale, single-step, direct solvothermal method and have successfully prepared high aspect ratio single crystalline transition metal (Co, Cu, Fe, Ni, Mn) doped ZnO NWs. The solvothermal synthesis process presented here can be scaled up to macroscale production and the fact that NWs need no further modification increases the technological potential of oxide semiconductor NW suspension-based devices electro-optical smart window devices.

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FLEXIBLE SUPERCAPACITORS BASED ON MOLYBDENUM OXIDE

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Recently, flexible and ultralight and wearable supercapacitors have attracted great interests in energy storage because of their potential applications in portable electronic devices, flexible displays, mobile phone and smart clothes. Supercapacitors show higher energy density than that of conventional capacitor, faster rates of charge/discharge and great life cycles than that of batteries. The self-supporting and binder-free electrode with robust mechanical strength and large capacitance is a vital factor for flexible supercapacitors. Here, carbon paper was prepared easily by carbonizing fiber paper and used as substrate to grow molybdenum oxide. Compared to other materials, the carbon paper obtained with our method has the outstanding advantages of facile and large-scale synthesis from cheap, abundant and easily obtained natural source. The composition and structure of molybdenum oxide/carbon paper electrode was identified by XPS and XRD. The capacitive performance of the deposited oxides was evaluated using cyclic voltammetry in 3M KCl solution. The pseudocapacitive characteristics of molybdenum oxide/carbon paper electrodes associated with variation of the Mo oxidation state during the charge and discharge cycles were elucidated using *in-situ* X-ray absorption near-edge structure (XANES) spectra.

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EVOLUTION OF THE VERWEY TEMPERATURE DURING THE BIOMINERALIZATION PROCESS OF MAGNETITE NANOPARTICLES

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Magnetite is one of the most popular and studied ferrimagnetic compounds. In fact, it was already used by early navigators. This crystalline solid presents a characteristic sudden change in lattice symmetry and electric conductivity around 120 K. This temperature is known as Verwey temperature and depends on the compound stoichiometry. Although considerable progress has been made in the last years, the physics of this phenomenon is still under debate [1,2]. In this work, we are focusing in magnetite nanoparticles, and the goal is to identify possible influences of the particle size in the Verwey transition. However, magnetite nanoparticles are especially sensitive to oxidation, which leads to stoichiometry changes.

Magnetotactic bacteria *Magnetospirillum gryphiswaldense* biosynthesizes magnetite nanoparticles of high structural and chemical quality allowing the bacteria to orientate in the geomagnetic field, working as a “magnetic compass”. The highly precise biological control determines the shape, size, and magnetic properties of the so-called magnetosome, which consists of a magnetite nanoparticle surrounded by a 3-4 nm thick lipid bilayer membrane [3].

In this work, we exploit the well defined genetically controlled stoichiometry of the magnetite nanoparticles to study the dependence between the Verwey temperature and the nanoparticle size. We follow the biomineralization process and perform a time-resolved study, analysing particles at different times after Fe incubation [4]. The particle size is determined by transmission electron microscopy, finding a narrow size distribution, which has an evolution on time from 16 nm to 45 nm -at the end of the biomineralization process-. Magnetic characterization consists of measurements of magnetization as a function of temperature, which are performed using DC and AC (0.03-1000 Hz) magnetic susceptibility measurements in SQUID.

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REDUCTION OF THE MEAN MAGNETIC MOMENT OF NI CLUSTERS EMBEDDED IN AG

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Magnetic properties of materials change drastically from the bulk size to the nanoscale [1]. This is due to surface effects, which become increasingly important and need to be taken into account when analyzing the magnetic properties at the nanoscale.

In this work we combine experimental results with Density Functional Theory (DFT) calculations to show that Ni clusters embedded in an Ag matrix become non-magnetic below a cluster size of around 6 atoms. Experimental measurements have been performed on a DC-sputtered Ni_6Ag_{94} nanogranular thin film. The film structure investigated by means of Extended X-ray Absorption Fine Structure (EXAFS) confirms that the film is composed of sub-nanometre sized Ni particles. The magnetic analysis highlights a strongly reduced magnetic signal that is 62% lower than the bulk value. DFT calculations performed on Ni_m clusters of selected sizes (m=1 to 6, 10 and 13) embedded in an Ag bulk matrix confirm that Ni clusters below 6 atoms become non-magnetic due to charge transfer between the Ni *sp* and *d* orbitals. This explains the loss of magnetic signal observed experimentally as being due to the coexistence of small non-magnetic Ni clusters together with slightly larger ones that do hold a full magnetic moment.

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MAGNETIC NANOPARTICLES IN THE ENVIRONMENT: ORIGIN, IDENTIFICATION; AND APPLICATIONS

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Iron is the fourth most abundant element in the Earth crust, where it occurs as constituent of various minerals such as silicates, oxides, and sulphides. A small fraction of such minerals has ferrimagnetic properties and is responsible for the recording of the Earth magnetic field in past epochs. Such so-called paleomagnetic records play a fundamental role in the reconstruction of the dynamic history of our planet.

Of particular interest for Earth scientists are nano-sized ferrimagneitc iron minerals produced by environmental processes on land and in the oceans. These nanoparticles can provide very stable paleomagnetic records. Furthermore, they represent the signature of specific biogeochemical processes that are modulated by the geologic and climatic history of our planet. Notable examples are (1) the formation of maghemite (γ-Fe_2O_3) nanoparticles in soils, whose concentration in continental dust deposits reflects the alternation of cold-dry and warm-humid climates, and (2) the production of magnetite (Fe_3O_4) in freshwater and marine sediments, inorganically and by so-called magnetotactic bacteria, which is modulated by variations of the sedimentary environment, e.g. in terms of organic matter and oxygen availability.

The study of natural magnetic nanoparticles is extremely challenging because of low concentrations (1 ppm to ~1%) and co-existence of different groups of particles in terms of composition, domain states (i.e. single-domain vs. pseudo-single domain and multidomain), shape, and dispersion in a non-magnetic matrix. Recent techniques based on high-resolution first-order reversal curves (FORC) provided important improvements in the characterization of highly disordered dispersions of magnetic particles as they occur in nature. Such techniques are important for discriminating different magnetic mineral sources and the processes responsible for their formation, transport, and accumulation.

Special focus is given to some topic examples demonstrating the interdisciplinary approach needed to understand natural magnetic nanoparticles - from Earth processes to magnetic property models.

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FERRITE AND HYBRID FERRITIN-BASED NANOPARTICLES FOR BIOMEDICAL APPLICATIONS

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Magnetic nanoparticles (NPs) are excellent building-blocks for the development of innovative nanodevices with theranostic properties to be employed in biomedicine as heat mediators for magnetic fluid hyperthermia (MFH), contrast agents for Magnetic Resonance Imaging (CA-MRI) and for targeting tumor cells. The most investigated materials for these applications are ferrite NPs, whose properties can be tuned by varying size, shape and chemical composition. In this contribution, we focus on the magnetic properties and hyperthermic efficiency of various highly monodisperse mixed ferrite based nanomaterials with average size of few nanometers [1].

A key point for the use of magnetic NPs for biomedical applications is to ensure the biocompatibility of the magnetic core by a proper functionalization. In this framework, the mineralization of iron oxide (magnetite/maghemite) NPs inside the internal cavity of the human protein ferritin (NPs@HFt) represents a viable route, thanks to the high biocompatibility and the large functionalization capability of the HFt shell. However, the size constraint imposed by the internal shell diameter limits the use of this system for MFH, since, if made of pure iron oxide, NPs of 8 nm mean size are too small to provide a sizable temperature increase under an alternating magnetic field. To overcome this drawback, we developed two different strategies to improve the hyperthermic efficiency still exploiting the advantages offered by HFt. In the first approach, we increased the magnetic anisotropy of 6-7 nm NPs@HFt by doping the magnetite core with Co^{2+} (**Co-NPs@HFt**) [2]. The second approach was based on **HFt-NPs** constructs, obtained by conjugation of larger magnetite NPs (15-18 nm) from chemical synthesis with *apo*-HFt. The Specific Absorption Rate (SAR) of both materials were investigated through calorimetric techniques and correlated with structural features and magnetic properties. Both approaches were found to increase the hyperthermic efficiency of the material with respect to NPs@HFt and to ensure a high biocompatibility of the material. Moreover, *in vitro* tests highlight the importance of the cell internalization of NPs for the successful outcome of the hyperthermic treatment.

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REMOVAL OF PHTHALATE ESTERS AND PHARMACEUTICALS IN RIVER SEDIMENT BY FENTON-LIKE REACTION USING NANOSCALE SCHWERTMANNITE AS A CATALYST

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The objective of this study was to evaluate the performance of nanoscale schwertmannite on catalysis of hydrogen peroxide to generate OH· free radicals in oxidation of selected emerging contaminants (ECs). *In situ* Fenton-like process has been proven to be technologically feasible for remediation of sites contaminated by various organic compounds. In Fenton-like process, generally, iron minerals like goethite and hematite are active catalysts for decomposition of hydrogen peroxide and generation of active oxygen species, which in turn are used for oxidation of organic contaminants in contact. Recently, an iron-oxyhydroxysulfate mineral named schwertmannite was used as a new Fenton-like catalyst in the oxidation of phenol by H_2O_2 with satisfaction [1]. Thus, the novel Fenton-like reaction with lab-prepared nanoscale schwertmannite (nano-SHM) was tested in this work for oxidation of phthalate esters and pharmaceuticals in top sediment (0-10 cm below the sediment surface) collected from a river in Taiwan. To study the pH effects on contaminants removal, preliminary tests were carried out in model solutions (with pHs of 2, 7, and 10) using a mole ratio of 1:20 between nano-SHM and 0.05% H_2O_2. Experimental results showed that the novel Fenton-like reaction was effective in oxidation of target contaminants over a wide pH range. However, the performance slightly deteriorated at higher pHs. This finding further confirms that the novel Fenton-like reaction is suitable for *in situ* chemical oxidation of various organic compounds in the aquatic environment. Thus, the novel Fenton-like reaction with nano-SHM was further tested for remediation of ECs of concern in river sediment (pH = 7.53). Using a mole ratio of 1: 20 between nano-SHM and 1% H_2O_2 and a reaction time of 5 d in batch tests, it was found the removal efficiencies for di-n-butyl phthalate (DnBP), di-2-ethylhexyl phthalate (DEHP), diisononyl phthalate (DiNP), and acetaminophen (ACE) were 94%, 56%, 53%, and 100%, respectively. Therefore, the novel Fenton-like reaction with nano-SHM is considered as a viable technology for remediation of phthalate esters, pharmaceuticals, and perhaps other organic compounds in river sediments.

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MICROWAVE ASSISTED HYDROTHERMAL SYNTHESIS OF CONTROLLED SHAPE MAGNETITE NANOPARTICLES

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Magnetite nanoparticles have been investigated by several research groups due to their potential applications in mechanical engineering [1-3] and in biomedical fields [4]. Moreover, magnetite nanoparticles have recently emerged as a versatile support for catalyst immobilization, since they are inexpensive, non-toxic, chemically stable, and easily prepared from low-cost precursors [5]. It is well-established that the magnetic properties of nanoparticles are strongly dependent on their size and shape. For example, magnetic nanoparticles with non spherical shapes showed interesting anisotropic magnetic properties [6]. In this contribution, a microwave-assisted hydrothermal method for the synthesis of size and shape-controlled magnetite nanoparticles to be used as catalyst support was described. The syntheses were carried out also using oleic acid, polyvinylpyrrolidone and trisodium citrate as surfactants in order to investigate their effect on the size distribution, the morphology and the functionalization of the magnetite nanoparticles. X-ray diffraction, Fourier Transform Infrared, Thermogravimetric, Transmission Electron Microscopy analyses were performed to characterize the chemical and morphological features of the nanoparticles. On the basis of the different reaction conditions, the synthesis could be directed towards the formation of either hexagonal magnetite nanoplates with diagonal of 139±55 nm and a saturation magnetization of 65 emu/g or irregular octahedron nanoparticles with size of 60±25 nm with higher saturation magnetization up to 80 emu/g. The latter material is therefore promising for applications as transportable catalyst support.

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SYNTHESIS OF MAGNETIC ZEOLITE USING FLY ASH AND RED MUD MIXTURE

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In this study, two waste materials (red mud and fly ash) were used to synthesize magnetic zeolites at low incubation temperature. The novelty of the process is based on the use of fly ash and red mud as precursors for the one-step synthesis of zeolites with good magnetic properties, without the addition of iron oxide magnetic nanoparticles [1]. Magnetic zeolites, in fact, are generally synthesized using two methods. The first refers to precipitation of magnetic nanoparticles on the zeolite surface [2], the second involves the modification of zeolite with magnetic particles [3]. In both the cases, the addition of iron oxide magnetic nanoparticles is considered.

Red mud form during the production of alumina when the bauxite ores are subject to caustic leaching. The use of this waste material for zeolite synthesis has not been previously reported. Fly ash is a by-product of thermal power plants partly used in concrete and cement manufacturing, but in the last few years it has being used for the synthesis of zeolites [4]. The structural, microstructural and magnetic properties of precursors and synthetic zeolites formed from these two waste materials were investigated. Different types of zeolites were obtained from different fly ash/red mud mixtures and all of them exhibit sufficiently high magnetic moments, coercivity and remanence. The origins of the ferro(ferri)magnetic behavior have been correlated to the properties of precursors. The magnetic zeolites were also investigated by SEM, XRD and TEM in order to determine the crystal structure and the morphology of these synthetic products.

Magnetic zeolites are successfully used in removing contaminants from polluted water, because they can be easily separated from the medium using an external magnetic field, making the wastewater treatment simpler than applying centrifugation or filtration.

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THE COMPLEX CASE OF OBSIDIAN: STRUCTURE, MORPHOLOGY AND MAGNETISM OF MONTE ARCI OBISIDIAN

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Obsidian, also known as the *Neolithic black gold*, has been one of the most important raw material during the Neolithic, due to its mechanical properties and its workability [1]. Although it is commonly defined as a natural volcanic glass, obsidian is actually a very complex material to be studied due to the duality of its nature, i.e. amorphous and crystalline. In fact, a low fraction of crystalline phases, as either occlusions or inclusions, can be found together with a glassy matrix. In addition, the crystalline phases can be *micro-* and *nano*-structured. Therefore, obsidian can be better described as a composite material in which microcrystalline and nanocrystalline phases are dispersed into/over a glassy matrix. With the aim of studying in depth its microstructural and magnetic properties, this work proposes a multitechnique study of Monte Arci (Sardinia) obsidian based on the combined use of X-ray diffraction (XRD) and Rietveld refinement, ^{57}Fe Mössbauer Spectroscopy, magnetic measurements and Transmission Electron Microscopy (TEM and High Resolution-TEM) [2]. Rietveld analysis on XRD data highlights the dual nature of obsidian identifying, besides the main amorphous component, different crystalline phases and quantifying their content. Among the crystalline phases, iron-containing phases like biotite and a nanostructured spinel oxide phase have been revealed. In this framework, ^{57}Fe Mössbauer Spectroscopy (also under intense magnetic field), has been extremely useful because it allows us to associate a magnetic complexity to the structural one revealing the coexistence of paramagnetic, superparamagnetic and ferrimagnetic iron-based phases. Temperature dependence of magnetization, by Zero field cooled (ZFC) and field cooled (FC) protocols, and M vs H curves confirm this picture. A further level of complexity has been observed by TEM and HR-TEM analyses and related to the morphology (size and shape) and distribution of the crystalline phases into/over the glassy matrix. As a result of these observations, an exhaustive definition of obsidian should take account of all the aspects of its complexity, i.e. structure, morphology and magnetism.

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SUPERANTIFERROMAGNETISM IN MAGNETIC NANOPARTICLES

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Magnetic nanoparticles have been object of renewed interest in the last years due to their multidisciplinary interest [1, 2]. In the case of a well-isolated ensemble, the particles behave following a superparamagnetic behaviour. When interactions are present, the magnetic relaxation becomes more complex [3]. One of the first approaches in this field was carried out in goethite, a very common Fe-oxi-hydroxide for which the superantiferromagnetism (SAFM) term was coined. This mineral presents several transitions, which have been studied in detail, some of them connected to the magnetic anisotropy [4]. However, this mineral appears too complex to consider it as a case example of SAFM.

We have selected a more simple SAFM system. This is constituted by a series of Rare Earth nanoalloys of $TbCu_2$, which have been produced by inert-atmosphere milling. They have been characterised by TEM and X-ray diffraction (with sizes from 23 nm to 6 nm). An important advantage is that the use of Rare Earth elements lowers the Néel transition below RT ($T_N = 49$ K), enabling an easier characterisation [5]. To establish their magnetic character a thorough static and dynamic susceptibility analysis has been accomplished. The microscopic study has been completed with Neutron diffraction. The magnetic structure retains the bulk structure and there is an increased effect due to a moment canting ($T_f \leq 20$ K) at the surface when the particle size becomes more and more reduced. From a macroscopic point of view, there is a coexistence of antiferromagnetism in the nanoparticle core with the spin glass disorder at the shell.

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MECHANOCHEMICAL SYNTHESIS OF NANOCRYSTALLINE TERNARY METAL CHALCOGENIDES BY HIGH-ENERGY MILLING

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Ternary metal chalcogenides of the I-III-VI_2 group with extraordinary properties are suitable semiconductor materials due to their possible applications in biolabelling, photocatalysis, solar energy conversion, and light-emitting devices. Mechanochemical synthesis of nanocrystalline ternary metal chalcogenides may be a contribution into nanotechnology and materials engineering. Nanocrystalline ternary metal chalcogenides have been synthesized from corresponding metals and chalcogen powders by high-energy ball milling in a planetary mill in an argon atmosphere. Structural, surface and morphological properties were investigated by X-ray diffraction (XRD), low temperature nitrogen sorption, scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDX), high-resolution transmission electron microscopy (HRTEM) and particle size distribution method. The optical properties were also studied using UV-vis absorption and photoluminescence (PL) spectroscopy. The controlled mechanochemical synthesis of ternary semiconducting chalcogenides can be considered environmentally friendly, because a solvent-free mechanochemical procedure was performed under ambient temperature and atmospheric pressure. Therefore, it is a promising candidate for the production of nanocrystalline materials.

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MINERAL REALGAR (As_4S_4) AS AN ADVANCED NANOMATERIAL FOR APPLICATION IN MEDICINE

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Arsenic sulphide compounds have a long history of application in traditional medicine. In recent years, realgar (As_4S_4) has been studied as a promising drug in cancer treatment. The nanoparticles of mineral realgar and its combination with ZnS were prepared by one-step mechanochemical route in a planetary mill (Fritsch). The successful synthesis and structural changes were confirmed and followed via XRD and FTIR spectroscopy. Morphology of the particles was studied via SEM and HRTEM methods and the presence of nanocrystallites was verified. Their optical properties were also studied.

For biological testing the prepared As_4S_4/ZnS nanocomposites were further milled in a circulation mill (Netzsch) in the water solution of Poloxamer 407 (0.5 wt%) in order to obtain stabile nanosuspensions. Size of the particles in the nanosuspensions were ~150 nm determined by photon cross-correlation spectroscopy method. The stability of the nanosuspensions was determined via particle size distribution and zeta potential measurements, confirming their stability without provoking any physico-chemical changes for several months. The anti-cancer effects were tested on two melanoma cell lines A375 and Bowes.

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EFFECT OF HEAT TREATMENT ON THE STRUCTURAL AND TEXTURAL PROPERTIES OF HALLOYSITE

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Halloysite the naturally occured nanotube, is a dioctahedral 1:1 clay mineral. The crystal structure of halloysite consists of SiO_4 tetrahedral layer and AlO_6 octahedral layer. There are water molecules between these two layers. Halloysite has widely used in many industrially applications as adsorbent and catalyst. Recently, investigations on halloysite gained a growing importance due to its nanotubular structure. [1-4]

In this study, the natural halloysite was obtained from Eczacıbasi Esan Co Ltd., Turkey. The chemical composition is SiO_2 = 43% and Al_2O_3 = 38%. The effects of heat treatment on the structural and textural properties of halloysite has been investigated. Calcination temperature (200, 400, 650 and 900 °C), calcination time (2, 4, 6 hr), and heating rate (10, 20, 40 °C/min) was selected as parameters. After heat treatment, samples were characterized by XRD, FT-IR, SEM and nitrogen adsorption/desorption.

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SULPHATE REMOVAL OVER CHEMICALLY MODIFIED ALUMINOSILICATE MINERALS

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Sulphate removal from mine waters is a current problem. There are several methods to treat the sulphate contaminated effluents such as chemical precipitation, biological treatment, membrane technologies (reverse osmosis, electrodialysis), ion exchange and adsorption but these methods have some disadvantages and limitations. Traditional and widely used chemical precipitation, for example, is not able to remove all sulphates from mine waters and in addition, it creates sediment as a secondary waste. On the other hand, adsorption is not suitable method as only method for wastewaters that contain up to thousands milligrams per litre of sulphate [1,2]. Therefore, adsorption could be finishing treatment after chemical precipitation.

Zeolites are well known for their ion exchange capacity. Zeolites are hydrated aluminosilicate minerals having cage-like structures (Si-O-Al framework) with large internal and external surface areas. There are more than 50 different natural zeolite types and many others have been synthesised [3-5]. Similar to zeolites, geopolymers also consist of a polymeric Si-O-Al framework. The main difference from zeolite is that geopolymers are amorphous instead of crystalline. Geopolymers are formed by the polymerization of aluminosilicate mineral in an alkaline solution. For example metakaolin or wastes such as fly ashes, active clays and slags can be used as raw material for manufacture geopolymers [6-8].

In this study, the ability of chemically modified aluminosilicate minerals (zeolites and geopolymers) to uptake sulphate from aqueous solutions via sorption was studied. Sorption experiments were carried out in a batch reactor. The effects of different variables (initial pH, initial sulphate ion concentration, adsorbent dosage, temperature and time) on the removal of sulphate were studied. Experiments were done by using model solutions and by mine waste water, which was pretreated with precipitation. Sulphate concentration in this mine water was 800-900 mg/L. The effect of pH on sulphate removal was studied over a range of 2-10. The effect of initial solution concentration was studied at optimum pH with different initial concentrations ranging from 25 to 1000 mg/L of sulphate. The rate of sorption of sulphate was studied at different time intervals between 1-1440 min. Also the effect of temperature (10, 23 and 40 °C) and adsorbent dosage were studied (0.5-25 g/L). Sorbent was separated from the solution and sulphate concentrations were analysed by ion chromatography.

Based on the results, chemically modified aluminosilicate minerals are promising materials in the removal of sulphate.

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INFLUENCE OF POLYELECTROLYTES ON DISPERSION STABILITY OF LAYERED TITANATE NANOWIRES

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Multifunctional layered titanate nanowires are used in several applications ranging from sensing through solar cells to catalysis. Although they have been extensively investigated in solid state, there is a lack of reliable studies focusing on their dispersion characteristics. Formulation of such colloids plays a key role in applications relying on stable dispersions of the titanate nanowires, however, the removal of the nanowires from heterogeneous systems by aggregation and subsequent sedimentation can be an important issue in others. To deal with this challenge, the present study focuses on formulation of aqueous titanate nanowire dispersions with polyelectrolytes which are one of the most powerful stabilizing agents for aqueous dispersed systems consisting of charged particles.

The titanate nanowires were positively charged at low pH and they reverse their charge under alkaline conditions. Accordingly, positively charged poly(diallyldimethyl ammonium) chloride polyelectrolytes adsorbed strongly on the nanowires of negative surface charge at pH 9 leading to charge neutralization and subsequent charge reversal at appropriately high polyelectrolyte doses as it was revealed in electrophoretic measurements. The adsorbed amount increased with the ionic strength due to the reduced repulsion between the adsorbed polyelectrolyte chains at higher salt concentrations. These surface phenomena resulted that the titanate nanowire dispersions were stable at low and high polyelectrolyte doses where the particles possessed charge as indicated by high stability ratio values determined in time-resolved dynamic light scattering experiments. The stability ratios were close to unity, i.e., the nanowires aggregated rapidly, near the charge neutralization point where the nanowires had an overall charge of zero. These interparticle interactions can be explained qualitatively well with repulsive double layer and attractive van der Waals forces as predicted by the classical theory developed by Derjaguin, Landau, Verwey and Owerbeek. If one covers the nanowires' surface with polyelectrolytes, one of the main advantages of such coating was found to be that the polyelectrolyte coverage resulted in a higher stability of the dispersions, i.e., higher salt concentration was needed to aggregate the covered titanate nanowires than the bare ones. Similar results obtained with the positively charged nanowires in the presence of poly(styrene sulfonate) polyelectrolyte of negative charge under acidic conditions at pH 3 indicating a generic nature of these findings. In summary, aggregation of layered titanate nanowires in aqueous dispersions can be tuned with appropriate amount of polyelectrolytes and such samples can be formulated according to the desired goals.

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KEROLITES AND SILICA SMECTITE MIXTURES: RELATION BETWEEN STRUCTURES AND APPLICATIONS WITH FOCUS ON PURIFICATION AND SEPARATION PROCESSES

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Two types of unique clays are presented with respect to their structure and their applications, clays exhibiting according to the literature kerolite-stevensite [1-4] and clays with structure, which can be described as a natural mixture of smectite with silica [5-7]. For both clays first the results of a detailed clay chemical structure characterization are presented. Then it will be derived, how the structures lead to the suitability for special applications in purification and separation process.

The kerolite based clays exhibit a high specific surface (typical BET surface area 280 m^2/g) in connection with a very low negative layer charge, making them suitable for adsorption of organic molecules from aqueous solutions. Applications in the field of mycotoxin adsorption in animal feed as well as enzymatic reactions have been identified for such clays.

Clay based on natural silica smectite mixtures also exhibit a high porosity and a high BET surface area (typically 240 m^2/g). The connection of the cation exchange capacity, typical for montmorillonites, with the high porosity and a low extend of swelling make these clay suitable for separation processes in aqueous systems, e.g. for removal and separation of protein, as well as for separation and purification processes in organic media like solvents, edible oil and biodiesel. An example for the latter case is the removal of impurities and side products from biodiesel.

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COMPOSITE FIBROUS STRUCTURES FOR REDUCTION OF BIOFOULING IN DEEP-BED WATER FILTERS

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Growing demand for water, combined with rapidly increasing population, makes the world eventually seriously consider the issues of water reclamation and reuse. Investment in treatment technologies requires developing new products to meet limited high-quality fresh water demand [1]. Low throughputs from membrane based filtration processes and expensive high-pressure fluid pumping drive engineers to explore highly porous depth media to remove particulate matter as well as pathogens. With a good understanding of bacteria's and solid particle's behavior in depth filters it is possible to broaden the application of this low-pressure separation technique. Fibrous composite depth filters are used for efficient, low-pressure drop, removal of microorganisms and abiotic particulate matter. One of the unsolved problems in the process is the reduction of fouling and biofouling effects that significantly reduce the filter performance. In our solution the problem is solved with fiber surface modification of with antibacterial/antifouling substances, such as Ag and/or ZnO nanostructures. Two methods of modification were used. The melt-blown technique enables direct introduction of nanoparticles towards fiber surface when composite granules of polymer and nanoparticles, prepared in another process as the precursor, are processed in the extrusion and fiber formation. The surface structure of the composite fiber is controlled. Another technique of fiber surface modification is connected with the formation of ZnO nanowires. Pure polymer fibers obtained in the melt-blown process first were pre-treated in argon plasma environment causing extensive etching and implantation of oxygen and hydrogen containing polar groups. After nucleation of ZnO nanoseeds, the controlled nanowire growth in the hydrothermal process commenced. A composite polypropylene fiber with a varied surface morphology was examined in antibacterial/antifouling tests via a growth inhibition assay. E.coli and B. subtilis were chosen as model microorganisms to grow in Luria-Bertani broth. Biofilms removed from the fiber were examined with OD_{550} and FTIR tests. The inhibition curves, for different samples of pure and composite polymer fibers were obtained. The best morphology of the composites of polypropylene with ZnO and Ag nanoparticles on the surface and composites with ZnO nanowires were used for the production of regular, commercial filter cartridges. Filters made of regular and composite fibers using our technology [2] were tested in the purification of Chriesbach (Dubendorf, Switzerland) river water. Results show a significant reduction of the filter fouling for composite fibrous structures during long-term tests.

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SEM EDS SILICATES RECOGNITION IN HISTOLOGICAL SAMPLES OF HUMAN NEOPLASIA

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Biological samples from 4 patients affected by carcinoma were investigated from a mineralogical point of view in order to ascertain presence of solid particles that could have caused their disease. These patients during their life have had frequent contact with dusty environments with probable presence of asbestos minerals, heavy metals particles and other potentially dangerous substances.

Four histological samples were prepared from the suspected carcinoma masses removed from kidney (2 patients) and from colon (2 patients).

SEM investigations revealed the presence of various particles, from 200 nm up to 30 µm in size, containing metals, metal alloys, and minerals (sulfates, phosphates and silicates). In particular there were recognized very little particle of metals (Al, Zn, Ti, Ni) and metal alloys (Cu-Zn, Cu-Fe-Sn, Ni-Cu-Zn, Fe-Cu) that were always associated with silicates, the most commons being feldspars and Mg-Fe silicates.

Quantitative chemical analyses of the silicates have been performed on the basis of cationic proportions. Difference with respect to theoretical were ascribed to the presence of nanoparticles forming the analysed grain (as it was the case of complex silicate phases containing Al, Mg, Na, K, Ca, Fe, Ti, and S) or to the intense mineral alteration during its permanence in the human body.

The chemical composition of these particles can be related to minerals as talc, biotite, amphiboles (amosite, richterite(?)), pyroxene, olivine, wollastonite, feldspars (albitic and andesinic plagioclase), zircon, chrysotile, apatite, barite, and xenotime (sometimes with appreciable Eu quantities).

There were observed the presence of many rounded shaped particles having compositions comparable with amphiboles. Rare acicular fibres (likely amosite and chrysotile), with length from 6 to 32 µm, were observed only in the histological specimen of the patient that underwent surgery for colorectal cancer. These observations and the very rare occurrence of finer asbestos' fibers with respect to other silicates (i.e. pyroxenes, amphiboles, feldspars, and zircon) might be related to their different degree of alteration.

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THE CONTRIBUTION OF XANES SPECTROSCOPY TO PALEOCLIMATE RECONSTRUCTIONS FROM ANTARCTIC ICE CORES

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Mineral dust aerosol has an important effect on the Earth's radiation budget, as it can both scatter sunlight back to space (negative radiative forcing), and absorb solar and infrared radiation (positive forcing). Thus, in opposition to the greenhouse gases, the combination of absorption and reflection of solar radiation caused by dust microparticles can lead to a net (longwave and shortwave) negative radiative forcing at the surface and at the top of atmosphere.

Mineral dust transported long-range from the Southern Hemisphere continental landmasses to the remote East Antarctic plateau travels in the high troposphere and interacts with climate. Aeolian processes occurring during atmospheric transport from source areas to polar ice sheets are responsible for the strong reduction of dust concentration and size in the polar atmosphere; besides concentration and grain size, other properties that influence the dust radiative effect such as mineralogy and shape of minerals are still very poorly known.

On such challenging samples, we performed synchrotron radiation spectroscopic analyses as X-ray Absorption Near Edge Structure (XANES), which can provide new information inaccessible with other standard analytical techniques. We present new data from Talos Dome (72°49'S, 159°110'E; 2315 m a.s.l.) spanning the last two climate cycles (ca. 250 kyrs) and reconstruct dust geochemistry and elemental coordination state in selected climatic periods. Dust composition changes in time provide an important contribution to the scientific knowledge on palaeoclimate changes in near coastal regions of the Antarctic ice sheet and novel information on possible changes occurred at the source areas.

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ARCHAEOMETRIC AND TECHNOLOGICAL INVESTIGATIONS OF "SANT'IMBENIA AMPHORAE" FROM THE NURAGIC SITE OF SANT'IMBENIA (ALGHERO, SARDINIA)

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The Nuragic site of Sant'Imbenia in Alghero (north-western Sardinia, Italy) was approximately inhabited between the 14th and the 7th century BC. During the last period of its life, in Sant'Imbenia lived natives together with foreign people, i.e. Phoenicians and, probably, Greeks. Exchanges among them, together goods, involved also cultural aspects and technologies [1].

The aim of the work is to identify the trades and contacts of this settlement through the provenance of clays and the technology of ceramic.

Particularly, the study takes into account the results of the archaeometric analyses of the so-called "Sant'Imbenia Amphorae" found in the site during the excavations carried out in 2008, 2009, 2010, 2011, 2012 and 2013. Sant'Imbenia Amphorae, in fact, are considered "an open question" by the archaeologists either for production area and chronology [1-5]. Their production is dated back from the end of 9th century BC until, at least the 7th century BC. Craftsmen inspired to oriental models and amphorae were probably also used to store and trade wine. In fact, these types of amphorae have been recovered in various sites of Sardinia as well in Mediterranean coasts, as for example in Cartago and in Southern Spain [4].

Ceramic samples were observed under a stereomicroscope to identify the treatments applied by potters to smooth the surfaces. A first determination of samples colour and texture was carried out by means of Munsell® Soil Color Charts. A portable Minolta CM700d spectrophotometer was used to determine the chromatic coordinates of ceramic fragments and to detect possible differences between samples in terms of their composition or production process. Later the artifacts were studied by X-ray fluorescence, X-ray powder diffraction and optical microscopy to analyze their chemical, mineralogical and textural features and compare them with local raw materials.

Our results reveal that the amphorae are characterized by four different typologies. The first and the second, more abundant, are compatible with a local production which results relevant and specialized, the other two suggest an import from different sites. The four groups differ in the raw materials used and in the quantity of non-plastic component added. The groups we consider of local production are characterized by a high quantity of non-plastic component with irregular shapes and dimensions, while the other two have a lesser amount of non-plastic component and a better morphological distribution. It seems there are no differences in the surface treatments: amphorae can show a slip, an engobe or be smoothed.

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EFFECT OF ALUMINA FILLER ON PROPERTIES OF BOROSILICATE GLASS COMPOSITE SEALANTS

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The effects of Al_2O_3 filler on thermal (viscosity and coefficient of thermal expansion) and electrical conductivity of SrO-La_2O_3-SiO_2-B_2O_3-Al_2O_3-R_2O (R= Na and K) glasses have been studied with a view to use as sealants of planar solid oxide fuel cells. The interaction of fillers with glass after sintering and further heat treatment has also been investigated by XRD, electrical conductivity and FTIR spectroscopy analysis. All of the FTIR data showed that the filler partially dissolved in the glass during sintering and heat treatment resulted in strengthening of glass structure via conversion of non-bridging oxygen to bridging oxygen. Electrical conductivity measurements also supported the role of the alumina filler in strengthening of glass structure. Addition of alumina filler found to be useful for long-term high temperature operation of glass-based sealants for solid oxide fuel cell application.

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