ZEOLITE 2014

9th International Conference on the Occurrence,
Properties and Utilization of Natural Zeolites

Book of Abstracts

Edited by Aleksandra Daković, Marina Trgo
and Alessio Langella

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Preface

This volume contains abstracts submitted for oral and poster presentations at Zeolite 2014, the 9th International Conference on the Occurrence, Properties and Utilization of Natural Zeolites. The conference was held 8th - 13th June 2014 at Chamber of Commerce and Industry of Serbia in Belgrade, Serbia.

Zeolite 2014 is the latest in a series of conferences organized under auspices of the International Natural Zeolite Association (INZA), formerly the International Committee on Natural Zeolites (ICNZ). The initial conference was in Tucson, Arizona, USA (Zeolite '76); subsequent conferences were held in Budapest, Hungary (Zeolite '85); Havana, Cuba (Zeolite '91); Boise, Idaho, USA (Zeolite '93); Ischia (Naples), Italy (Zeolite '97); Thessaloniki, Greece (Zeolite '02); Socorro, New Mexico, USA (Zeolite '06); and Sofia, Bulgaria (Zeolite 2010).

The abstracts herein are organized alphabetically by first author. An author index at the end of the volume lists the page number of each author's abstract(s).
This Book of Abstracts contains the contributions of researchers from 40 countries around the world.

This volume of Zeolite 2014 abstracts is dedicated to the memory of Dimiter I. Tchernev, who had an important role in the birth of the ICNZ and INZA, in which he officiated as Secretary-Treasurer for many years.

Marina Trgo
Aleksandra Daković
Belgrade, Serbia
June 2014

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In Memoriam

Dimiter I. Tchernev (1930-2012)

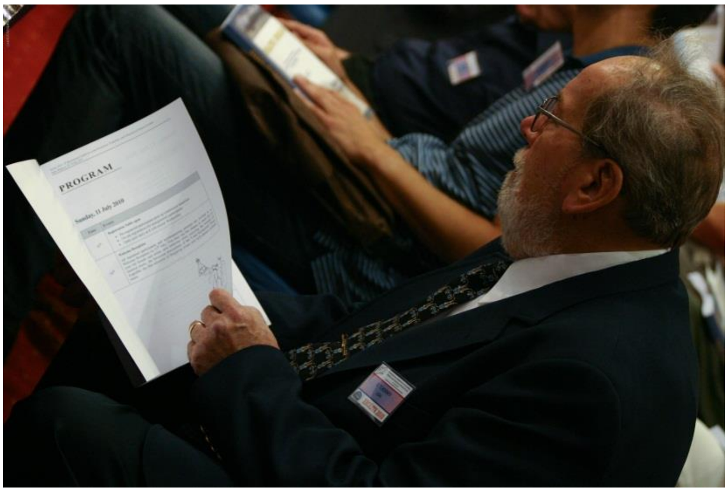
Dimiter Tchernev was born in Bulgaria in 1930 and spent most of his life in the US. He received his doctorate in electrical engineering from Massachusetts Institute of Technology (MIT) in 1965 and became interested in solar energy in 1970, when he was teaching at the University of Texas, Austin. His great passion for this field of research ultimately led to the foundation of the Zeopower Company of Natick, MA, that saw him as the Chief Executive Officer (CEO) until his death on 5th September 2012.

He liked to recall that this passion was, as it often happens, fortuitous. “One of my students threw a pellet of zeolite, loaded with water, into the hot furnace. After the dust cleared up from the explosion, I decided there was an awful lot of energy stored in that little pellet. It must be good for something…”. This led to his invention of a refrigerator powered exclusively by solar energy. The device, shaped like a wishing well, had solar collectors on its small pitched roof and a four-cubic-foot storage compartment underneath. This idea led him to deposit several patents on solar refrigerator systems and heat pumps energized by low-grade heat sources.

His strong connection with natural zeolites is also witnessed by a large number of scientific reports in International Journals, making him one of the most active researchers on this peculiar type of minerals. He also had an important role in the birth of the International Committee on Natural Zeolites (ICNZ) that was subsequently replaced by the International Natural Zeolite Association (INZA), in which he officiated as Secretary-Treasurer until his death.

We remember Dimiter as a kind, brilliant man and scientist who had a wonderful sense of humor and a great willingness to contribute his time and energy to ICNZ and INZA.

Alessio Langella
INZA President



Frederick A. Mumpton (1932-2004)

INZA has been without its founder and leader emeritus, Professor Fred Mumpton, for over ten years, yet we recognize his contributions and feel his influence to this day. As many INZA members recall, the predecessor of INZA, ICNZ, was formed at Zeolite ’76 in Tucson, Arizona, by Fred and his colleagues (making INZA 38 years old during Zeolite 2014). It was during Fred’s career that geologists recognized that zeolites were more than “white minerals in black rocks,” that they existed in large, massive deposits that were of economic and geologic importance. Fred dedicated the latter part of his career to advancing natural zeolite science and to encouraging scientists, young and old, in their studies of these fascinating minerals. On this 38th birthday of INZA, we remember Fred’s continued dedication to natural zeolite studies and to the premise that INZA is open to any person interested in any aspect of natural zeolites.

David L. Bish
Bloomington, Indiana, USA

Invited Papers

Applications of zeolite science to problems in rare earth element research

L. S. Campbell[1], A. Dyer[2], N. J. G. Pearce[3] and S. Chenery[4]

[1]*Sch. Earth, Atmospheric and Environmental Sciences, University of Manchester, Williamson Building, Oxford Road, Manchester M13 9PL, UK; E-mail: linda.campbell@manchester.ac.uk*
[2]*Dept. Chemistry, Loughborough University, Ashby Road, Loughborough, Leicestershire LE11 3TU, UK.*
[3]*Dept. Geography and Earth Sciences, Aberystwyth University, Penglais, Aberystwyth, Wales, SY23 3DB, UK.*
[4]*British Geological Survey, Keyworth, Nottingham, NG12 5GG, UK.*

Introduction

Twenty-first century technological advances have dramatically accelerated the global demand for rare earth element (REE) resources. Although ore grades and reserves of many REE deposits worldwide are known, the dominant producer remains as just one country, China. In recent years, dramatic price fluctuations have intensified attention on the security of supply of REE resources, and although such geopolitical factors are important, other issues have been also been recognized. These include ore deposit locations, the complexity and diversity of geological occurrences, understanding geochemical mobilities, mineralogical constraints (intergrowths, refractory phases, associated radionuclides), element separation challenges, and all the concomitant environmental and economic risks connected with extraction and mineral processing.

Zeolite science, and in particular the natural zeolite research community, are well-placed to address some of these problems due to decades of high quality research on zeolite minerals and alkaline environments. Here we describe some research in progress which aims to examine REE behaviours in alkaline fluid-mineral-rock systems. Our approaches include trace element analysis of zeolite minerals (a) in volcanic tuffs and (b) in hydrothermal "cavity" type zeolites. The intention is to be able to align these data with the advanced understandings of zeolite stabilities in relation to major element compositions, pH and temperature constraints (e.g. Chipera and Apps, 2001, Langella et al., 2013), ultimately to lead to additional predictive value from zeolitic trace element signatures. Fundamental studies of ion exchange characteristics are also being undertaken in experiments to determine mineral-fluid distribution coefficients for individual rare earths.

Analytical Methods and Challenges

Zeolitized tuffs from Italy and Tanzania were impregnated with an ultra-clean, low-viscosity resin, then cut as 50-100 μm thick sections and gently polished. Vein and other cavity zeolite samples were similarly prepared as multiple grain-mounts. Preparatory optical and electron microscopy determined locations for analysis. Although at present unavailable, a fully quantitative electron microprobe method (wavelength dispersive spectrometry, WDS) is being developed. This will closely address analytical challenges specific to zeolites; beam damage related to their hydrated nature, quantification of light elements (Na and O), variations in R (Si/(Si+Al), and potential peak overlaps.

Two distinct laser-ablation (LA)-ICPMS methods were used in the present study, according to the different priorities of the samples. For the tuffs, the microcrystallinity, textural and mineralogical diversity required high spatial resolution (14μm ablation craters) and high trace element sensitivity and so we applied the volcanic glass method of Pearce et al., (2011) to zeolites, *in situ*.

For the grain mounted cavity zeolites, larger craters (100μm) helped to achieve a compromise between trace element detectability and the possibility of simultaneous determination of a wider range of analytes. In the absence of Al data (tuffs), all results were calibrated using Si as the internal standard.

Results and Discussion

Relationships of the REE to the alkali elements were examined (Figure 1). In the Italian Tufo Lionato, an apparent coupling between Cs and the REE was found, to a maximum threshold level of REE. The Tanzanian phillipsite tuff displayed a positive correlation between Ba-Sr, but no clear patterns with the alkalis. For hydrothermal phillipsites from various world locations, K-REE substitution is suggested.

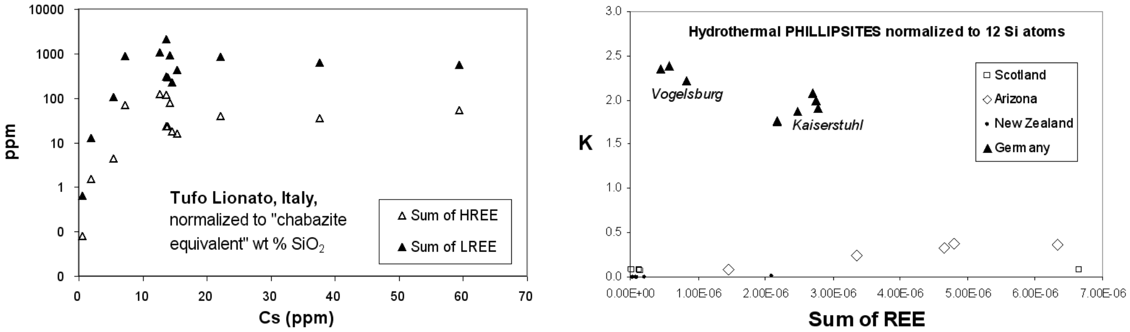


Figure 1. Left: shows an apparent coupling between the alkali elements and the REE; Right: gives K-REE substitution relationships in various hydrothermal phillipsites

All tuff samples displayed light-REE enriched chondrite normalized patterns, and generally low Gd/Lu ratios. Preliminary evaluation of high field strength element (HFSE) data from the tuffs is suggestive of the presence of micro-inclusions of HFSE minerals as separate phases; e.g. oxides and silicates such as ilmenite and zircon. There are insufficient data to be able to further interpret the signatures, but if accompanying data for unreacted volcanic glass becomes available, reaction processes and fates of different trace elements might be elucidated. The roles of alkali cations and different anionic ligands for REE mobility are of particular interest.

This reconnaissance study demonstrates considerable diversity in natural zeolite trace element compositions from around the world, indicating major opportunities for research development. Clarification is needed with microprobe and other data as to exactly what the signatures represent. However, it has been established that both tuff and cavity zeolite minerals and their ion-selective properties have the potential to contribute to fluid modelling studies for understanding fractionation and transportation processes of the REE during fluid-rock interaction. Applications of these studies could extend to greenfield resource exploration when used in conjunction with “Earth system” geological context information (Campbell et al., 2012).

Acknowledgments

Italian tuffs were collected with the assistance of *Goldschmidt Geochemistry 2013* field leaders, Conticelli, Avanzinelli, Giordano and Cioni, and the Tanzanian sample was supplied by the University of Berkeley, USA (collected by the late R. Hay). Academic and technical colleagues at the University of Manchester are thanked for preparations and discussion. The support of the UK Mineral Industry Research Organization and NERC grant NE/L002418/1, together with the kind invitation of the INZA are gratefully acknowledged.

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Natural zeolites - A treasure in zeolite science

R. X. Fischer

Fachbereich Geowissenschaften, Universität Bremen, Klagenfurter Straße, D-28359 Bremen;
E-mail: rfischer@uni-bremen.de

Zeolites belong to the most important classes of materials with main applications as catalysts, e.g., in oil refinery, adsorbents and as ion exchangers, e.g., for the softening of water with a production of more than 1 million metric tons per year just as an additive to laundry detergents. Similarly, it is used for drying and purifying gasses, cleaning up nuclear wastes, adsorbing odors, and even for clotting blood applied to large open wounds. The first crystal structure determination of a zeolite-type compound was published by Jaeger (1929). More than 80 years later Masters and Maschmeyer (2011) pointed out that zeolites are a technological cornerstone of our age because of their outstanding properties, especially in catalysis and ion exchange. The basis of their usefulness is their porous structure.

Despite the fact, that most of the commercially available zeolites are synthetic products, our knowledge on the crystal chemistry of zeolites is based to a large extent on natural zeolites due to their appearance as single crystals suitable for X-ray and neutron diffraction studies. About 1,500 crystal-structure descriptions of zeolite-type minerals are published in the literature as listed in the database ZeoBase (Baur and Fischer, 2010). The systematics of natural zeolites is described in a standardized form and main findings are summarized. The problem of interpreting occupancies of statistically distributed atoms is addressed and possible solutions for their evaluation are presented.

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Natural zeolites in extraterrestrial environments and potential implications

V. J. Inglezakis[1] and A. A. Zorpas[2]

[1] *Nazarbayev University, School of Engineering, Chemical Engineering Department, Astana, Republic of Kazakhstan; E-mail: vasileios.inglezakis@nu.edu.kz*
[2] *Cyprus Open University, Faculty of Pure and Applied Science, Environmental Conservation and Management, Nicosia, Cyprus*

This paper presents the potential space applications and occurrence of zeolites and similar minerals in extraterrestrial environments and the implications of such discoveries. The paper focuses on the Mars case but available data on Moon and Titan are also discussed. The relevance of asteroids is also discussed. The available research demonstrates the amazing implications of the existence of zeolites in other bodies in our solar system and the equally extraordinary potential for utilization of these minerals for sustaining human settlements in such hash and hostile environments.

Porous materials as host of active products: experimental and theoretical studies

A. Rivera

Zeolites Engineering Laboratory, Institute of Science and Technology of Materials (IMRE), University of Havana, 10400 Havana, Cuba; E-mail: aramis@fisica.uh.cu; aramis@imre.oc.uh.cu

The use of porous materials in different areas is a topic of great interest in today's materials science. Among them, zeolites and clays are attractive options due to their exciting properties and low cost. They have shown to be friendly with both the human body and the environment.

This work reviews current and potential applications in medicine of drugs based on porous minerals such as Cuban natural zeolites and their modified forms, and clays. Also their use in the removal of organic pollutants. Our goal is to offer a broad picture of our main results aimed at the development of new porous materials with potential pharmaceutical and environmental applications through ion exchange and adsorption processes.

We first examine zeolite-based antacids, in particular natural clinoptilolite, and their interactions with conventional drugs. Next, we discuss the potential of modified natural zeolites to slowly release ions of medical interest, and also as drug-carriers for the slow release of conventional drugs. We also present preliminary evidence pointing to the anti-tumor potential of Cuban natural clinoptilolite. We then approach our studies on the use of acid natural clinoptilolite in the adsorption/separation of *n*-paraffins, and the effect of acid treatments on the structure of the natural and sodium clinoptilolite in connection with its physical chemical properties involved with practical applications. Finally, we evaluate the use of clays as model drug support for slow release systems, and in the capture of organic contaminants from waste water.

Contributed Papers

Adsorption of eriochrome black T on MnO_2 – coated zeolite

D. M. Aguila, M. V. Ligaray, R. V. Mariano, H. D. Mendoza, E. M. Olegario and R. J. Pagdingalan

Department of Mining, Metallurgical and Materials Engineering University of the Philippines, Diliman, Quezon City, Philippines; [1]E-mail: eleanor.olegario@gmail.com

Introduction

Azo dyes, the most widely used organic colorants, are utilized in textile, cosmetic, dyestuff and paper industries (Püntener and Page, 2004). Their molecular structure has one or more nitrogen-nitrogen double bonds, which can form amines. Some amines are harmful to humans due to their carcinogenic potential. Many processes are employed in color removal, and one of them is adsorption (Weber, 1974). Commonly used adsorbents are activated carbon, chitin, sand and zeolites. Zeolite has been widely used in adsorption studies (Akgül & Karabakan, 2011). Its surface can be modified for higher selectivity, also adsorbent coated with Mn has larger surface area and is more efficient than uncoated adsorbent (Djomgoue et al., 2012 and Guha et al., 2001).

The objective of this study is to determine the effectivity of manganese oxide-coated zeolite (MOZ) in removing an azo dye Eriochrome Black T (EBT) in a wastewater model at its natural pH. Kinetic and isotherm studies have been performed using batch process.

Experimental Methods

1. Adsorbent preparation. Powdered zeolite sample mainly composed of mordenite was received from Saile Industries, Philippines. Placed in a beaker, the zeolite was contacted with boiling $KMnO_4$. Then, HCl (37.5% -wHCl/-wH_2O) was added dropwise to form MnO_2. After stirring for 1 h, it was then filtered and washed with distilled water until pH 7.0 was reached. It was dried at room temperature and stored in a pp bottle until further use. **2. Adsorbate**. EBT was used to prepare 1000 ppm stock solution by dissolving 1 g of the dye in 1 L distilled water in a volumetric flask. From the stock solution, 20, 40, 60, 80 and 100 ppm solutions were made. **3. Batch Adsorption**. Batch adsorption experiments were performed in agitated vials in shaking water bath at constant temperature (30˚C) and at 150 rpm. A volume of 25 ml of the model wastewater with 20 ppm EBT and 0.1 g of the adsorbent was put in the vials with varying time. The isotherm experiment was evaluated by contacting 0.1 gram of MOZ and 25 ml of the pollutant at different concentrations (40, 60, 80 and 100 ppm) for 12 hours. **4. Analytical methods**. EBT concentrations of adsorbed samples were determined using UV-vis spectrophotometer (Shimadzu UV-Vis Mini 1240) set at 530 nm wavelength.

Results and Discussion

The batch adsorption studies in Figure 1(a), shows the removal of EBT dye by MOZ, a zeolite composite, reached up to ~80 % removal. This indicates the presence of readily available functional groups of the adsorbent. The adsorbate attaches itself to the binding sites on the surface of MOZ until it became saturated. This slowed down the EBT uptake of the MOZ until the system reached equilibrium after 12 hours and remained constant until 24 hours (Akgül & Karabakan, 2011).

Table 1. Rate of adsorption, correlation coefficient, and theoretical EBT uptake of pseudo-first order, pseudo-second order, and intra-particle diffusion models

Pseudo-first			Pseudo-second			Intra-particle		
k_1	R^2	qe_{theo}	k_2	R^2	qe_{theo}	k_i	R^2	qe_{theo}
0.499	0.980	3.86	0.126	0.833	3.56	3.428	0.948	8.37

The pseudo-first order kinetic model has the highest correlation coefficient, R^2, with a value of 0.98, which indicates that physical adsorption is the rate-limiting mechanism of the EBT/MOZ system.

The theoretical values of the adsorption capacities of the kinetic models at a given time were compared to the actual values which were shown in Figure 1(b). Adsorption capacity is defined as the EBT uptake of MOZ.

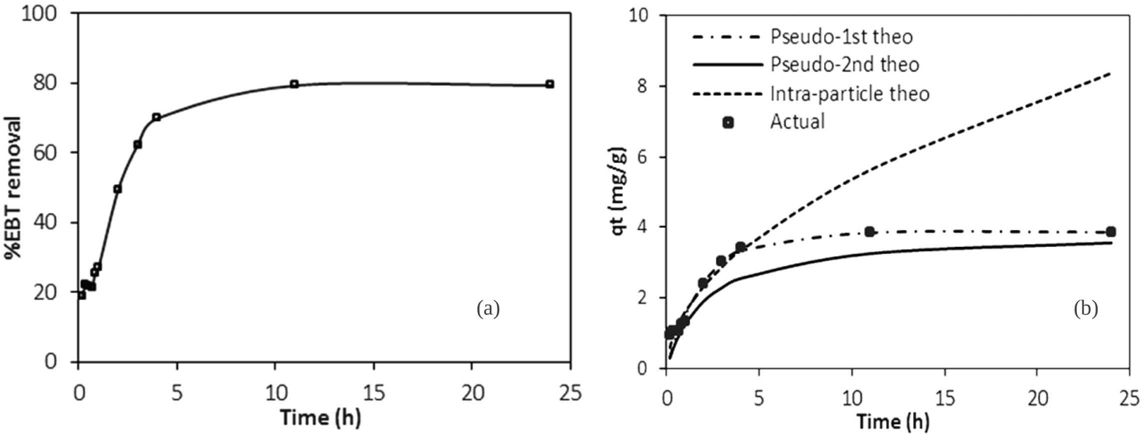

Figure 1. (a) Removal percentage of EBT at a given time by MOZ and (b) Adsorption capacity of MOZ

The energy of adsorption was calculated from Dubinin-Radushkevich (D-R) model of adsorption which resulted to 0.01 J/mol. This indicates physical adsorption (< 8kJ/mol). Since the kinetic studies determined that physical adsorption was the rate-limiting mechanism, this confirms that only physical adsorption occurred during the process.

Isotherm studies, on the other hand, were done using Langmuir, Freundlich and D-R isotherm models to fit the results.

Table 2. Adsorption parameters and correlation coefficients of Langmuir, Freundlich, and Dubinin-Radushkevich isotherm models

Langmuir			Freundlich			D-R			
K_L	q_{max}	R^2	K_F	1/n	R^2	β	qm	R^2	E
0.011	12.35	0.096	0.342	0.654	0.408	5E-5	4.768	0.287	0.01

Table 2 shows the parameters and correlation coefficient of the isotherm studies of the three previously introduced models. Freundlich showed the highest R^2 which has the best fit with an R^2 of 0.408. This indicates that more than two functional groups are present on the surface of the adsorbent, MOZ, and attract the EBT molecules. FTIR studies from literature (cite proper reference) have shown that hydroxyl groups, NO_2 groups, –C=C– aromatic, and $–SO^{3-}$ groups from the adsorbent which was investigated exhibited band changes portraying possible occurrence of adsorption of EBT (Crupi et al, 2006 and Mohan et al, 2006). This means that it is possible for EBT to attach itself to more than two functional groups.

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Simultaneous removal of *Escherichia coli* and heavy metals from water in batch and fixed bed column systems using silver modified clinoptilolite

L. O. Akhigbe, S. K. Ouki and D. P. Saroj

University of Surrey, Guildford, Surrey, UK GU2 7XH; E-mail: l.akhigbe@surrey.ac.uk

Introduction

The use of silver modified zeolites for water and wastewater disinfection has been investigated and reported in literature (De la Rosa Gomez et al., 2008; Copcia et al., 2011; Krishnani et al., 2012). Natural zeolites are effective adsorbents which are highly selective towards metal ions (Wang and Peng, 2010).

In this study batch and column experiments were conducted to investigate the performance of silver modified clinoptilolite for the simultaneous removal of *Escherichia coli* and heavy metals from water.

Experimental Methods

Silver modified clinoptilolite (SC) prepared by an ion exchange method in a silver nitrate solution was used to treat water spiked with 0.5 mg/l of each metal (Pb^{2+}, Cd^{2+} and Zn^{2+}) and 10^8-10^{10} CFU/100ml of *E. coli*. Batch experiments were conducted by shaking 0.2 g of zeolite in 100 ml solution at pH 5 to avoid metal precipitation. The fixed bed column experiment was performed using a column filled with 2 g of SC (bed height = 1cm) with the influent continuously fed at a flow rate of 2ml/min. Membrane filtration method was used for enumeration of *E. coli* and metal analysis was performed using inductively coupled plasma-optical emission spectrometry (ICP-OES).

Results and Discussion

The results of the batch experiments indicate that the SC exhibited antibacterial activity with 100% removal of *E. coli* within 15 minutes of contact as shown in Figure 1. The metal ions were rapidly taken up by the zeolites within the first 15 minutes of contact and more than 95% metal removal was achieved after 60 minutes indicating the absence of significant competition for metal sorption sites under the experimental conditions of this study.

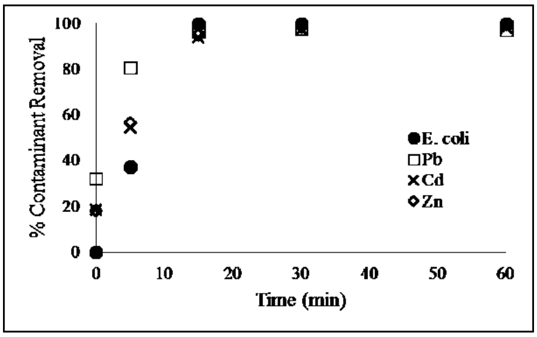

Figure 1. Simultaneous removal of *E. coli*, lead, cadmium and zinc ions by silver modified clinoptilolite in batch system as a function of contact time

Control experiments showed that unmodified zeolites did not exhibit any antibacterial properties and metal ions in the blanks did not result in any significant elimination of bacterial cells at the concentration levels used in this study. This suggests that as metal ions were being taken up by SC, the silver ions being released into the solution were taken up by the bacterial cells resulting in cell death.

The percentage breakthrough of contaminants in the fixed bed column system as a function of contact time is shown in Figure 2.

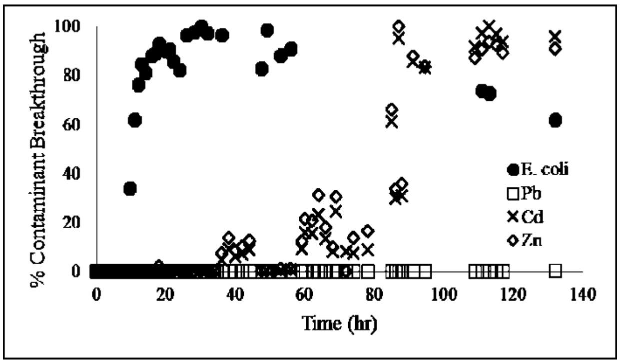

Figure 2. Simultaneous removal of *E. coli*, lead, cadmium and zinc ions by silver modified clinoptilolite in fixed bed column system as a function of contact time

In the column system, 100% disinfection and metal removal efficiency was achieved within the first 9 hours of operation. However after 9.5 hours *E. coli* breakthrough was observed. The disinfection efficiency decreased as the amount of silver released from the system decreased until 90% of the initial *E. coli* cells was detected in the effluent after 17 hours. This further indicates that disinfection was due to the silver ions released from the silver modified clinoptilolite. Breakthrough of Cd and Zn was observed after 26 and 28 hours respectively and more than 90% breakthrough of both metals after 111 hours. However the zeolite was more selective towards Pb^{2+}, hence breakthrough was observed after 132 hours of continuous operation at which point the experiment had to be stopped as the accumulation of cell debris and biofilm formation due to the loss of disinfection efficiency resulted in bed clogging. In conclusion, the results of the batch and fixed bed column studies suggest that silver modified clinoptilolite could potentially be used for the removal of *E. coli* and metals from wastewater.

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Effect of using natural substrate on elimination of heavy metals from industrial wastewater using pitcher irrigation

K. Asgari[1], W. M. Cornelis[2], N. Samadi[3] and P. Najafi[4]

[1] *Department of Soil Management, Ghent University, Belgium; E-mail kamran.asgari@stu.sku.ac.ir*
[2] *Department of Soil Management - UNESCO Chair on Eremology, Ghent University, Belgium*
[3] *Department of Renewable Resources, University of Alberta, Edmonton, Canada*
[4] *Department of Water Engineering, Khorasgan (Isfahan) Branch, Islamic Azad University, Isfahan, Iran*

Introduction

Water experts and politicians agree that there is a critical water shortage in the Mediterranean and the Middle East regions (Turker et al., 2009). Therefore, governments and the private sector have initiated wastewater treatment plants to reduce the imbalance between water supply and demand. On the other hand, applying alternative irrigation systems with higher efficiency has priority for governments and farmers. Pitcher irrigation is a low cost and simple method with high potential of water saving (Bainbridge, 2001). Combination of pitcher irrigation with drip irrigation system could result in extending the secondary treatment period, as it could be an efficient system to treat municipal and industrial wastewater and reduce total dissolved elements. However, the mixture of substrates inside the pitcher is important for the success of the combined system. Natural minerals possess selective adsorption, cation exchange, dehydration–rehydration, and catalytic properties, which contribute directly to their industrial applications. Natural minerals and rocks such as zeolites, perlite and vermiculite are proper and cost effective options to use as a substrate inside the pitcher. Their most important feature in agricultural application is the ion exchange capacity without major changes of structure (Mumpton and Fishman, 1977; Street, 1994). Zeolite structure has a negative charge which allows adsorption of cations in micropores channels and cavities by means of ion exchange. Lead, Cd and Hg cations are typical toxic heavy metals that can be adsorbed by zeolitic materials (Kazemian et al., 2001; Ansari 2007). Absorption of heavy metals from industrial, municipal and agricultural wastewater using zeolite has been widely studied (Perić et al., 2004, Inglezakis et al., 1999). Clinoptilolite (simplified ideal formula: (Na, K) $6Si_{30}Al_6O_{72}\cdot nH_2O$), is the most abundant zeolite mineral in sedimentary rocks of volcanic origin having a tremendous commercial interest because of its purity, stability and accessibility. Kazemian et al. (2001) studied absorption of heavy metals by clinoptilolite from different regions of Iran. In this study we examine and assess the performance of a clinoptilolite as compared to perlite and vermiculite for elimination of heavy metals from industrial wastewater in a pitcher irrigation system.

Experimental Methods

The study area is located in the grape garden of the Esfahan steel company at the city of Esfahan, Iran (32°37′ N 51°43′ E and 1590 m above sea level). Esfahan is situated on the semi-arid plateau of central Iran, with dry and hot summers and mild winters. The soil used was a clay loam with low amount of organic matter. An experiment was conducted with three treatments: natural zeolite clinoptilolite (NZ), perlite (P) and vermiculite (V) filled half of the volume of the clay pitcher in 15 replications. Beside each tree, one pitcher was placed at 50 cm depth. The soil of each hole was collected and used as an initial sample and was transported in air-tight bags to the laboratory. A drip irrigation system was installed with emitters inside the pitchers. The top of the pitchers was closed with plastic caps to prevent dust and insects. The pitchers were irrigated with industrial wastewater 60 times (1500 cc per each irrigation event) over a period of six months. Afterwards, the pitchers were removed and samples were taken from the substrate inside the pitcher and from soil near the wall and floor of the holes. The samples were transported to the laboratory. Soil and substrate samples were used to measure heavy metal concentration according to standard procedures (Carter and Gregorich, 2006) prior to and after irrigation with wastewater. To determine total concentrations of Fe, Cd, Cr, Cu, Pb, Mn and Zn in the soil, 0.100 g of dried soil was digested and the elemental concentrations were determined with an atomic absorption spectrophotometer (Perkin-Elmer, USA). All determinations were repeated three times to minimize the risk of error. The data were statistically analyzed. Statistical significance was detected using the independent-samples t-test and analysis of variance at $\alpha=0.05$.

Results and Discussion

The final concentration of the measured elements in the soil and substrates compared with the initial values are shown in Figure 1. After six months of continuous irrigation with industrial wastewater, the cumulative amounts of Zn and Pb were perceptibly increased in the substrates, in accordance with Erdem et al. (2004) which show that natural zeolites hold great potential to remove cationic heavy metal species(Cu^{2+} , Zn^{2+} and Mn^{2+}) from industrial wastewater. Absorption of Zn in vermiculite was significantly higher than other substrates, whereas natural zeolite and perlite showed almost the same values. Natural zeolite and perlite showed high ability to eliminate Pb from the industrial wastewater, but vermiculite was not successful. This is supported by findings of Halimoon et al. (2010) and Vukojević Medvidovic et al. (2006) which showed that zeolite has high capacity to remove heavy metals from wastewater. Natural zeolite also showed medium ability to adsorb Fe and Cd from wastewater, enabling substantial was amounts to be transferred to the soil surrounding the pitchers. No substrate showed capacity of filtering Cu, Mn and Cr, in accordance with Erdem et al. (2004). Consequently, soluble heavy metals were passing the filtration setup without being adsorbed, hence their concentrations increased in the soil around the pitchers.

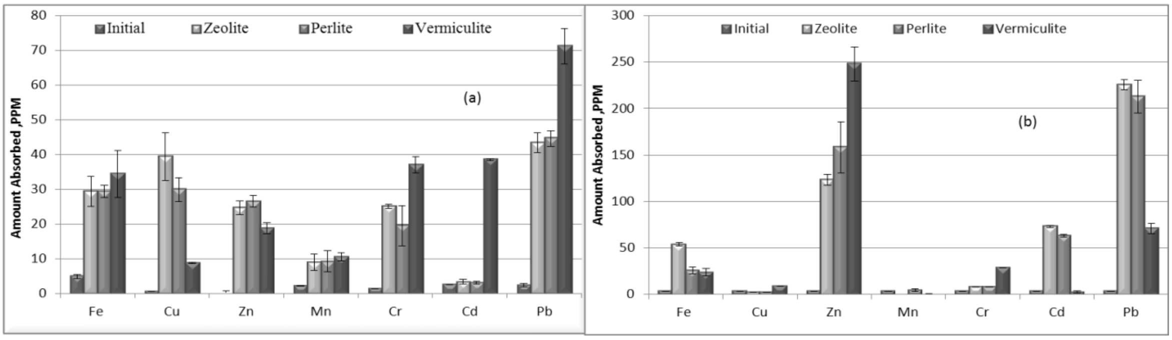

Figure 1. Comparison of initial and final concentration of elements in (a) soils and (b) substrates

In spite of the fact that the substrates used in this experiment have high ability to adsorb heavy metals, especially Pb and Zn, an increase of these two elements in the soil nearby the pitcher indicate that the used substrates have limitations in adsorption capacity for these heavy metal cations. As this is related to their cation exchange capacity and specific surface area, application of a nano form of the substrates such as nano zeolite might remarkably increase their cation exchange capacity and specific surface area.

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Natural clinoptilolite nanoparticles: an adsorbent for removal of heavy metals from landfill leachate

M. J. Askari[1], H. Kazemian[2] and P. Najafi[3]

[1]*Young Researchers and Elite Club, Khorasgan (Isfahan) Branch, Islamic Azad University, Isfahan, Iran; E-mail: asgari627@gmail.com*
[2]*Department of Chemical & Biochemical Engineering, Faculty of Engineering, Western University, London, ON, Canada N6B 5B9*
[3]*Faculty of Agriculture, Islamic Azad University, Khorasgan (Isfahan) Branch, Isfahan, Iran*

Introduction

Landfills leachate is a serious threat for the surrounding area including soil and ground water (Renou et al., 2008). Among the possible landfill leachate threats, heavy metals are one of them (Carriazo et al., 2007). Cation exchange-based technique using naturally accruing adsorbents such as bentonite, kaolinite, zeolites, lime, and gypsum has been proved to be one of the most promising approaches. Clinoptilolite is of tremendous commercial interest because of its high CEC, purity, stability and accessibility (AnsariMahabadi et al., 2007; Faghihian et al., 1999; Kazemian et al., 2001).

In this paperwe are reporting a wet ball milling approach of decreasing the particle size of a natural clinoptilolite. Furthermore, cation exchange behavior of the produced zeolite nanoparticles was studied. The starting material and the products (nano-sized materials) were characterized by means of several techniques and finally, the produced zeolite nano-powders were tested for removal of Zn and Fe cations from an actual landfill leachate.

Experimental Methods

Clinoptilolite (140 μm) with SiO_2/Al_2O_3 ratio of 5.7 from Semnan region of Iran was used as the feed of the wet ball milling process. Clinoptilolite properties are summarized in Table 1.

Table1. Properties of natural clinoptilolite used as feed for grinding (Chemical composition is based on EDX results obtained from SEM analysis)

CEC (meq/100g)	pH	EC (ds/m)	Al_2O_3	SiO_2	K_2O	CaO	Fe_2O_3	Na_2O	TiO_2	LOI
95.62	10.13	0.46	11.8%	67.5%	2.62%	3.02%	0.60%	1.23%	0.39%	12.50%

Mechanical size reduction was carried out by a planetary ball mill. In order to produce zeolitic nanoparticles with minimum particle size and narrower size distribution as well as maximum crystallinity, the wet milling conditions under inert atmosphere of argon was executed (Akcay et al., 2004; Charkhi et al., 2010; SalavatiNiasari et al., 2009). The zeolitic nanopowder prepared under wet milling process was tested using XRD, SEM and TEM techniques.

To evaluate the ion exchange property of the products for Fe (II & III; total) and Zn (II) in the landfill leachate that was taken from eastern district of Isfahan city, Iran, and was aged for 14 days in aerobic situation to stabilize and for particles deposition. Cation concentration was measured by means of atomic absorption technique. For all of the ion exchange tests, the zeolite to solution ratio was 1:50 and adsorption test carried out at different contact time of 70, 90 and 110 minutes.

Results and Discussion

The XRD patterns of the samples pulverized using ball diameter of 20 mm and 2-3 mm are shown in Figure 1. It was determined that after 2 h of grinding by 20 mm zirconium balls, the characteristic peaks of clinoptilolite remained intact, which means that crystallinity of the zeolitic sample was unchanged.

High crystallinity of the size-reduced sample can be attributed to the high Si/Al ratio of the tested clinoptilolite. Overall, the wet grinding mode has several advantages over dry grinding including higher energy efficiency, lower magnitude of excess enthalpy, elimination of dust formation, and decrease of the destruction of zeolite structures (Akcay et al., 2004; Feng et al., 2000; Frances et al., 1996). The average size of the produced nanoparticles (i.e. nanocrystallites) was 44 nm. The TEM studies on morphology and particle size of the size-reduced samples showed that both separate particles and larger agglomerates are recognizable in pulverized sample of zeolitic nanopowders with particles size less than 100 nm.

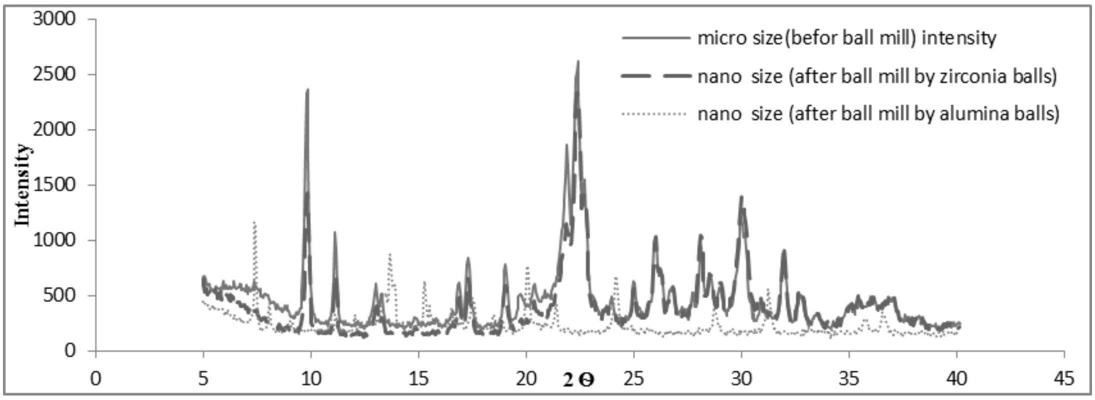

Figure1. Comparison of XRD patterns of micro- and nanoparticles of zeolite prepared by alumina and zirconia balls

To compare the ion exchange property of the produced nanoparticles and the micron-sized sample, we measured their sorption efficiency in real landfill leachate, whose chemical properties are summarized in Table 2 (Turan et al., 2011). According to the results, the mechanically produced nano-zeolite showed remarkably shorter equilibrium time for both of the tested heavy metals of Zn (II) and Fe (total) compared to the micro-size zeolite, which can be attributed to its larger surface area and easier accessibility of the ion-exchange sites resulting in faster reaction rate.

Table 2. The chemical composition of tested landfill leachate

pH	EC	Fe	Zn	Cr^{3+}	Cu^{2+}	Cd^{2+}	Pb^{2+}	Ni^{2+}	Mg^{2+}	Ca^{2+}	Na^+	NO_3	NH_4^+
	ds/m							mg/l					
7.23	77	79	5.4	0.330	0.35	0.149	1.410	2.807	1.81	14.91	12.8	740.8	365.1

The ion exchange tests revealed that despite the fact that the produced nano-sized sample has lost its crystallinity by 13%, its cation exchange capacity increased by 70% (i.e. 162 meq/100g for nanoparticles compared to 95.6 meq/100g for the micron-size sample). Despite the complexity of the chemical composition of the landfill leachate, the mechanically produced nanozeolite showed remarkable shorter equilibrium time and higher adsorption capacity for the studied heavy metal cations of Zn (II) and Fe (II and III).

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Sorption of selected petroleum products by clinoptilolite and synthetic zeolites

L. Bandura, M. Franus and W. Franus

Department of Geotechnics, Lublin University of Technology, Nadbystrzycka 40, 20-618 Lublin, Poland,
E-mail: w.franus@pollub.pl

Introduction

Petroleum products (gasoline, diesel fuels, motor oils, greases etc.) are one of the main sources of environmental pollution these days (Carmody et al., 2008). Progressive industrialization and development of automotive industry are undeniably related to an increasing demand for such hazardous substances. This, in turn, leads to an increase in the potential risks associated with the aforementioned negative impacts of those petroleum substances on the environment and living organisms (Aguilera et al., 2010). In the era of growing industrialization and rising demand for petroleum products it is extremely important to search for the effective methods for the removal of oil from contaminated sites.

The most popular methods used for the removal of oil leakages are adsorption techniques that use various kinds of adsorbents (Carmody, 2008; Wahi et al., 2013). Among natural mineral adsorbents, zeolites play a significant role. They are porous aluminosilicates with a crystal structure, containing a system of channels and chambers. Their structure provides them with unique surface properties; such as ion exchange, adsorption, molecular-sieves and catalytic capabilities (Franus, 2012). Therefore, those mineral resources are widely used in many fields. So far, a variety of applications of natural and synthetic zeolites was described (Franus and Wdowin, 2010; Misaelides, 2011; Chałupnik et al., 2013). However, zeolites have not been used as sorbents of petroleum substances yet. Their sorption properties and porous structure indicate the possibility of their application as adsorbents of this kind of substances.

Experimental Methods

A natural occurring zeolite clinoptilolite, and synthetic zeolites Na-P1 and Na-X type were used in this study. Natural zeolite originated from the mine tuffs in Sokirnica (Ukraine). In order to obtain synthetic zeolites F-class fly ash with sodium hydroxide was used and later it underwent the hydrothermal conversion. Fly ash originated from Kozienice Power Plant (Poland).

Na-P1 zeolite type material was obtained with the use of technological line for the production of zeolites from fly ashes. For one synthesis, there were 20 kg fly ash, 12 kg NaOH and 90 dm^3 of water used. The synthesis was conducted at the temperature of 80 °C during 24 h. Na-X zeolite type material was obtained in the laboratory scale with the use of the following proportions of substrates: 0,02 kg of fly ash, 0,06 kg NaOH and 0,5 dm^3 of water. The temperature and duration of both reactions was 80 °C and 24 h, respectively.

For zeolite material the following tests were performed: mineralogical (XRD), morphological (SEM) and textural (specific surface S_{BET} and porosity). Moreover, the physical parameters such as bulk density and particle size distribution were determined.

The sorption capacities of the materials were evaluated with the three following petroleum products of different density and viscosity: diesel fuels Verva ON and Biodiesel (PKN Orlen) and also used motor oil. For that purpose 10 g of each sorbent material was placed in a tea bag and then immersed into the petroleum product for 12 h. Then, the samples were taken out of oils and left for about 24 h to drain the excess of oil off them. The percentage of adsorbed hydrocarbons in each sample was measured by CHN element analysis. Obtained values were converted in the adsorbents sorption capacities. Experiments were conducted in room temperature.

Results and Discussion

Specific surface area of clinoptilolite is much smaller than the one that synthetic zeolites Na-P1 and Na-X are characterized by. S_{BET} of clinoptilolite is 18 m^2/g. When it comes to the specific surface area of synthetic zeolites, they are 87 m^2/g for Na-P1 and 236 m^2/g for Na-X (Table 1).

Table 1. Textural parameters of studied zeolites

Material	S_{BET} m^2/g	V_{mic} cm^3/g	S_{mic} m^2/g	V_{mes} cm^3/g	S_{mes} m^2/g	D_p nm
clinoptilolite	18.3	0.05	7.68	0.0046	10.65	10.5
Na-P1	86.8	0.32	54.01	0.0143	32.84	11.6
Na-X	236.4	0.21	62.99	0.077	173.45	3.6

where: S_{BET} - specific surface area; V_{mic}/V_{mes} - volume of micropores/mesopores; S_{mic}/S_{mes} - surface of micropores/mesopores; D_p - the average pore diameter

Na-X is characterized by the highest surface area due to its high contribution of micropores. As for zeolite Na-P1, it has both micro- and mesopores. However, the share of micropores is much smaller in relation to the Na-X zeolite.

The results of sorption experiments are presented in Figure 1. Synthetic zeolites exhibit higher sorption capacity than natural zeolites. It is due to their more developed surface area. Sorption of Biodiesel, Verva ON and used oil by clinoptilolite was 33%, 26% and 35% respectively. Na-P1 sorption capacity was 60, 46 and 76% with respect to Biodiesel, Verva On and used oil respectively. Sorption capacity of Na-X was 64% for Biodieslel, 63% for Verva ON and 84% for used oil.

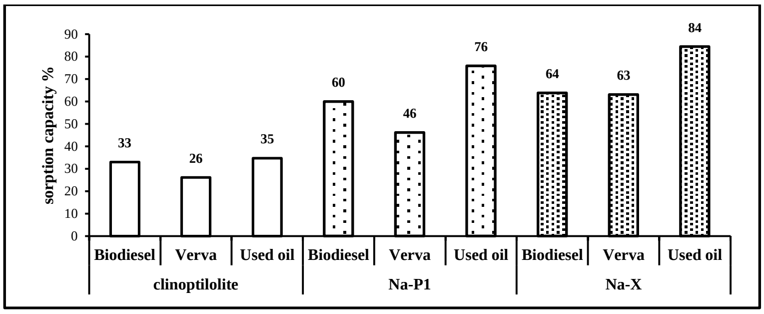

Figure 1. Oil sorption capacity (%) of zeolites

What is more, a correlation between the sorption capacity of materials and the density of the used oils was observed. Oil having the lowest density of 0.83 g/cm^3 (Verva ON) is characterized by the lowest sorption, oil having a density of 0.87 g/cm^3 (Biodiesel) intermediate sorption, whereas the oil with the highest density of 0.89 g/cm^3 (used oil) was sorbed in the largest quantities by examined zeolites.

The examined zeolites possess high adsorption properties to oils and can constitute an effective sorbent for the removal of petroleum substances leakeges that appear, for example, during road accidents.

Acknowledgement

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Use of natural zeolites to produce basic reclaimed water for industrial use from the effluents of sewage treatment plants

F. Borsatto[1], G. N. Almeida[1], F. Machdo[2], M. L. R. P. Fernandes[2] and A. M. Matsumoto[2]

[1]*Indústrias Celta Brasil Ltda.; Cotia, São Paulo; Brazil; E-mail: fernandoborsatto@celtabrasil.com.br*
[2]*Companhia de Saneamento Básico do Estado de São Paulo – SABESP; São Paulo; Brazil*

Introduction

The Water and Sanitation Company of the State of São Paulo - SABESP is responsible for providing drinking water and sewage collection, transportation and treatment, either from municipal and industrial sites. Five large plants using the activated sludge technology and a number of smaller plants, compose the complex sewage treatment in the Metropolitan Region of São Paulo.

The significant volume of drinking water supplied along with the fact that the metropolitan region suffers from water scarcity, has motivated SABESP to invest in the treatment of the final effluent generated in activated sludge plants for further urban and industrial reuse.

The basic reclaimed water can be produced by SABESP using different technologies according to the water quality requirements regarding to the intended use. In many cases, the reuse of effluents produced in activated sludge sewage treatment plants is restricted to processes such as: filtration and chlorination, and it can be complemented by coagulation.

However, if the intended use for the basic reclaimed water demands a higher quality standard, such as industrial processes, it is necessary to incorporate more sophisticated treatment technologies.

Experimental Methods

This study evaluated the efficiency of natural zeolites in two applications tests performed directly to SABESP's sewage treatment plants. These applications will be called Case 1 and Case 2. In both situations the reclaimed water had as its goal the use by textil industrial process.

In case 1, it was evaluated the removal of iron, manganese and color. The treatment was done directly on the final effluent of the activated sludge treatment plant, whose treatment was supplemented by coagulation / sedimentation.

In this case, it was used a natural clinoptilolite modified by oxidation of impregnated manganese through ion exchange process (Higarashi *et al.*, 2006), herein called ZF, which has the following characteristics: 74.01% SiO_2, 11.56% Al_2O_3, density of 0.98 g / cm³ and particle size of 0.4-1.0 mm.

The treatment aimed to obtain a specific quality standard of water (Total Fe < 0.1 mg / l, total Mn < 0.05 mg/L and color < 5 uC). It was used in this test, a filtration column measuring 22 mm in diameter, filled with 80 cm in height of ZF zeolite as filter bed and a backwashing empty space about 50 cm.

The basic water to be processed by filtration in the column containing the modified ZF zeolite, showed the following average levels considering the parameters defined for this study: Total Fe ranged from 0.87 to 0.22 mg/L, Total Mn ranged from 0.28 to 0.21 mg/L and color ranged from 20.40 to 12.00 UC. The pH ranged from 6.90 to 6.60.

In case 2, the treatment was done in basic water constituted by the final effluent of an activated sludge treatment plant and whose treatment was supplemented by coagulation and filtration.

In this case it was used a sodium modified natural clinoptilolite zeolite, herein called ZS, which has the following characteristics: 74,01 % SiO_2, 11,56% de Al_2O_3, 6,0% Na_2O, uniformity coefficient of 1.30, effective size of 0.67 mm, porosity of 48.14% and particle size of 0.4-1.0 mm.

The treatment aimed to obtain a specific quality standard of water (Total Hardness < 20 mgCaCO$_3$/L, and Ammonia < 5 mg/L).

It was used in this test a fiber filter measuring 0.53 m mm in diameter, total height of 1.57 m, area of 0.22 m^2 filled with 0.67 m in height of ZS zeolite as filter bed and and expansion rate of 42.25%.The total mass of ZS used was 150 kg.

The basic water to be processed by the fiber filter containing the modified ZS zeolite, showed the following average levels considering the parameters defined for this study: Ammonia ranged from 18.21 to 16.01 mg/L and total hardness ranged from 38.10 to 35.70 mg CaCO$_3$/L.

Results and Discussion

Table 1 presents the results of case 1 and the total concentration of iron and manganese in the basic water filtered through the column containing ZF zeolite.

Table 1. Fe and Mn concentrations after passing through zeolite ZF

Fe total mg/L		Mn total mg/L		Color uC	
Influent	Effluent	Influent	Effluent	Influent	Effluent
0.87 – 0.22	0.08 – 0.01	0.28 – 0.21	0.10 – 0.08	20.40 – 12.00	12.26 – 4.44

The tests were conducted at pH ranging from 6.90 to 6.60.It is observed that the removal of iron reaches the entire specific quality standard (Total iron < 0.1 mg/L) in all tests. However the removal of manganese and total color is often presented above the desired pattern.

Table 2 presents the results of case 2 and the total concentration of ammonia and hardness in the basic water filtered through the fiber filter containing ZS zeolite.

Table 2. Ammonia and hardness concentrations after passing through zeolite ZS

Ammonia mg/L		Hardness mg $CaCO_3$/L	
Influent	Effluent	Influent	Effluent
18.21 – 16.01	4.17 – 1.00	38.10 – 35.7	< 10

The results were obtained in 3 days of filter operation and it is possible to identify that in this case both parameters are below the requirement. During this period, the proportion of removed ammonia was 2.1 mg per gram of ZS zeolite and 3.6 mg $CaCO_3$ per gram of ZS.

Comparing this study with a previous project performed with swine waste (Nucci, 1985) and using clinoptilolite-modernite zeolite, the following proportion were obtained: 1.41 mg ammonia per gram of clinoptilolite-modernite at pH 6.0 and 1.32 mg per gram of clinoptilolite-modernite at pH 7.0.

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Use of natural zeolites (FERTCEL) in the treatment of municipal solid waste (MSW)

F. Borsatto and J. A. Febles

Industrias Celta Brasil, Rua Iris Memberg 200,Cotia, SP, Brasil;
E-mail: fernandoborsatto@celtabrasil.com.br

Introduction

Landfill disposal generates a large volume of gas emissions from anaerobic digestion of the organic matter. By installing energy plants using biogas generated in landfills twice environmental objective is achieved, using organic matter for energy and reducing emissions of gases that contribute to cause the greenhouse effect is achieved.

The 5th Action Programme Environment and Sustainable Development (R2) In section 5.7 Waste Management states that: "... the waste is not only a potential source of contamination, but it can become further secondary raw materials".

Among the fundamental problems limiting the application of anaerobic processes for biogas from liquid and solid waste include: prolonged periods of rush the process; relatively large hydraulic retention or small organic loads used for design of digesters, which involves the construction of large digesters. Montalvo et al. (1993) demonstrated the influence of the zeolite on the biogas production process with very positive results in anaerobic processes achieving increases in efficiency between 10-15% in batch processes.

Experimental Methods

For the development of the experiments 2.5L capacity reactors in batch systems (batch) have been fed with synthetic wastewater to the corresponding doses of nitrogen and zeolite was added. To this reactor were further added an inoculum of 10% of the reactor volume, resulting in 2 experimental series:

1. In the first series was added a feeding 10 g/L of COD, one organic nitrogen dose (NT): 1000 mg/L in and three different doses of zeolite, 500, 1000 and 1500 mg/L.
2. The second series was added a feeding of 10 g/L of COD, a dose of zeolite 1000 mg/L to 4 nitrogen, 1750, 2000, 2250 and 2500 mg/L.

The zeolite used in all experiments is coming from deposits of Tasajera whose mineralogical composition is 61% zeolitic material with a grain size less than 1.00mm.

Another experiment was the anaerobic digestion of organic waste without zeolite mineral and 1% relative to the total mass of sludge digestion.

Results and Discussion

Experimental series # 1

The main results of this series are shown in Table 1.

Table 1. Effect of zeolite production of biogas

Dose of zeolite (mg/L)	0	500	1000	1500
Volume of gas produced (Vg) (ml)	1855	1980	2017	2108
% Increase in Vg	-	6.31	7.99	12.0

The digestion time in this series was 30 days, assuming the presence of zeolite improved process generally, and increase of 12% methane when incorporated in 1500 mg / L of mineral.

Experimental series # 2
Table 2 shows the results obtained in the experimental series.

Table 2. Conversion of organic nitrogen in ammonium

Nitrogen Dose (mg/L)	1750		2000		2250		2500	
Dose of zeolite (mg/L)	0	1000	0	1000	0	1000	0	1000
Vg (mL)	8950	9508	8958	9158	6750	7158	6858	7075
% Increase in Vg	-	6.23	-	3.23	-	6.04	-	3.16
% Increase in ST	75.72	89.88	88.78	88.84	87.40	89.22	91.65	92.22
% Removal in SV	77.75	86.13	90.71	92.92	89.94	91.34	93.89	94.17
% removal in DQO	93.18	97.72	90.62	96.09	84.85	95.45	96.03	97.62

The digestion time was of 32 days confirming that the presence of the zeolite increases the efficiency of the anaerobic process. The concentration of ammonia nitrogen (NH_4^+) at the beginning of the process was 100 mg/L and the end was in all digesters between 1200 and 2100 mg/L which shows the high conversion of organic nitrogen to ammonia during anaerobic process

The removal of organic matter when zeolite is used is higher compared to the system without zeolite. This result confirms improving the process by adding of zeolite due to increased micro-substrate contact, with a conversion of over 95% of the ammonium nitrogen form.

In comparative experiment of digestion of pig waste in the presence of zeolite was obtained similar to municipal waste results as seen in Figure 1.

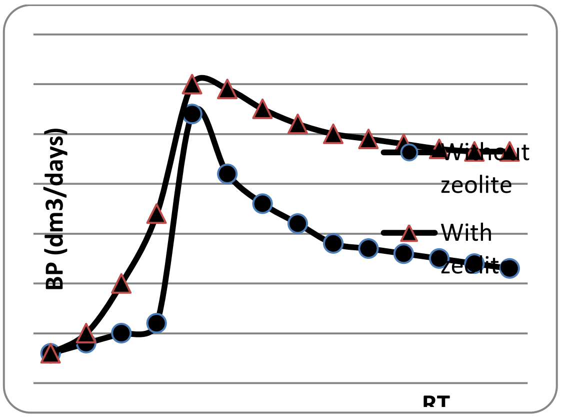

Figure 1. Production of Biogas

The biogas production (BP) in relation to the retention time (RT) of digesters used with and without zeolite (Figure 1), shows that both exhibit fluctuations in gas production rate, motivated by fluctuations in temperature (24 to 28^{0}C). This graph shows that the digester containing zeolite has a higher rate of production of biogas presenting a higher bacterial activity, and the time of appearance of the peak gas production is lower. Analyze the composition of biogas digesters in both gas chromatography, we see that the content of methane in the digester gas zeolite is 1.39 larger than the zeolite without.

The presence of natural zeolite powder enhances the biodegradation of organic matter during anaerobic process implying the increase in biogas production. The percentage of biogas in all cases was always greater than 70.

There a significant difference in relation to organic matter removal in reactors operating with and without zeolite (about 12% more reactors with zeolites). This not only confirms the positive influence of this mineral in the process, but also reduces the negative effect of increased nitrogen.

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Efficacy of thermal treatments in inactivating exhausted clinoptilolite-based Pb-exchangers

A. Brundu and G. Cerri

Dipartimento di Scienze della Natura e del Territorio, Università di Sassari, Via Piandanna 4 – 07100 Sassari, Italy; E-mail: abrundu@uniss.it

Introduction

The high selectivity of clinoptilolite toward Pb^{2+} has stimulated many studies focused on possible environmental applications, and the metal uptake has been assessed under several different experimental conditions. Conversely, issues related to the management of the exhausted exchangers have not received an analogous attention. This aspect is not trivial because such materials, if not properly treated, could become a source of pollution. It should be considered that only a fraction of the lead adsorbed by clinoptilolite during a wastewater treatment could be recovered with profit by a regeneration process, but a complete reconditioning of the zeolite would be not feasible. Consequently, both fully-exploited and partially reconditioned exchangers represent an environmental concern, indeed some authors have started to study the problems related to the mobility and plant-availability of Pb^{2+} adsorbed on clinoptilolite (Hamidpour et al., 2010). Thermal treatments can inactivate the exhausted exchangers because heating affects zeolite structure, inhibiting the desorption of the cation.

An extensive research has been started to evaluate the effects of thermal treatments at high temperatures on a clinoptilolite conducted both partially and fully in Pb-form. Here are presented the results concerning the efficacy of the process of lead immobilization in the exchangers, evaluated through prolonged leaching tests.

Experimental Methods

A Sardinian cineritic epiclastite, Oligo-Aquitanian in age, already characterized in previous works (Cerri et al., 2002; Cerri et al., 2004), has been used in this study. The rock, with a clinoptilolite content of 66±4wt.%, has been subjected to a slight beneficiation process, carried out through a granulation in a jaw crusher, followed by an autogenous comminution (performed with a planetary mill deprived of the ball grinding elements), and by sieving, recovering the fraction between 250 and 125 μm for the subsequent experiments.

A quantitative XRD analysis of this material has been performed using a Siemens D5000 diffractometer, equipped with a Cu tube and a graphite monochromator on the secondary beam, at the following operating conditions: 40 kV, 30 mA, 2θ range 2-70°, step size 0.020°, time per step 2s. Diffraction data have been evaluated using the Bruker Diffrac^{PLUS} package. Rietveld refinement has been accomplished by Bruker Topas 4.2 software.

The exhausted Pb-exchanger has been obtained through a Na preconditioning (five cycles of exchange in batch, 2 hours each, with a 1 M $NaCH_3COO$ solution, solid/liquid ratio=30 g/l, T=65°C, continuous stirring), followed by an exchange in a 0.5 M $Pb(CH_3COO)_2$ solution (two cycles in batch, other parameters as above). This material has been marked P-ex.

Three partially reconditioned exchangers (respectively, PN-ex, PK-ex and PA-ex) have been prepared starting from P-ex, put in contact with three different solutions of $NaCH_3COO$, KCH_3COO and NH_4CH_3COO. The three exchanges have been performed employing the same experimental conditions (2 hours under continuous stirring at 25°C, s/l ratio = 30 g/l).

The prepared materials have been analyzed by ICP-MS at Actlabs (Ontario, Canada).

An aliquot of each material has been heated at 1000°C for four hours in platinum crucibles. The relative products have been marked P-1000, PN-1000, PK-1000 and PA-1000.

X-ray diffraction analyses (at the same conditions specified above) of unheated and heated materials have been performed to evaluate phase transformations after the thermal treatment.

Leaching tests have been carried out on PN-ex, PK-ex, PA-ex and on all heated materials, through two exchanges executed in sequence, the first of seven and the second of fourteen days. Experiments have been conducted at 25°C, with a s/l ratio of 30 g/l, under continuous stirring. PA-ex and PA-1000 have been tested in a 0.5 M $NaCH_3COO$ solution, the other samples in a 0.5 M NH_4CH_3COO solution. To determine the Pb^{2+} released, blank solutions and elutes have been analyzed by AAS (Actlabs).

Results and Discussion

After the beneficiation process the material has attained a 77±3wt.% of clinoptilolite percentage.

Lead content of P-ex (1.89 meq/g) testifies the achievement of a near end-member of Pb-clinoptilolite, considering the results previously obtained on the same material (Brundu et al., 2008; Brundu and Cerri, 2012).

Lead contents of the other materials (PN-ex = 1.07; PK-ex = 0.91; PA-ex = 0.70 meq/g) indicates that the efficacy in metal recovering has followed clinoptilolite's sequence of selectivity ($NH_4^+ > K^+ > Na^+$).

The lead released from unheated samples at the end of the leaching tests (PN-ex = 0.52, PK-ex = 0.38, PA-ex = 0.20 meq/g) show that the potential dangerousness of the partially reconditioned exchangers is directly related to their Pb-content. After the test, the metal still contained in the samples is similar, but still in the order PN-ex (0.55) > PK-ex (0.53) > PA-ex (0.50 meq/g).

Thermal treatments have greatly affected the mobility of lead contained in the exchangers. In particular, at the end of leaching tests P-1000, PN-1000 and PK-1000 have released, respectively, 0.04, 0.02 and 0.01 meq/g, that is about 2% of their initial Pb^{2+} content, whereas PA-1000 has liberated 0.02 meq/g (3%). The inhibition of metal release is due to the destruction of zeolite framework and consequent immobilization of the lead in the structure of heating products. XRD analyses have evidenced the presence of Pb-feldspar and tridymite in P-1000, confirming the data reported by Brundu et al. (2008). PK-1000 is essentially amorphous, and only weak peaks related to traces of tridymite, Pb-feldspar and K-feldspar can be detected in the diffraction pattern. In PN-1000, essentially amorphous too, peaks of tridymite are more evident and Na-feldspar (instead of K-feldspar) is detectable, whereas Pb-feldspars reflections are similar to those in PK-1000. PA-1000 differs from PN-1000 and PK-1000 because is mainly composed by crystalline phases: Pb-feldspar, tridymite and mullite. The thermal transformation of an ideal "hybrid" dehydrated (NH_4,Pb)-clinoptilolite can be described as follow:

$$3Pb_2(NH_4)_2[Al_6Si_{30}O_{72}] \rightarrow 6NH_3\uparrow + \ 3Pb_2H_2[Al_6Si_{30}O_{72}] \rightarrow 3H_2O\uparrow + 6PbAl_2Si_2O_8 + Al_6Si_2O_{13} + 38SiO_2$$

This study provides data useful to evaluate the efficacy of thermal treatments in inactivating exhausted clinoptilolite-based Pb-exchangers.

Acknowledgment

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Zeolitized tuffs in Pedotechnique for the reclamation of abandoned quarries. A case study in the Campania region (Italy)

A. Buondonno[1], E. Grilli[2], G. F. Capra[3], C. Glorioso[1], A. Langella[4], A. P. Leone[5], N. Leone[4], P. Odierna[1], S. Vacca[3] and R. C. Vigliotti[2]

[1] *Seconda Università degli Studi di Napoli, Abazia San Lorenzo ad Septimum, Borgo San Lorenzo 81031, Aversa (CE), Italy. E-mail: andrea.buonodonno@unina2.it*
[2]*Seconda Università degli Studi di Napoli, Via Vivaldi n° 43, 81100 Caserta, Italy*
[3]*Università degli Studi di Sassari, Via Colombo n° 1, 08100 Nuoro, Italy*
[4]*Università degli Studi del Sannio, via dei Mulini n°59°, 82100Benevento, Italy*
[5]*Centro Nazionale delle Ricerche – Istituto per i Sistemi Agricoli e Forestali del Mediterraneo, via Patacca n°85, 80056 Ercolano (NA), Italy*

Introduction

The functional recovery of post-mining quarries is an important issue in the Campania region (Italy), where over 600 quarries are currently distributed, especially on carbonatic mountains in the Caserta province. Complex regional legislation on mining practices (Regione Campania, 2006a, 2006b) dictates reclamation interventions at the end of mining activities. This regulation states that soil rebuilding is the overriding and necessary action for environmental restoration. One possible approach for the reclamation and management of abandoned quarries is *ex novo* soil building, that implies a total or partial return of the ecosystem to its original state and land-use (Séré *et al.*, 2008). The soil can be built by co-utilizing several organic and inorganic matrices, such as building materials, industrial by-products, amendment and compost (Buondonno *et al.*, 2013). As shown by Buondonno et al. (2002), zeolitized tuffs are promising materials in reconstructive pedotechniques to *ex-novo* built soils, also designed as "*proto-horizons*" or "*embryonic*" soils (Buondonno *et al.*, 2007, 2013; Bucci *et al.*, 2005).

Our study aims at evaluating the evolution of different model *proto-horizons* made up by co-utilizing the Phlegraean Yellow Tuff (PYT), the zeolitized yellow facies of Campanian Ignimbrite, with phillipsite > chabazite (Grilli *et al.*, 2011). Attention was paid to the stability and modification of soil Organic Matter (OM) to best support plant growth.

Experimental Methods

We considered four model proto-horizons for the possible establishment and stabilization of pasture/grass as a starting step for limestone quarries restoration: i) limestone gravel (LG) as a representative natural substrate of limestone quarries; ii) straight zeolitized tuff (PYT); iii) PYT + commercial compost (CC); and iv) PYT + phosphorite (PH) + poultry manure (PM). All models were assembled and monitored for nine months under controlled (pot) conditions. One gram of pasture/grass for pot was sowed (Buondonno *et al.*, 2013).

The OM variability and evolution was estimated measuring Total Organic Carbon (TOC), total extractable carbon (TEC), humic and fulvic acids (HA+FA) and humin (HUM). To make the overall evaluation and comparison easier, all parameters applying to OM have also been expressed as percent variation (Δ%) in the final proto-horizons with respect to their initial value.

Results and Discussion

Stressed seed germination occurred in the reference proto-horizon (LG), and the plants quickly wilted within a few days even before cotyledons developed. To consider such a model as the paradigmatic benchmark to assess both plant development and pedogenesis progress was clearly unrealistic. Accordingly, the results and discussions will focus only on straight-, amendment-, and fertilized-tuff proto-horizons.

PYT-based proto-horizons were characterized by a good crop production, following the order PYT < PYT+CC < PYT+PH+PM (data not showed).

As expected, the largest amounts of TOC, TEC, HA+FA and HUM were detected in the amendment-tuff proto-horizon (PYT+CC). However, a dramatic relative decrease was observed with respect to their content in the starting proto-horizons (Fig. 1) equal to -59, -74, -81 and -40%, respectively. In addition, a dramatic decrease in total N content occurred, with a relative increase (Fig. 1) of -80%.

However, a remarkable rise in TOC, TEC, HUM and, to a lesser extent, HA+FA, was observed in the straight- and fertilized-tuff proto-horizons. The rise was more notable in the straight-tuff proto-horizon, which showed the largest relative increase in these parameters and in N content (83%) (Fig. 1).

As before mentioned, carbonatic proto-horizons were clearly incapable of sustaining significant plant growth. On the opposite, the PYT exhibited a relevant suitability and efficiency as a pedogenic substrate in all of the examined model proto-horizons. The straight-tuff supported plant growth while inducing accumulation of OM as a result of root activity. The fertilized-tuff, initially containing scarce amounts of OM and N, maintained the best plant performance in terms of dry matter yield and plant cover. By contrast, the amendment-tuff, containing important initial amounts of both OM and N, produced the poorest plant response. Overall, our results confirm that zeolitized tuffs are suitable materials for pedotechnical interventions. Specifically, a proto-horizon built of PYT with a minimum supply of low-cost N and P shows potential for effective, environmentally safe quarry restoration.

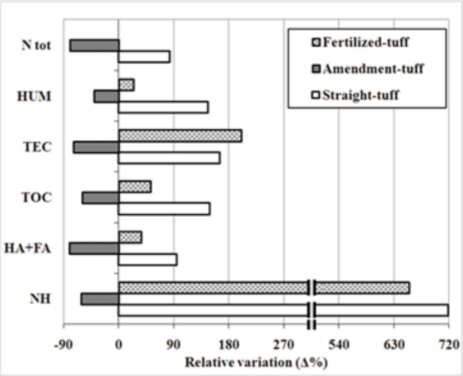

Figure 1. Relative variation (Δ%) of total nitrogen and soil organic matter fractions in the final model proto-horizons with respect to their initial values

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Impregnation of natural clinoptilolite with zinc

G. D. Calabria[1], F. Borsatto[1] and M. C. Shinzato[2]

[1]Indústrias Celta Brasil Ltda.; Cotia, São Paulo; Brazil; E-mail: giovanna@celtabrasil.com.br
[2]Departamento de Ciências Exatas e da Terra – Universidade Federal de São Paulo; Diadema, São Paulo; Brazil.

Introduction

The cation exchange capacity (CEC) of zeolites is limited by the diameter of channels of the crystal structure, ionic radius, ionic charge and concentration of electrolytic solution (Barrer, 1978). In general, zeolites with low Si/Al ratio have greater CEC. For zeolites with high ratio of Si/Al as clinoptilolite, there is also greater selectivity for ions of lower charge (monovalent cations) than for divalent ones (Sherry, 1969). So, the cation exchange of natural clinoptilolite with zinc is not so effective at low temperature (60°C – 100°C), therefore the solution of zinc salts in clinoptilolite requires a long contact time for a high cation exchange (Dimowa *et al.*, 2012).

Zinc has bactericidal properties and within the clinoptilolite structure can be used as a filter media, so the objective of this research is to improve the impregnation of zinc in the natural zeolite sample, composed by clinoptilolite and mordenite, by using zinc solutions and also molten-exchange process with a zinc salt.

Experimental

The studied zeolites samples come from Cuba deposits and are comprised of 98% of clinoptilolite and 2% of mordenite.

To compare the efficiency of some methods to retain zinc in the zeolite structure three tests were performed. The first one was carried out in batch tests mixing 1 g of natural zeolite (ZN) in 5 mL of solution with different concentrations of zinc (10 to 1100 mg L^{-1}) at ambient temperature (25°C). After a period of 42 hours these mixtures were filtered and washed with distilled water and the concentration of zinc in the resulting solutions was analyzed by spectrophotometer (Smart Spectro/Policontrol). In the second test the same process was repeated, but the zeolites samples waere heated at 300°C (Z300) for 4 hours. The third test was based on the molten-exchange method proposed by Dimowa *et al.* (2012), where the zeolites and $ZnCl_2$ salt (proportion of 1:1) were mixed and heated at 380°C for 4 hours in a muffle oven. The resulted material was washed with distilled water and dried at 110°C and analyzed by X-ray fluorescence (XRF-1800/Shimadzu) and X-ray diffraction (Xpert Pro/Panalytical) techniques.

Results and Discussion

The results of the first and second batch tests indicate that the concentration of the retained zinc in the mineral structure increased with the zinc concentration. The maximum value of zinc retained by ZN was 2.9 mg g^{-1} (in a solution with 1000 mg L^{-1} of Zn). For Z300 samples, at the same concentration (1000 mg L^{-1}), the adsorbed zinc was 3.4 mg g^{-1} and at 1400 mg L^{-1} was 4.1 mg g^{-1} (Fig. 1).

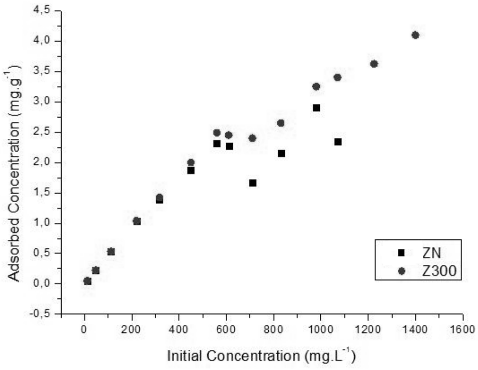

Figure 1. Zinc adsorption by zeolites samples (ZN and Z300)

The chemical composition determined by X-ray fluorescence analysis (Table 1) indicated that the natural clinoptilolite (ZN) treated with a solution of 1000 mg L^{-1} of zinc presented 2 wt% of ZnO, and those samples heated at 300°C (Z300) and treated with 1400 mg.L^{-1} of zinc in solution contained about 5 wt% of ZnO.

Table 1. Chemical composition of zeolites samples treated in batch and molten experiments

Oxides	ZN	Batch experiments ZN	Batch experiments Z300	Molten-process
		(wt %)		
SiO_2	70.29	68.69	64.21	53.46
Al_2O_3	11.57	11.22	10.44	8.77
Fe_2O_3	1.66	1.51	1.39	1.12
TiO_2	0.25	0.22	0.27	0.20
CaO	2.79	2.21	2.40	1.04
MgO	0.79	0.60	0.68	0.47
Na_2O	1.08	1.18	1.19	1.38
K_2O	1.51	1.49	0.90	2.03
MnO	<0.01	<0.01	<0.01	<0.01
P_2O_5	0.05	0.05	0.06	0.04
ZnO	0.01	2.04	5.07	14.94
LOI	10.00	10.30	12.62	15.86

The samples obtained by the molten-exchange process presented a higher percentage of ZnO (almost 15 wt%), and also a high value of LOI (15.8 wt%). However, the Al_2O_3 and SiO_2 concentrations decreased during this heating treatment. Dimowa *et al* (2012) also verified similar values of ZnO in their study: 14.32 wt% in clinoptilolite treated by molten-process and 2.2 wt% in the liquid ion-exchange. Besides the chemical composition changes, it was also observed that the XRD patterns of the original zeolites (ZN) changed after the molten-process. The analysis of these X-ray diffractions indicated that the high temperature converted all modernite and a small part of clinoptilolite (2%) to stilbite crystal structure. It is possible that the high Si/Al ratio and the presence of K^+ ions in the clinoptilolite composition favored to increase the stability of this mineral crystal structure upon heating (Ates & Hardacre, 2012). According to Elaiopoulos *et al*., (2008) clinoptilolite is also thermally stable at temperatures exceeding 450°C. So, the structural change may be related to the behavior that different type of zeolites may exhibit towards the dealumination methods (Elaiopoulos *et al*., 2010).

As Dimowa *et al.* (2012) observed, the incorporation of zinc in the clinoptilolite structure may change the intensities of some diffraction peaks and also made some other ones disappeared.

The experimental data confirms that the molten-exchange process of natural zeolites with $ZnCl_2$ can retain more zinc than the treatments using solutions with zinc.

Acknowledgment

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A new approach to fast modify the zeolite surface: high speed disperser technique in the preparation of great SMZ amount

P. Cappelletti[1], L. Catalanotti[2], A. Langella[3], M. Mercurio[3], B. de' Gennaro[2], M. Rosella[3] and A. Daković[4]

[1] *DiSTAR, University of Naples Federico II, Naples, Italy*
[2] *DICMAPI, University of Naples, Federico II, Naples, Italy: brdegenn@unina.it*
[3] *Department of Science and Technologies, University of Sannio, Benevento, Italy*
[4] *Institute for Technology of Nuclear and Other Mineral Raw Materials, P.O. Box 390, Belgrade, Serbia*

Introduction

A variety of minerals have been used as excipients in pharmaceutical preparations as they have certain desirable physical and physico-chemical properties, such as high adsorption capacity, specific surface area, swelling capacity, water solubility and dispersivity, hygroscopicity and thixotropy (Carretero and Pozo, 2009; Krajišnik et al., 2011). The mineral-organic interaction can also be used to control the release of active ingredients (drugs) with improved therapeutic properties. In this perspective, zeolite-rich rocks, having large specific surface area and high adsorption capacity, are emerging as materials for biomedical applications due to their adsorptive, ion exchange, and catalytic properties (Pavelic et al., 2001). Moreover, the zeolite modification with long chain organic cations results in an increased hydrophobicity of the mineral surface providing a high affinity for drug molecules. The enhanced adsorption of drug molecules on solid–surfactant complexes may lead to innovative zeolite applications, such as new drug delivery systems (Rivera and Farias, 2005; Farias et al., 2010). Among the main issues related with the preparation of large amounts of *carrier* for drug delivery, is the time required to modify the zeolitic support surface with surfactant molecules leading to the surface bilayer formation. In the present work, the adsorption of cetylpyridinium chloride (CPC) onto natural clinoptilolite- (CLI_SK) and phillipsite-rich rocks (PHI_SAV) was investigated, with the aim of setting a useful method for assessment of the External Cation Exchange Capacity (ECEC) and therefore for preparing large modified zeolite amounts in the shortest possible time.

Experimental Methods

The materials used in this study for the surfactant modified zeolite preparation were a clinoptilolite-rich rock from Slovakia, named CLI_SK, and a phillipsite-rich rock from Campania (Italy), named PHI_SAV. The mineralogical composition of the investigated samples, carried out by qualitative X-Ray Powder Diffraction (XRPD) and quantitative mineralogical characterization using the RIR/Rietveld method with internal standard, are reported in Table 1. The ECEC values, estimated through batch method (Li and Bowman, 1997), were 0.13 and 0.18 meq/g for CLI_SK and PHI_SAV, respectively.

Table 1. Quantitative mineralogical evaluation for the selected samples

	Clinoptilolite	Cristobalite	Chabasite	Phillipsite	Analcime	Pyroxene	Feldspar	Quartz	Mica	Amorph*
CLI_SK	55.7	6.3					12.6	4.2	1.9	19.4
PHI_SAV			4.5	69.6	3.3	3.3	13.3		Tr	6.0*

*Amorphous matter also includes partially or disordered phases

The sorption reactions were carried out in two different ways: (1) by mixing with a high speed disperser (IKA-ULTRA TURRAX-T25 digital) at 8000rpm and fixed time ~ 10 min, a suitable amount of zeolitized rock sample in a solution containing the ionic surfactant (cetylpyridinium chloride, CPC) (solid to liquid ratio = 1/50), with concentration 25 - 200% of the rocks ECEC; and (2) by mixing with the same disperser, a suitable amount of zeolite rock sample in a CPC solution (solid to liquid ratio = 1/50) with concentration of 150% ECEC, at different times (from 15 to 90 min.) and at the previous speed. After dispersion, the suspensions were filtered and the supernatants were used for determination of cations released and surfactant concentration. In order to ensure the complete bilayer formation, the same runs were repeated increasing the disperser rate up to 18000 rpm.

Results and Discussion

Figures 1 and 2 report the amounts of the released cations as a function of ECEC percentage (figure 1) and/or time (figure 2). The fixed speed (8000 rpm) seems not to be sufficient to attain the monolayer formation within 10 minutes (Figure 1). In fact the concentration of the released cation corresponding to 100% of the ECEC (0.10 meq/g and 0.13 meq/g for CLI_SK and PHI_SAV, respectively) is lower than the ECEC value, which was attained only at 200% of surfactant concentration in solution. Moreover the released cation for sample initial concentration ranging from 100% to 200% of the ECEC did not reach the expected plateau. Moreover neither at 150% nor at 200% ECEC surfactant concentrations the bilayer formation occurs. In fact the curves are rather linear, thus probably indicating that 8000 rpm and 10 minutes are not sufficient to use the total external cation exchange capacity and to induce the bilayer formation.

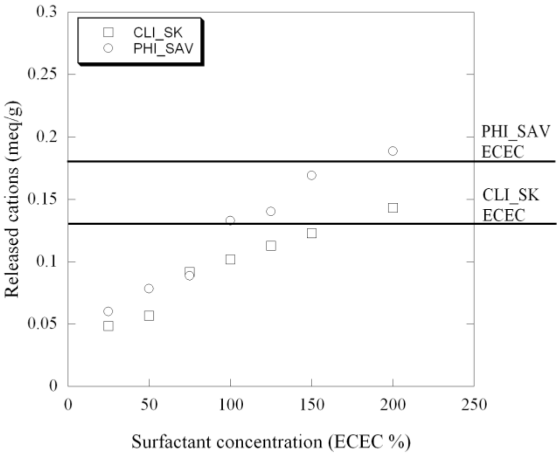

Figure 1. Released cations as a function of CPC concentration in solution in % of the ECEC. Effect of concentration on the surfactant modified zeolite formation

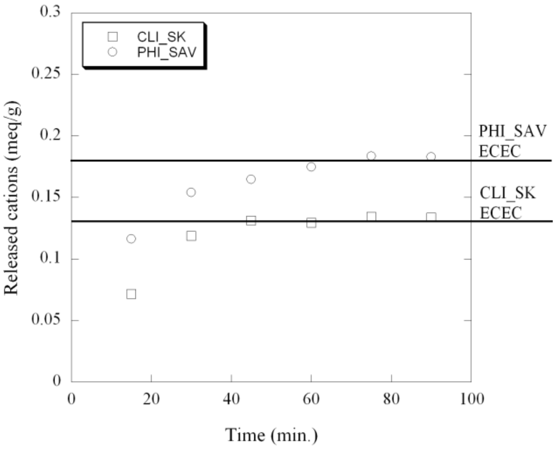

Figure 2. Released cations as a function of Time. Effect of time on the surfactant modified zeolite formation

On the contrary, the ICP-OES analysis of the released cations as function of time (Figure 2), for both zeolite samples highlighted the External Cation Exchange Capacity saturation after about 1 hour. Moreover, the surfactant analysis from liquid chromatography confirmed the bilayer formation using a 150% CPC solution at about 90 minutes.

With the aim of making the method quite general regardless of the structure of the selected zeolite material, and therefore of its External Cation Exchange Capacity, by optimizing the considered parameters, the experiments were performed by increasing the stirring rate from 10000 up to 18000 rpm, always at the same concentration values and at increasing times. The results confirmed that the higher the stirring rate, the lower the exchange time also for that zeolite-rich rocks having greater external cation exchange capacity.

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Use of surface modified natural zeolite (SMNZ) in pharmaceutical preparations Part 1. Mineralogical and technological characterization of some industrial zeolite-rich rocks

P. Cappelletti[1], L. Catalanotti[2], A. Langella[3], A. Colella[1], M. Mercurio[3], V. Monetti[1] and B. de' Gennaro[2]

[1] *DiSTAR, University of Naples Federico II, Naples, Italy*
[2] *DICMAPI, University of Naples, Federico II, Naples, Italy; brdegenn@unina.it*
[3] *Department of Science and Technologies, University of Sannio, Benevento, Italy*

Introduction

Some geomaterials (kaolins, bentonites, clinoptilolite-rich rocks) have been widely used in the pharmaceutical and cosmetic areas for a number of purposes (excipients, carriers, etc.) (Veniale, 1997). As far as zeolites are concerned, literature data has shown that their alkaline composition, molecular adsorption and cationic exchange properties induced positive therapeutic effects. Moreover the ability to functionalize the surface of zeolite-rich materials with long-chain organic molecules (HDTMA-Br/Cl, BC-Cl, CP-Cl), provides systems capable of exchanging anionic molecules or adsorb organic compounds (Sharma, 1999). Previous papers, investigating the interaction between a surface modified clinoptilolite and two non-steroidal anti-inflammatory drugs for *in vivo* use, verified both the non-toxicity and chemical and thermal stability of these systems (Krajisnik et al., 2010). However, the possibility of using surface-modified systems in vivo requires further study on the technological preparation of the carrier, the potential toxicity of these systems, and the effect of surface changes in the drug-matrix interaction. As a consequence, the use of natural zeolites in the biomedical field cannot be separated from a preliminary and accurate mineralogical characterization. Therefore, this study was aimed at defining the mineralogical and technological features of some natural zeolites, which might have potential use in the pharmaceutical sector.

Experimental Methods

The present research preliminarily accounted for an accurate selection of representative samples from zeolitized deposits in different world geographical areas commonly mined and marketed by American and European mining companies. These geomaterials displayed high levels of clinoptilolite, phillipsite, and chabazite and were characterized utilizing mineralogical (XRPD, XRF, SEM/EDS, OM), chemical and technological (FTIR, Surface Area through BET method, Cation Exchange Capacity and External Cation Exchange Capacity). Preliminary quality control on the selected materials determined the undesirable elements (Ni, Cd, Pb, As, Zn, Hg), which were evaluated after leaching with 5% w/w nitric acid at its boiling point. Moreover, the batch sorption isotherms were prepared to evaluate the surfactant sorption plateau (maximum amount of surfactant sorbed) as a function of surfactant counterion. For this purpose, selected zeolite samples were treated with the surfactant agents (HDTMA-Br/Cl, BC-Cl and CP-Cl) having initial concentrations ranging from 25% to 400% of the sorption plateau as a function of the ECEC. After equilibrium, the mixture was centrifuged and the supernatant solution analyzed via liquid-chromatography.

Results and Discussion

Table 1 reports the quantitative mineralogical analyses of the selected samples. CLI_SK, CLI_BG, CLI_NM and CLI_CA are all clinoptilolite-rich samples (ranging between 56% and 80 %) along with cristobalite, K-feldspar, quartz, and a micaceous phase, in decreasing amounts. An amorphous component, including smectite (poorly ordered) and hydrated glass, also occurs in amounts ranging between 3.3% (CHA_SM) and 22.3% (CLI_BG). The CHA_SM sample shows chabazite content slightly higher than 70% along with several percent of phillipsite, which is usually found in these Italian volcaniclastic deposits. K-feldspar (approximately 16%) should be considered as a pyrogenic phase. Pyroxene, mica, and amorphous matter also occur in minor amounts. The PHI_SAV sample comes from the NYT formation, which is generally characterized by a total zeolite content rarely exceeding 50%. In order to increase phillipsite content, a bland enrichment process was carried out by gently crushing the specimen and operating a magnetic separation (Frantz Isodynamic Separator). This treatment increased the phillipsite content to approximately 70 wt.%.

Table 1. Quantitative mineralogical evaluation for the selected samples

	CLI_SK	CLI_BG	CLI_NM	CLI_CA	CHA_SM	PHI_SAV
Clinoptilolite	55.7	62.7	60.1	80.2		
Cristobalite	6.3	7.8	2.3	2.9		
Chabazite					71.2	4.5
Phillipsite					5.2	69.6
Analcime						3.3
Pyroxene					3.1	3.3
K-feldspar	12.6	4.7	12.4	2.3	16.2	13.3
Quartz	4.2	Tr.	4.7	tr		
Mica	1.9	2.0	1.5	2.0	1	tr
Amorphous	19.4	22.3	18.9	11.8	3.3	6.0*

*Amorphous matter also includes partially or disordered phases

For the selected samples, the ECEC did not seem to be influenced by the surfactant used in the evaluation, but strongly depended on the zeolite content and type. Comparing different zeolites with the same content (CLI_CA= 0.477 meq/g; CHA_SM= 0.229 meq/g; PHI_SAV= 0.144 meq/g) it is clear how the ECEC is strongly affected by the zeolite framework.

Following mineralogical and chemical characterization, four zeolite-rich rocks: Two clinoptilolite-rich rocks from Slovakia and California, respectively and the chabazite- and phillipsite-rich rocks from the Campania region were selected. Surfactant sorption thermodynamic tests indicated that different zeolite frameworks (clinoptilolite-, chabazite- , phillipsite-rich rocks) seem to show similar interaction mechanisms (figure 1), thus showing bilayer formation mechanisms which only depend on the anionic species which balances the surfactant, and not on the kind of surfactant. The only sample which diverged from this scheme was CLI_CA where the sorption sequence also seems to be influenced by the surfactant morphology (figure 2). Results provide good perspectives on the use of zeolite-rich rocks in pharmaceutics.

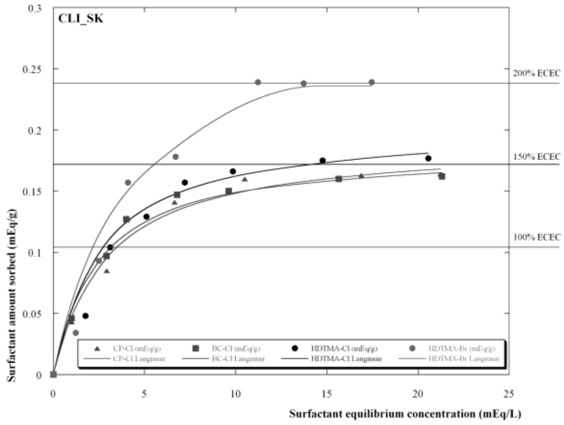

Figure 1. Thermodynamic runs of the surfactant sorption between CLI_SK and different surfactants in concentration ranging from 25% and 400% of the ECEC

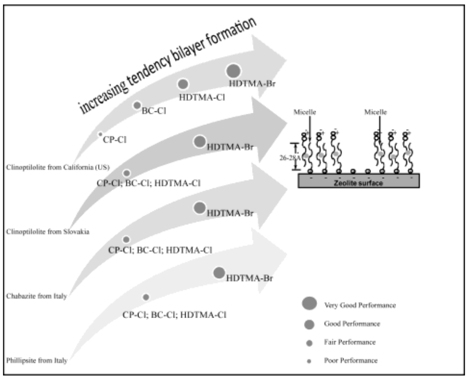

Figure 2. Synoptic scheme representing the surfactant sorption affinity sequence for the selected systems

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The "Tufo Giallo della Via Tiberina" (Sabatini Volcanic District, Central Italy): a complex system of lithification in a pyroclastic current deposit

P. Cappelletti[1], P. Petrosino[1], M. de' Gennaro[1], A. Colella[1], S.F. Graziano[1], M. D'Amore[1], M. Mercurio[2], G. Cerri[3], R. de' Gennaro[4], G. Rapisardo[1], A. Langella[2]

[1] *Dipartimento di Scienze della Terra, dell'Ambiente e delle Risorse (DISTAR), Università Federico II di Napoli. Via Mezzocannone 8, 80134-Napoli. Italy; E-mail: piergiulio.cappelletti@unina.it*
[2] *Dipartimento di Scienze e Tecnologie, Università degli Studi del Sannio. Via dei Mulini 59/A, 82100-Benevento, Italy*
[3] *Dipartimento di Scienze Botaniche, Ecologiche e Geologiche, Università di Sassari. Via Muroni 25, 07100-Sassari, Italy*
[4] *CISAG, Università Federico II di Napoli, Via Mezzocannone 8, 80134-Napoli, Italy*

Introduction

Zeolitization processes in pyroclastic deposits of central-southern Italy (i.e. Campanian Ignimbrite and Neapolitan Yellow Tuff from Campi Flegrei) were found to be strictly related to a) eruptive mechanisms and b) thermodynamic conditions occurring after the emplacement (de' Gennaro et al., 2000; Cappelletti et al., 2003; Langella et al., 2013). The present research deals with the characterization of the authigenic mineralization in the Upper Tufo Giallo della Via Tiberina, a pyroclastic deposit cropping out in a widespread area north of Rome. Previous works TGVT products show that they are rich in zeolites (chabazite and phillipsite) derived from post-emplacement transformation of volcanic glass (Cappelletti et al., 1999; Lombardi and Meucci, 2006). Aim of this multidisciplinary investigation was hypothesizing a model able to explain genesis and stability fields of zeolites (including chabazite, phillipsite, and analcime) in the TGVT.

Experimental Methods

A detailed field investigation was carried out, selecting suitable sampling sites in terms of outcrop representativeness. Mineralogy of samples was investigated by X-ray powder diffraction (XRPD); chemical analyses of bulk-rock samples were obtained by X-ray fluorescence (XRF). Optical microscopy (OM) and scanning electron microscopy (SEM) observations were performed and chemical analyses of minerals and glasses were obtained by EDS microanalysis and subsequently elaborated for thermodynamic modeling.

Results and Discussion

The mineralogical and chemical characterization of the main units of UTGVT allowed to reconstruct minerogenetic processes leading to lithification of this formation. In a reconstructed type section of lithified layers, zeolite contents shows a clear predominance of chabazite which occurs in quite high amounts (ca. 40 wt.%) for thicknesses of around 10 meters in the central portion of the deposit. Phillipsite, always subordinate to chabazite, is constant and rarely exceeds 10 wt.%. Feldspar content, although slightly variable, ranges between 5-10 wt.% accounting for the overall amount of this primary phase. Moving downwards in the volcanic sequence, chabazite slowly but constantly decreases accompanied by an as well as constant and slow increase of feldspar. An attempt to correlate such a minerogenetic reconstruction keeping into account the chemical compositions of the glass precursor and the authigenic phases was also carried out. As far as zeolites are considered, it is remarkable to highlight an homogeneous composition of phillipsites which cluster in a defined portion of the diagram of fig. 1 (left). Phillipsite is a K-rich phase with subordinate contents of Na, although a slight Ca-enrichment of this phase was recorded. Quite different is the question concerning chabazites which show a large chemical variability. In particular, the representative points widely scatter along the K÷Ca+Mg side so that a progressive chemical evolution should be hypothesized for this zeolite. Although a hydromagmatic origin has not been accounted for the TGVT eruption, a variable contribution of external water, both meteoric or derived from the surficial stream network, can be hypothesized due to the diffuse presence of accretionary lapilli, mainly in the basal parts of the aggrading deposit. No data has been produced so far about the emplacement temperatures of the TGVT pyroclastic currents but the frequent occurrence of un-burnt wood trunks in the basal layers of the deposit (e.g. base of the succession) makes it possible to hypothesize emplacement temperatures for the front of the flows lower than 250 °C, the ignition temperature of wood (Hudspith et al., 2010). After the emplacement, temperature was preserved for a period of time strongly dependant on thicknesses/grain size/water content/permeability etc. of the deposit and that conditioned the evolution of the minerogenetic process.

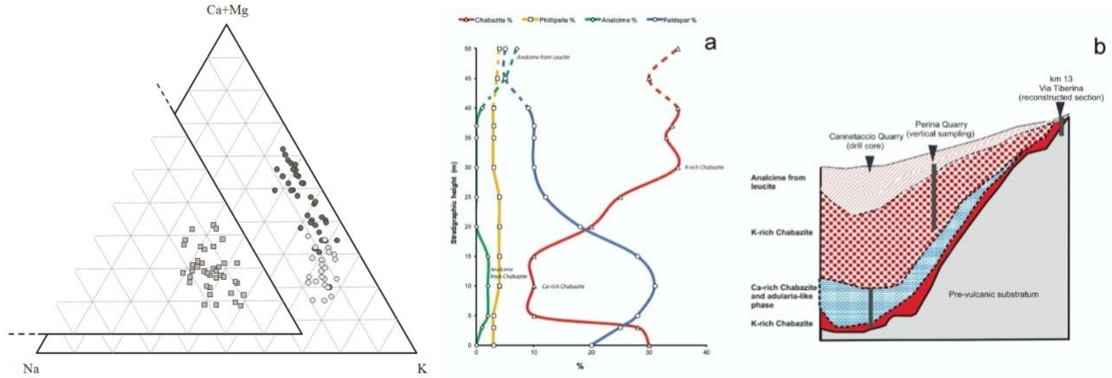

Figure 1. Extraframework cations (Na, K, Ca+Mg) in phillipsites (square) and chabazites (circle), left; . Reconstruction of: a) a type section with vertical variation of the authigenic phases (chabazite, phillipsite, analcime, feldspar); b) a sketch section of the investigated sequences (thickness not to scale) related to the variation of the main authigenic phases, right

Chemical composition of fluids (mostly water) and of the glass precursor defined a pH increase above neutral possibly with the contribution of the calcareous clasts. Higher temperatures persisting in the innermost portion of the deposit (Fig. 1, right) favoured the progression of the minerogenetic process leading to the transformation of the former chabazite in a more stable phase such as adularia. Here the residual chabazite, which was not affected by this phase conversion, is strongly enriched in Ca. This could be explained to a Ca exchange process of chabazite due to the availability of this cation in solution released by chabazite itself during its transformation in K-feldspar, and/or by calcite dissolution from the lithic clasts at higher T °C. Evidence that this portion of the deposit is affected by higher T °C, is the presence, not recorded so far, of analcime, in agreement with a transformation process of a metastable phase (chabazite) in a more stable one (analcime/adularia). In this process analcime could represent an intermediate product of transformation between chabazite and a more evolved/stable phase (K-feldspar) (Langella et al., 2001; de Gennaro et al., 1999). A synthesis of these considerations is given by the thermodynamic model carried out to calculate stability fields of all zeolites(chabazite, phillipsite, and analcime). This reconstruction, although providing a reliable minerogenetic model for UTGVT, also evidences that lithification within this volcanic formation cannot be ascribed only to zeolitization process but also as a consequence of a dissolution of the carbonaceous clasts largely occurring in the deposits and the following re-precipitation of calcite as secondary phase.

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Sorption-regeneration cycles of ammonium by a salt-activated clinoptilolite

M. G. Cardoso, L. M. Paim, I. C. Tessaro and L. A. Féris

Engineer Luis Englert Street, Central Campus of Federal University of Rio Grande do Sul, Department of Chemical Engineering, Postcode: 90040-040 – Porto Alegre – RS – Brazil
E-mail: manuelagc@gmail.com

Introduction

The presence of high ammonia loading in surface and ground waters is a serious environmental impact associated to problems such as eutrophication and toxicity of aqueous system (Zheng et al., 2008). Considering the constant search for processes that promote higher efficiencies with lower costs, the adsorption has become an attractive alternative for wastewater treatment.

It is already known that zeolites are capable of accomplish sorption through ion exchange process with high affinity to ammonium ion (Alshameri et al., 2013). Despite the great interest in ion exchange using zeolites, few data exist in respect of successive adsorption-regeneration cycles by a salt-activated zeolite.

In this work, it was aimed to know the ammonium sorption capacity by a salt-activated clinoptilolite through successive adsorption-regeneration cycles. Additionally, comparative experiments were conducted with and without the reuse of regenerative saline solution. Such a study enables to establish the reduction of the effluent volume achieved by the sorption technique.

Experimental Methods

The salt-activated clinoptilolite (ZS) used in this study was supplied from Celta Brazil Company, São Paulo, Brazil, with a particle size of 0.4-1.0 mm. This material was superficial treated by the referred company, through immersion of the natural zeolite in a batch mixer reactor containing NaCl solution.

The ZS as received was sieved to remove powder, present in a large quantity on the commercial product, and to select a shorter range of size (0.7-1.0 mm). Analytical grade ammonium sulfate $(NH_4^+)_2SO_4$, sodium chloride NaCl and deionized water were used in the preparation of solutions.

The adsorption tests were performed in a shaker bath in the ammonium concentration of 1,200 $mg.L^{-1}$, contact time of 1.25 h, temperature of 25°C, pH of 5.0±1.0 and 0.5 g zeolite in 40 mL of ammonium solution. The regeneration step was conducted with NaCl concentrations of 0.5, 1.0, 1.5, 2.0, 2.5 and 3.0 $mol.L^{-1}$, 0.5 g zeolite in 20 mL of NaCl solution, at the same pH, contact time and temperature of adsorption tests. An ultraviolet spectrophotometer was used to determine the ammonium concentration (APHA et al., 1999).

At the end of adsorption experiments, the solution was discarded and zeolite was dried in oven at 70°C. The dried material was then placed in contact with NaCl solution for regeneration. After regeneration, the NaCl solution was discarded (or collected in the case of reuse of regeneration solution) and zeolite was again subjected to drying. After drying, the zeolite was submitted to new cycles of adsorption.

Percentage of regeneration (%) at each adsorption-regeneration-adsorption cycle was calculated according to the equation:

$$\text{Percentage of regeneration (\%)} = \frac{q_{e,n}}{q_{e,virgin}}.100 \tag{1}$$

where n represents the number of the cycle, $q_{e,n}$ and $q_{e,virgin}$ are the amount adsorbed (mg/g) in the nth regeneration cycle and the amount adsorbed by the zeolite in its first use (virgin material), respectively.

Results and Discussion

Table 1 shows the percentage of regeneration for each cycle of adsorption-regeneration-adsorption performed with concentrations of NaCl from 0.5 to 3.0 mol L^{-1}. This test was done without the reuse of regenerative solution. Some values are above 100%, which indicates that after the regeneration treatment done in laboratory, the amount adsorbed by zeolite (mg/g) were higher from in its first use. It was also observed an increase on values to concentrations from 0.5 to 3.0 $mol.L^{-1}$ for all cycles of regeneration, except in the second cycle where there was an oscilation in the values to concentrations from 1.5 to 3.0 $mol.L^{-1}$.

Table 1. Percentage of regeneration (%) by the salt activated clinoptilolite through the successive cycles of regeneration

Cycle	1	2	3	4	5	Mean
NaCl (mol L^{-1})	Percentage of regeneration (%)					
0.5	88.0	88.3	74.6	75.2	74.8	80.2
1.0	94.9	96.9	86.5	88.4	83.0	89.9
1.5	100.7	113.7	93.9	91.2	92.2	98.3
2.0	104.5	103.1	96.9	94.4	94.3	98.7
2.5	104.0	98.3	100.9	103.8	100.0	101.4
3.0	105.9	100.5	102.8	108.8	106.1	104.8

There was a higher improvement on percentage of regeneration when concentrations were increased from 0.5 to 1.0 and from 1.0 to 1.5 mol.L^{-1} than in the sequent increases, especially for the 4th and 5th cycles. This leads to conclusion that the NaCl solution of 1.5 mol.L^{-1} is economically the best choice to regeneration step.

Figure 1 shows the result of the regeneration study making the reuse of regeneration solution (NaCl 1.0 mol.L^{-1}). The results obtained with NaCl 1.0 mol.L^{-1} solution, presented in Table 1, are included in the Figure for comparison.

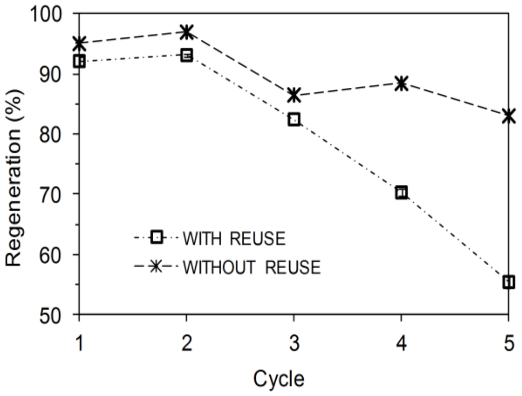

Figure 1. Regeneration of the adsorbent (%) with and without reuse of NaCl solution 1.0 mol L^{-1}

Figure 1 shows that the difference in the regeneration of the zeolite obtained in the tests with and without reuse of NaCl solution was less than 4% until the third cycle. However, from the 4th cycle, the NaCl reused solution was not efficiently able on regenerating the zeolite. Therefore, it was concluded that it is possible to regenerates the zeolite for up to 3 cycles using the same NaCl solution, obtaining approximately 80% of its original capacity. Considering that 40 mL were used to adsorption tests and 20 mL were used in the regeneration step, it can be concluded that it is possible to treat 160 mL (first adsorption plus three cycles) of ammonium solution using only 20 mL of NaCl solution, reducing the effluent volume in 88%. Until the present moment no data was found where the reuse of the regeneration solution to sorption with zeolites is being investigated, which consists in a fundamental feature in wastewater treatment.

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Zeolitization of pyroclastic flows: the case of the "Orvieto-Bagnoregio Ignimbrite", Central Italy

G. Cerri[1], A. Brundu[1], P. Mameli[1], P. Cappelletti[2], A. Langella[3], P. Petrosino[2], G. Rapisardo[2], R. de' Gennaro[2], A. Colella[2], M. D'Amore[2] and M. de' Gennaro[2]

[1]*Dipartimento di Scienze della Natura e del Territorio, Università di Sassari, Via Piandanna 4 – 07100 Sassari (Italy); E-mail: gcerri@uniss.it*
[2]*Dipartimento di Scienze della Terra, dell'Ambiente e delle Risorse, Università "Federico II" di Napoli, Via Mezzocannone 8 – 80138 Napoli (Italy)*
[3]*Dipartimento di Scienze per la Biologia, la Geologia e l'Ambiente, Università degli Studi del Sannio, 82100 – Benevento (Italy)*

Introduction

The "Orvieto-Bagnoregio Ignimbrite" (OBI) is an assemblage of Quaternary pyroclastic flows located 80 km NNW of Rome that stretches over a wide area. In detail it is constituted by two main silica under-saturated pyroclastic flows often containing chabazite and phillipsite. In spite of the large amount of commercial and petrographic knowledge of this rock, which has been largely exploited for dimension stones, no studies have concentrated specifically on understanding the process(es) that led to zeolitization of the flows. Previous research (Passaglia and Vezzalini, 1985; Granato et al., 1991; de'Gennaro and Langella, 1996) generally focused on the crystal-chemistry of zeolites (and sometime of glass) and the extent of zeolitization through the formation. Because authigenic processes can be strongly influenced by local conditions, detailed sampling is required to detect small chemical-mineralogical variations that otherwise would be missed. The aim of this work is to formulate a zeolitization model that is consistent with the detailed vertical mineralogic variations of the OBI.

Experimental Methods

After a preliminary survey and study over the outcrop area of the OBI, the best-exposed section was sampled on a face of the Palombara quarry (Viterbo province). The section presents two facies belonging to a single pyroclastic flow, grey and poorly consolidated at the bottom and yellow-orange and lithified at the top. The change in color is sharp and occurs along an irregular, sub-horizontal surface. On the quarrying front, a climber collected nineteen samples, one per meter, along a vertical line. Total mineralogy was investigated by X-ray powder diffraction (XRD), utilizing a Siemens D5000 diffractometer, and by scanning electron microscopy (SEM), utilizing a ZEISS LS10 instrument. Chemical analyses of the single phases have been performed with an Oxford INCA energy-dispersive spectrometer (EDS). Rietveld quantitative mineral analyses were carried out using XRD data with Bruker Topas 4.2 software package, and amorphous content was determined using an α-Al_2O_3 internal standard (20 wt%, 1μm, Buehler Micropolish). Rock chemistry was investigated by X-ray fluorescence (XRF) and atomic absorption spectroscopy (AAS) utilizing a Panalytical Axios apparatus with superQ Panalytical software, respectively.

Results and Discussion

XRD analyses detected zeolites only in the yellow-orange facies. The lowest zeolite content was recorded at the top (13 wt.%), and the zeolite content never exceeded 40 wt.% (*avg.*: 34 wt.%). Chabazite always prevailed over phillipsite (*avg.*: 29 and 4 wt.%, respectively). The feldspar content in the yellow facies is greater than in the grey facies (*avg.*: 43 wt.% vs. 34 wt.%), whereas volcanic glass was more abundant in the latter (*avg.*: 17 wt.% vs. 66 wt.%).

Chemical analyses by XRF and atomic absorption spectroscopy revealed Na and K loss in the yellow-orange facies compared with the grey facies, as evidenced through the Log-plot used by Broxton et al. (1987), whereas Ca, Mg and Sr showed a gain. Na loss increased from the top to the middle of the zeolitized section, where the greatest loss was recorded. Ca and Sr gains, as well as the Na loss, were correlated with zeolite content along the section: R^2=0.8 (both Ca and Sr) and R^2=0.9 (Na). Determination of Fe^{3+}/Fe^{2+} ratios suggested that the different color of the two facies is linked to the higher iron oxidation in the yellow-orange facies.

SEM observations suggested a sequence of crystallization of the secondary phases in the yellow-orange facies: authigenic K-feldspar → chabazite → phillipsite.

Energy dispersive spectroscopy (EDS) analyses of primary feldspars, authigenic K-feldspars, and volcanic glass showed only minor variations in chemical composition that were unrelated to stratigraphic position. On the contrary, the chemical composition of chabazite and phillipsite revealed a distinct chemical variability linked to the stratigraphy, with zeolites in the central part of the yellow facies being poorer in Na.

Our data indicate that authigenic processes have been more intense in the central portion of the section, which is consistent with secondary mineralization governed by the progressive cooling of a pyroclastic flow. The base of the flow was not altered because it was cooled quickly by the substrate, giving the grey facies. The original top of the flow deposit, directly exposed to the atmosphere, also cooled quickly, acting – as did the bottom of the unit- as a thermal insulator for the core of the deposit (Riehle et al., 1995). In the hottest section, the phonolitic glass initially began to react to form K-feldspar (de'Gennaro et al., 2000; Langella et al., 2013), leaving an excess of Ca and Na available. Decrease in the aK^+/aCa^{++} ratio, the percolation of water, and progressive cooling resulted in conditions favorable for chabazite nucleation. As chabazite formation consumed more Ca than K, its formation continued until the aK^+/aCa^{++} ratio became favorable for phillipsite nucleation. Secondary mineralization ceased when the unit cooled, as indirectly demonstrated by the significant amount of residual unaltered glass in the zeolitized facies. Only later was the original top of the flow deposit progressively eroded because it was unlithified.

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Effect of zeolite treated water on the phytochrome system of plants

K. Chakalov and T. Popova

Balkan Plant Sciences Ltd, 34, Zlatovruh Str., 1164 Sofia, Bulgaria;
E-mail: konstantinchakalov@yahoo.com

Introduction

Several recent studies discuss the structure of zeolite water in single crystals of natural zeolite. Hydrated clinoptilolite is known to absorb electromagnetic radiation and the water dipoles in the crystal structure take different charges. Thereby, its increased mobility provides a practical tool that can influence various molecular-biological processes. The periodic potential of lattice forces allows water molecules to occupy the most favorable positions. Since the crystal is saturated by water molecules and there are more molecules than advantageous positions, the excessive molecules must occupy the interstitials. Thus, the elastic forces of the intermolecular interactions tend to establish a different order. The resulting equilibrium state of the chain is, therefore, a compromise between competing factors (Gabuda S. P., 2002).

In-depth analyses of dynamic and electronic properties of the water have shown that the water in the hydrophobic zeolite behaves as a nanodroplet. As such, it is constantly trying to close its hydrogen bonds by itself by using a few short-living dangling OH-groups. In contrast, the water in the hydrophilic zeolites opens up to form weak hydrogen bonds with the oxygen atoms of the framework. Finally, the dependence on the polarity of the dipoles of the water content of the zeolite is more important than the dependence on the number of cations (Francois-Xavier Coudert et al., 2009).

Apparently, the zeolite-treated water has a potential to accelerate some biological processes. Thus, an important issue is whether the self-polarisation of the water can be kept in zeolite-treated water. A related question is, therefore, whether it is possible to apply zeolite-treated water for regulation of some physiological processes in plants? The aim of the present study is to address these questions. Specifically, we attempted to determine the impact of clinoptilolite-treated water on the plant phytochrome system.

Experimental Methods

The studied zeolite samples (clinoptilotite type) are from “Beli Plast” (BP) deposit, Eastern Rhodopes, BG, with CEC = 95.25 meq/100g, and from “Golobradovo” (G) deposit, Eastern Rhodopes, BG, with CEC = 83.55 meq/100g (size 0.1-0.8 mm). The physiological activity of the zeolite-treated water is examined by a standard hypocotyls test with lettuce seeds as well as in an experiment with foliar spraying of Poinsettia plants – once a week, 4 times.

The scheme of treatment of water with zeolite (BP or G) is as follows: with untreated zeolite – filtered (FNZ) and unfiltered (NZ); with zeolite treated in 300^{o}C for 24h - filtered (FNZ 300) and unfiltered (NZ 300), and with zeolite treated in 750^{o}C for 24h filtered (FNZ 750) and unfiltered (NZ 750). Control – distillated water. For the hypocotyls tests filtered treated water only was used. The water was treated with 20g zeolite per liter.

Results and discussion

The effect on the stimulation or inhibition of the forming of phytochrome A in the seeds can be estimated by the difference between the growth of the hypocotyls in the dark and under radiation with red light (≈650nm). It is considered that the phytochrome system is one of the main receptive systems of the plants, participating in the hormone regulation and in particular - in the activation of the synthesis of auxins, gibberellins and cytokinins in plants. Since these reactions of the researched test organs are related to an exogenic influence, it should be possible to evaluate the inhibiting or stimulating role of the respective compounds on the growth of the hypocotyls of lettuce seeds. For instance, the auxins inhibit these processes, whereas the gibberellins (contained in the hypocotyls) help their growth. It can be assumed, therefore, that the formation of a chain of connected dipoles of water activated by zeolite is able to deliver its potential on the phytochrome system of plants.

The data presented in Figure 1 a) and b) show that the water treated with destroyed zeolite provides its effects by the chemical composition per se, instead by activating the phytochrome system. Conversely, the water activated by natural form or dehydrated zeolite increases the effect of the radiation with red light two times and does not depend on the CEC of the zeolites.

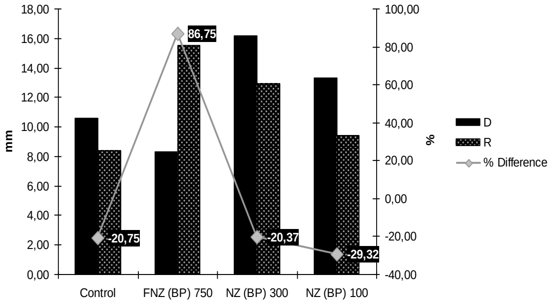

Figure 1.a) Influence of zeolite (BP) treated water on phytochrome system - standard hypocotyls lettuce test (Dark – p=0.0002; Red light – p <0.0001; % difference – p<0.0001)

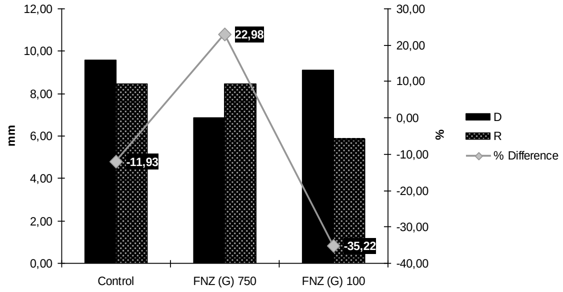

Figure 1.b) Influence of zeolite (G) treated water on phytochrome system - standard hypocotyls lettuce test (Dark – p<0.0001; Red light – p <0.005; % difference – p<0.0001)

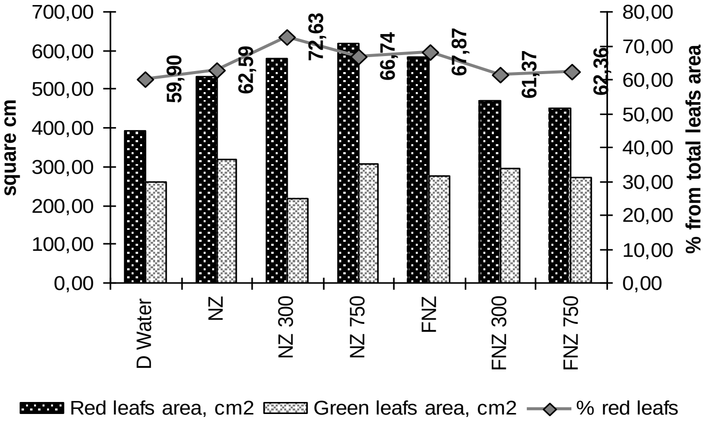

Figure 2. Influence of zeolite (BP) treated water on the forming of red leaves of Poinsettia plants (Green leaves area – p=0.2644; Red leaves area – p=0.0081)

Poinsettia has a genetic "circadian clock" in the DNA, which is activated by the phytochrome system. The coloring of leaves depends on these processes. Phytochrome is a major acceptor of photons. Probably, the water treated with NZ further activates the phytochrome system of the plants, whereas the water treated with NZ 300 and NZ 750 has a limited influence. The zeolite-activated water decreases the green leaves area of plants and increases the red leaves area with almost 48%. The present findings suggest that the water treated with zeolites retains the order of its charges as they are in the lattice and this significantly influences the ability of the phytochrome system to accept photons of red light. Thus water activated with clinoptilolite can stimulate the physiological processes in plants.

Conclusions

The water activated with natural clinoptilolite can stimulate the physiological processes in plants by supporting their phytochrome system. Probably, the CEC of zeolites has a slighter influence than their crystalline structure.

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Hydration Process and Strength Evolution of Air-cured Zeolite-rich Tuffs and Siltstone Blended Cement Pastes at low W/B Ratio

M. H. Cornejo[1,2], J. Elsen[2], C. Paredes[1] and H. Baykara[3]

[1] *Escuela Superior Politecnica del Litoral. Department of Mechanical Engineering and Production Sciences. Km. 30.5 Via Perimetral, Guayaquil, Ecuador.; E-mail: mcornejo@espol.edu.ec*
[2]*Katholieke Universiteit Leuven. Department of Earth and Environmental Sciences. Celestijnenlaan 200E B-3001 Heverlee, Belgium*
[3]*Siirt University, Department of Chemistry, Science and Art Faculty, 56100 Siirt-Turkey*

Introduction

The incorporation of natural zeolites into cement hydration leads to changes of the phase assemblages and the kinetic rate depending mainly on the type of zeolites, W/B ratio, and curing condition (Cornejo et al., 2013; Mertens et al., 2007; Snellings et al., 2010). A proper combination of mineral addition and low W/C allows to produce a high performance concrete, which is one of the most important engineering materials. These parameters have been investigated already for a long time (Estokova and Kovalcíková, 2013; Kocak et al., 2013; Mertens et al., 2009; Snellings et al., 2009); however, there are many shortcomings not solved yet.

We performed a multi-methodological study in order to answer to two open questions: 1.- What is the optimum value of dosage to achieve the highest mechanical performance of blended cement pastes in air curing condition and at low W/B ratio? 2.- What is the hydration pathway and pozzolanic reaction of two zeolite-rich tuffs and calcareous siltstone used as Supplementary Cementitious Materials in blended cement pastes under the aforementioned conditions?

Experimental Methods

This study was carried out with the following experimental protocol: the mechanical development and the hydration process of two zeolite-rich tuffs (coded as Zeo1 and Zeo2) and siltstone (coded as Limo), blended with Ordinary Portland Cement type I was evaluated through the uniaxial compressive strength (UCS), Quantitative X-ray diffraction analysis (QXRD), Thermogravimetric-Differential Scanning Calorimetry (TGA/DSC), and Scanning electron microscopy with energy dispersive system (SEM-EDS) varying proportions and curing days. In order to test the pozzolanic reaction in air curing condition, the specimens were cured in controlled-indoor lab environment at 25.6±1.6 °C and 68.6±3.9 % relative humidity during the whole experiment.

A completely randomize block experimental design has been carried out for identifying which proportion developed better mechanical performance than that of the control sample (0% of Zeolite) . Therefore the analysis was conducted with two slight different experimental settings. The reason for using two slight different experimental settings was to analyze small variations in proportioning and testing time, but simultaneously these results can be compared to verify the results over the whole experimental range. Phenomenologically speaking, the variation due to mineral addition can be estimated without repeating the same combination of factors and levels, allowing an analysis of more data under the same experimental condition. The first part called calibration (C) was carried out to identify the best mix using as dosage 5, 10, 15, 20, 25% by weight and 7, 14, 21 and 28 days as testing time, and a second part called replication (R) was done so as to confirm the calibration results using as proportioning 7.5, 12.5, 17.5, 22.5, 27.5 % and 4, 11, 18, 25 days as testing time. It is worth noting that an extensive experimental plan was carried out by testing 477 samples for compressive strength, 159 samples for TGA-DSC and density, 80 samples for QXRD, and some selected samples for SEM-EDS.

In the framework of this study, the following hydration parameters were monitored: content of CH per content of cement, content of CH consumed by pozzolanic reaction per content of cement, content of carbonated CH per content of cement, percentage of normalized water in hydrates, content of calcite, density, and secondary electron images of selected samples and compressive strength.

Results and Discussion

After analyzing the results, the following conclusions can be drawn:

- Two stages of hydration were identified: 1) early hydration vigorously producing CH, CSH, and other hydrates up to 14-21 days, and 2) mid and long-term hydration producing quite slowly CH, CSH and other hydrates; carbonation meaningfully proceeded. The amount of anhydrous cement phases remained almost constant after 7 days. Indeed, it was possible to identify C3S and C2S even at 91 days regardless the dosage.
- The higher the dosage, the higher the carbonation regardless the type of mineral addition.
- Normalized CH content in blended cement paste was generally higher than that of plain cement pastes. This could be due to the accelerating effect of SCM at early ages and additionally that plain cement pastes were more affected by air curing condition.
- Percentage of normalized water in hydrates increased as the dosage increased. Although its increase was clear at early ages, afterwards it remained almost constant over the time; only in a few cases, a slight decrease was observed.
- The higher the dosage, the lower the density. The density slowly increased over the time as hydration proceeded, suggesting that some hydrates were being produced.
- In terms of compressive strength, Zeo1 and Limo -blends performed better than Zeo2-blended cement pastes. In case of Zeo1-blended cement pastes, the best dosage was 5%, although 20% also performed well. In case of Zeo2-blended cement pastes, the best dosage was 5%, although 22.5% also performed well. In case of Limo-blended cement pastes, the best dosages were in the range of 10-12.5%. We also observed that plain cement pastes performed higher compressive strengths than pozzolana-blended cement pastes. This also suggests that the air-curing condition affected less at low replacement than at high ones, mainly at early ages. Apart from a lower compressive strength, a slow hardening rate was also noticed
- We can notice that all the values of the consumed CH amount by the pozzolanic reaction are negative, either for calibration or replication. It suggests that the pozzolanic reaction scarcely proceeded under air-curing condition. On the other hand, the amount of carbonated CH per amount of cement is about 0.1 mg CH / mg cement. This value is approximately 45% of the total amount of produced CH which should be carbonated at the age of 91 days. In other words, as a low water-to-blended ratio and air-curing conditions were used, the carbonation may play the major role during hydration consuming almost a half of total amount of CH produced.

Acknowledgment

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Mordenite from Spain and its application as pozzolana

J. L. Costafreda[1], B. Calvo[1], L. Gómez-Hortigüela[2], J. Pérez-Pariente[2] and I. Díaz[2]

[1] *Fundación Gómez Pardo. Escuela Técnica Superior de Ingenieros de Minas, Madrid, Spain.*
[2] *Instituto de Catálisis y Petroleoquímica, CSIC, Madrid, Spain; E-mail: idiaz@icp.csic.es*

Introduction

In Spain, natural zeolites have been only found in the volcanic areas of Canary Islands (San Gil, M.M., 1959). However, several years ago the study of the South Eastern region of continental Spain (Cabo de Gata) revealed the presence of a deposit of mordenite being industrially commercialized as bentonite. The deposit *San José-Los Escullos* is located in the concession registered as *Los Murcianos*, managed by *Bentonitas Especiales, S.A.* (BENESA) who was extracting bentonite while ignoring the presence of the zeolite. The name San José-Los Escullos refers to the discovery of mordenite in this deposit (Calvo Perez et al., 2005). The deposit is located in a volcanic area, constituted by pyroxenic andesites, breccias, tuffs, pyroclasts with andesitic and dacitic composition, largely altered by the hydrothermal solutions. The recent discovery of this zeolite with mordenite content up to 97%, has changed the initial vision about that deposit, and new possible uses of this mineral in the pozzolanic cement industry are foreseen. This work intends to give preliminary data on the characterization of this zeolite according to X-ray diffraction (XRD), ICP analyses, and scanning electron microscopy (SEM), as well as to emphasize the pozzolanic properties of this material, using both chemical and mechanical tests.

Location and geological setting

The only zeolite deposit studied in continental Spain, named San José-Los Escullos, is located in Almeria Province close to Rodalquilar, Los Escullos and San José district, over the coast line. Geographical coordinates are between 2º 4´ 08" W and 36º 46´ 42" N. The zeolite deposit is part of the main caldera complex of the southeastern volcanic region of Spain: Los Frailes, Rodalquilar, El Cinto y Lomilla de Las Palas (Arribas, A. 1992; Castroviejo, R. 1999), which are composed by a dacitic basement intruded and covered by dacitic domes, pyroxenic and hornblendic andesites, rhyolite and volcano-sedimentary materials (lapilli, tuff, ignimbrite, ash flow), in a wide hydrothermal alteration area (Costafreda, J.L., 2008). The composition of the volcanic area is mainly calc-alkaline (Lopez Ruiz and Rodríguez Badiola,1980). The main host rocks of the zeolitic mineralization are dacite and andesite. There is a strong metasomatic alteration in its contact with zeolite bodies, in which banded zeolite appears as a pseudomorphic product of both, plagioclase and pyroxene.

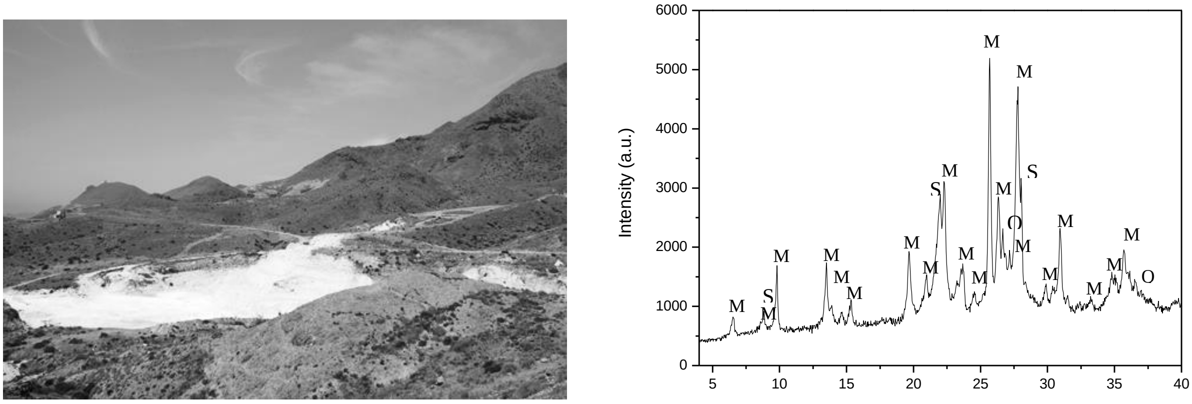

Figure 1. Left: View of the San José-Los Escullos deposit from south-east of the northwestern flank. (Photograph by: J. Costafreda/P. Riaza). Right: X ray pattern of the mordenite (M) sample from Spain, showing only impurities of smectite (S) and quartz (Q)

Experimental methods

The natural mordenite mineral found in the deposit of San José-Los Escullos in Spain, was initially identified by X ray diffraction. Figure 1 shows an image of the deposit along with a typical XRD profile which reveals a large amount of highly pure mordenite, with some impurities of smectite (S) and quartz (Q). Table 1 displays the chemical composition obtained from ICP (in weight %) showing a Si/Al ratio of 4.3 which lies in the range of 4 to 6 commonly observed in this type of natural zeolite, and a high content of Na^+; the corresponding approximate unit cell formula, excluding Fe, Ti and Mg contents and assuming that all the mineral corresponds to mordenite, is $Ca_{1.0}Na_{4.9}K_{1.8}Al_{8.6}Si_{39.4}O_{96}$.

Table 1. Composition of the natural mordenite (measured by ICP, in weight %)

Al	Ca	Mg	Fe	K	Na	Ti	Si
6.2	1.0	0.4	0.9	1.9	3.0	0.1	28.5

From this data the final oxides composition would be SiO_2 61wt%; Al_2O_3 11.7wt%; Na_2O 4wt%; K_2O 2.3wt%; CaO 1.4wt%; MgO 0.7wt%; Fe_2O_3 1.3wt%; TiO_2 0.2wt%, being the remaining 17% weight due to water.

The pozzolana behavior depends on the chemical composition, specifically on SiO_2 and Al_2O_3 contents, the level of grinding and the geometric homogeneity of the particles (Costafreda, J.L., 2008). The studies carried out on the Spanish zeolite from San José-Los Escullos deposit yield promising properties due to the high content of SiO_2, Al_2O_3, Na_2O and K_2O. On the other hand, low contents of MgO, SO_3 and chloride have been found (Costafreda, J.L. et al 2007). A great ion exchange capacity, structure stability, porosity, absorption and LOI capacity have been determined (Costafreda, J.L. et al, 2011). In addition, these minerals show an unusual percentage in both, reactive silica (>60%) and reactive CaO (>1.4%). All these properties were decisive in preparing cements, mortars and concretes, with low heat of hydration, and high strengths after ca. 28 days (> 50 MPa) (Costafreda, J.L., et al, 2011). The slower hydraulic reaction facilitates the complete hydration of dicalcium silicate. The pozzolanic character of this Spanish zeolite was shown through a multistage process in the solid-liquid and solid-solid interface (zeolite + cement + water), which starts with the reaction between zeolite and portlandite ($Ca(OH)_2$) providing a new reaction product: the tobermorite ($Ca_5Si_6O_{16}(OH)_2.4H_2O$). The appropriate reaction speed was reached due to previous sample crushing and grinding, up to grain sizes of 0.080 mm, 0.063 mm and 0.040 mm (Costafreda, J.L. 2008). From the industrial point of view, the zeolites have lower manufacturing costs associated, preventing excessive expansion and gas emissions, low reaction with sulphates and mineralized waters, as well as building of lighter structures.

Acknowledgment

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Use of natural zeolite as an ad-mixture for production of pozzolan cements

M. Daňko

Institution address: Zeocem a.s., Bystré 282, 094 34 Bystré, Slovakia. E-mail: zeocem@zeocem.com

Introduction

Many researchers have recently addressed the issue of finding portland clinker substitutes such as power station fly ash, silica fume, finely ground limestone, blast furnace slag or combinations of such materials. These studies have proven interesting from both environmental and technical points of view.

The objective of this work is to inovate existing products on the construction market such as pozzolan cements and special cements used to store radioactive materials by using natural zeolite. This work also researches the impact of zeolite in increasing the sulphate resistance of portland cement and the influence of zeolite on the mechanical strength of new pozzolan cements mixed and produced by Zeocem a.s.

Zeocem a.s. is a dynamically growing company with 60 years of experience in processing natural materials. Its production program and infrastructure are closely connected to the operation of a former cement plant in Bystré. A progressive move away from the production of construction materials has led it to become one of the most important producers of zeolite products in Europe. Zeocem, a.s. has its own quarries for natural, high quality zeolite and our meticulous processing method allows us to offer superior products based on natural zeolite.

Experimental Methods

The pozzolan activity of a material is based on the reaction of aluminosilicates with calcium hydroxide in an aqueous environment to calcium aluminium silicate hydrate (CASH). The creation of these crystal form hydrates may increase the strength of pozzolan cements in comparison with normal (slag) cement. The presence of natural zeolite (what type – clinoptilolite???) in the cement can prevent unwanted expansion of the concrete caused by the alkali-silica reaction.

The experimental section was tested in real production conditions for pozzolan cements with various levels of zeolite content, classified into strength classes and a set of design milling parameters was compiled.

Results and Discussion

The overall composition of the cements was defined and is shown in Table 1. The individual samples were prepared by milling zeolite together with the requisite clinker content and 6 wt % of gypsum in relation to the quantity of the clinker. The mechanical strength of the new pozzolan cements is higher in comparison with the strengths of similar cements. The increase in strength compared to the normal consistency proves that the zeolite contains active SiO_2 and Al_2O_3. A slight increasing trend in the strengths of these cements is expected. CEM V/A and CEM II/B-P class cements are used in the processing of radioactive waste (RAW) and are produced by Zeocem a.s. The former is used in the production of fibre-concrete containers, which are used for the temporary storage of solid and reinforced RAW and for the final storage of treated RAW. The latter is used in cementing treatment for liquid and solid RAW. The resulting product is cemented liquid RAW in cement group and cemented solid RAW (drums, mouldings, etc.) in fibre-concrete containers. The elimination of sulphate corrosion is ensured by applying a sulphate resistant portland cement with low C_3A (tricalcium aluminate - $3CaO \times Al_2O_3$) content (up to 3.5 %wt) or by applying pozzolan portland cement. Zeolite reacts with CaO using the pozzolanic reaction. This reduces the formation of $Ca(OH)_2$ and consequently its reaction with gypsum. This creates slightly hazardous gypsum. The ion exchange capacity of zeolite for Ca^{2+} ions is 1.82 mmol Ca^{2+} xg^{-1} or 0.073 g Ca^{2+}x g^{-1} of zeolite.

Table 1. Summary mechanical strength results and comparison with related types of cement

Type of cement	zeolite %	1 day		2 days		7 days		28 days		56 days (2 m)	
		Q1	T1	Q2	T2	Q7	T7	Q28	T28	Q56	T56
CEM II/A-P 42.5 N	15	4.17	15.0	5.09	22.1	7.4	38.6	9.80	62.7	10.38	65.0
CEM II/A-S 42.,5 N		3.18	11.5	4.74	19.9	6.74	28.8	9.74	46.7		
CEM II/B-P 42.5 N	25	2.45	8.7	3.50	15.3	6.3	30.4	10.02	57.6	10.59	60.3
CEM II/B-S 32.5 R		2.46	8.8	3.80	15.6	6.26	25.1	9.67	43.7		
CEM IV/A 42.5 N	35	3.00	11.2	3.78	16.3	6.4	29.2	9.67	61.9	9.97	61.3
CEM III/A 32.5 N				2.82	11.2	5.3	22.2	9.49	41.4		
CEM IV/B 32.5 N	45	1.60	7.0	2.35	9.3	4.1	19.8	8.52	48.4	9.37	53.5

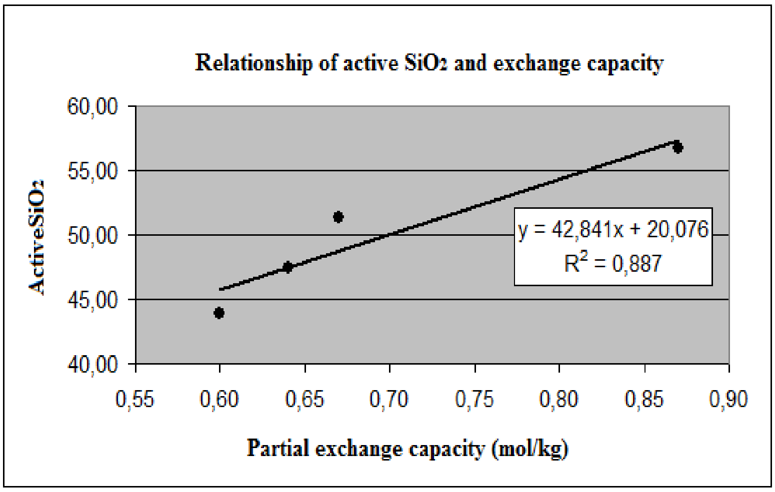

Figure 1. Relationship of active SiO_2 and exchange capacity of zeolite

Using zeolite as a partial replacement for portland cement decreases C_3A content in the cement and inhibits the formation of CSH_2 thereby eliminating the bulk reaction product – ettringite.

The achieved results indicate the ability to produce pozzolan mixtures of cements with zeolite content of up to 45 wt% in large volumes as well. In the production of pozzolan cements, we propose using a higher percentage of anhydrite ad-mixture – 8 % as hardening occurs in less time when compared to common types of cement and for CEM IV/B 32.5 N cement even at the minimum specified standards. It was determined that the application of 15 wt % of zeolite as a partial replacement for ordinary portland cement achieves the same level of sulphate resistance in mixed cement as sulphate-resistant portland cement. This cement may be classified as special portland pozzolan cement with sulphate resistance at a level of commonly available sulphate resistant portland cement.

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Natural Cuban zeolites for medical use and their histamine binding capacity

W. Dathe[1], T. Selvam[2] and W. Schwieger[2]

[1]*Heck Bio-Pharma, Karlstraße 5, D-73650 Winterbach, Germany; E-Mail: daweidoc@gmx.de*
[2]*Friedrich-Alexander-Universität Erlangen-Nürnberg, Institute of Chemical Reaction Engineering, Egerlandstraße 3, D-91058 Erlangen, Germany*

Introduction

Natural zeolites are microporous crystalline aluminosilicates with regular channels and cavities of molecular dimensions. They possess attractive properties such as adsorption, ion-exchange, molecular sieving and potential binding capacity for toxins and other harmful substances. Based on their bio-stability and biocompatibility, natural zeolites are finding increasing interest in research and use for application in human and veterinary medicine (Colella, 2011, Krajišnik et al 2013). However, it is worth to mention that most of the experiences have been made on the field of complementary medicine. The use of natural zeolites as medical product for human being requires a detailed analysis of their chemical composition, phase purity, ion exchange properties and microstructural harmlessness. Among the zeolite deposits available from around the world, the zeolite deposits from Cuba belong to the good investigated ones (Céspedes-Ortiz et al., 2011). These natural minerals are used for pharmaceutical formulations due to their high clinoptilolite content and extensively tested toxicological and pharmacological compatibility (Rodríguez-Fuentes et al., 2006). In the present study, we refer mainly to the natural Cuban zeolite deposit from San Andrés, which will be used as source of the natural zeolite drug Detoxsan® for different applications and galenical formulations. Special attention was paid to study the uptake of histamine by zeolite due to its important role as a regulator for human physiological processes, such as allergic inflammation, immune response and regulation of gastric acid formation.

Experimental Methods

The Cuban zeolites used in the present study were from San Andrés (particle size: ~40 μm) and Tasajeras (particle size: ~ 40-180 μm). The X-ray diffraction (XRD) patterns of the samples were recorded on a Philips X-ray diffractometer using Cu-Kα radiation. The XRD patterns were collected in the 2θ range between 2-50° at a scan rate of 0.2° 2θ per min. The quantification of the phases (clinoptilolite and mordenite) was done by using synthetic samples. The morphology of the zeolite deposits was studied using an Environmental Scanning Electron Microscope (FEI Quanta 200).

The BET surface areas of the samples were determined by an automated nitrogen adsorption analyser. The elemental compositions as well as environmental toxins of the samples were determined by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) and Gas Chromatography-High Resolution Mass Spectrometry (GC-HRMS), respectively.

Histamine uptake by natural zeolite was carried out at 36 °C. Typically, 0.3 g of histamine was dissolved in double distilled water or HCl solution (100 ml) in a polypropylene bottle. Zeolite sample (3 g) was dispersed into the above solution and the bottle was stoppered and then placed in a mechanical shaker (90 cps). Samples were collected at different times (15, 30, 60 and 120 min) by taking small aliquots (~10 ml) from the reaction mixture, filtered, dried at room temperature and analyzed by thermogravimetric analysis (TG-DTA) using TA instruments SDT 2960. The sample was heated up at a rate of 10 °C/min from room temperature to 900 °C under air atmosphere.

Results and Discussion

The total contents of the zeolite phases present in San Andrés and Tasajeras are 83% (clinoptilolite: 46% and mordenite: 37%) and 78% (clinoptilolite: 52% and mordenite: 26%), respectively. While the deposit of San Andrés seems to be free of other phases (Quartz <1%) in Tasajeras about 5% of each quartz and anorthite are present. The BET surface areas of zeolites of both deposits San Andrés and Tasajeras are 142 m^2g^{-1} and 90 m^2g^{-1}, respectively. The higher surface area of San Andrés zeolite could be due to the higher total zeolite content and the higher proportion of mordenite as a large-pore 12-membered ring zeolite (pore size: 6.5 x 7.0

Å); clinoptilolite is a medium-pore 10-membered ring zeolite (pore size:3.1 x 7.5 Å). The lower surface area of Tasajeras zeolite could also be due to the presence of the additional phases like quartz and anorthite.

The Scanning Electron Microscopy (SEM) images of both the samples from San Andrés and Tasajeras at different magnifications resulted in crystallites without definite morphology. It is quite evident that these samples are indeed free from fibrous materials such as asbestos and Erionite, which are known to be carcinogens (Carbone et al., 2011).

The uptake of histamine by both zeolites has reached a maximum within the first 15 minutes independent of the pH value (Table 1). The uptake capacity for histamine (at pH = 7) is similar by both zeolite deposits. The small differences in mineralogical composition seem to influence the histamine uptake capacity only slightly. Furthermore, the uptake capacity is about 20% higher under neutral (pH = 7) than under acidic (pH = 1) conditions. In order to get information about the stability of histamine within the zeolite, we treated the zeolite-histamine samples of San Andrés under two different pH conditions (pH = 3.5 and 7) at 36 ^{o}C for 3 h, and analyzed them by TG-DTA measurement. At both pH values, less than 18% of the adsorbed histamine was leached out indicating that histamine is strongly adsorbed onto natural zeolite of San Andrés (Selvam et al. 2014).

Table 1. Histamine uptake by natural Cuban zeolite obtained from San Andrés and Tasajeras under two different conditions[a]

Conditions	Incubation time, min	Histamine uptake, mg/g[b]	Histamine uptake, mg/g[b]
		San Andrés	Tasajeras
Hydrochloric acid	15	12.4	-[c]
(0.1 M, pH = 1)	30	11.4	-[c]
	60	12.4	-[c]
	120	12.9	-[c]
Double distilled water	15	15.7	14.1
(pH = 7)	30	13.7	15.5
	60	16.0	15.7
	120	15.7	15.5

[a]3 g of zeolite, 100 ml solution, 0.3 g histamine, temperature = 36.0 °C; [b]Determined by TG measurements in the temperature range of 350-600 °C; [c]Not determined.

Acknowledgment

BET surface areas of the samples were determined by Micromeritics Analytical Services Europe, Aachen, Germany and the elemental compositions as well as environmental toxins of the samples were determined by Wessling GmbH, Altenberge, Germany.

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Terephthalic acid (TPA) adsorption on natural zeolite supported titania composites

Ö. Deliismail[1], H. Banu Yener[2], M. Yılmaz[2], Ş.Ş. Helvacı[2] and F. Cakicioglu-Ozkan[1]

[1]Izmir Institute of Technology, Faculty of Engineering, Department of Chemical Engineering, Izmir, Turkey;
E-mail: fehimeozkan@iyte.edu.tr
[2]Ege University, Faculty of Engineering, Department of Chemical Engineering, Izmir, Turkey.

Introduction

Terephthalic acid (TPA) is the raw material commonly used for the manufacture of polyester fibers and films and also widely used in coating, adhesive, dye, plasticizer and other production industries (Wang at.el., 2011). In TPA production process, a large number of high concentration wastewater would be produced and thus this acid has been designated as pollutant. Due to its chemical structure, TPA cannot be removed completely by the natural processes. Thus, the investigations on TPA degradation are also of great importance.

In this study, the natural zeolite supported titania composite was synthesized in order to be used as a photocatalyst. Adsorption of TPA as the model organic pollutant on the synthesized composite was followed. Configuration of adsorbed acid on adsorbent is very important for degradation process Adsorption which is of significant importance for photocatalytic degradation kinetics was presented.

Experimental Methods

Natural zeolite supported titania composites were synthesized using titanium tetrachloride ($TiCl_4$) as TiO_2 precursor and clinoptilolite-rich natural zeolite from Gördes(Turkey) as support. The hydrolysis reaction was performed at 95° C, under reflux and at a constant stirring rate by the addition of aqueous acidic $TiCl_4$ solution onto the purified natural zeolite with the particle sizes less than 38 μm. Characterization of the synthesized zeolite supported titania composite was done by using XRD analysis, FEG-SEM analysis, FT-IR spectroscopy and by determination of the textural properties.

Terephthalic acid (TPA) was used as the model organic adsorptive substance and pollutant. The adsorption kinetics of TPA on the natural zeolite and natural zeolite supported titania composite was studied in the range of 0.1-1.5 g/L adsorbent concentration in the 20 ppm initial TPA concentration. The concentrations TPA in the supernatants were determined by UV-VIS spectroscopy at the characteristic wavelength of 241 nm. The measurements have continued up to equilibrium.

Results and Discussion

The XRD patterns and FEG-SEM images indicated the synthesis of rutile TiO_2 particles and spherical agglomerates, consisting of nano fibers, on zeolite support. TiO_2 particles were formed on the external surface of the support due to their sizes. The FT-IR spectra and TGA curves showed the inclusion of Ti^{4+} ions into the zeolite matrices and no structural change in the composites due to heating, respectively. It was observed that an increase in the BET surface area of the zeolites from 23 m^2/g to 210 m^2/g after the synthesis of TiO_2 particles.

Representative kinetic curves of TPA adsorption on synthesized zeolite supported titania composite for two different adsorbent concentration of solution is presented in Figure 1. Results showed that amount adsorption of acid incresed over time, at both concentration. It is observed that the amount of TPA adsorbed, q (g adsorbed TPA/ g adsorbent) was decreased with increasing the amount of adsorbent in suspension (Figure 1). This can be inferred as the consequence of the agglomeration of particles.

The percent adsorption (%), adsorbed percent of initial TPA in the solution did not altered with increasing adsorbent concentration of the solution. The percent adsorption on clinoptilolite-rich natural zeolite supported titania (%70) are higher than that of clinoptilolite-rich natural zeolite(%50) at equilibrium.

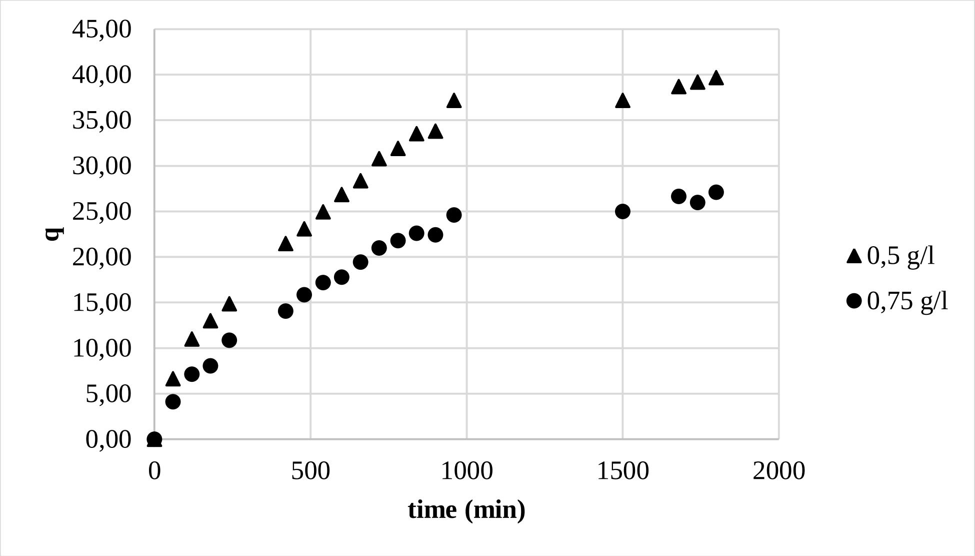

Figure 1. Effect of adsorbent amount (g adsorbent/L solution) on adsorption of terephthatic acid on clinoptilolite rich natural zeolite supported titania (initial TPA concentration: 20 ppm)

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Merlinoite synthesis from natural perlite precursor

L. Dimitrov, O. Petrov, M. Tarassov and V. Petkova

[1]*Institute of Mineralogy and Crystallography, Bulgarian Academy of Sciences, Sofia, Bulgaria;*
E-mail: opetrov@dir.bg

Introduction

The volcanic rock perlite is abundant raw material in Bulgaria (Yanev, 1987) and is an attractive low-cost source of silica and alumina for synthesis of molecular sieves with attractive potential.

Merlinoite is a rare natural zeolite. Its crystal structure consists of three-dimensional pore system of intersecting channels formed by 8-membered tetrahedral rings (Meier et al., 1996). It is a small pore, predominantly potassium-rich, alumosilicate, which, according to the nomenclature of the International Zeolite Association is with MER type topology. Recently, at temperatures 140-170°C, various zeolites were prepared from perlite at hydrothermal conditions. Depending on the SiO_2/Al_2O_3 ratio and NaOH concentration in the starting gel Kongkachuichay and Lohsoontorn (2006) prepared a phase diagram of the products - analcime, NaP1 and sodalite, synthesized form perlite. Additionally, analcime as a major product of perlite transformation at 140°C and 3N NaOH (1:5 solid/liquid ratio) and cancrinite (at solid/liquid ratio = 20) and NaP (at 100°C and atmospheric pressure) were also obtained (Tangkawanit and Rangsriwatananon, 2005).

The purpose of the present work is to investigate the possible hydrothermal synthesis of microporous phases using perlite from Schupenata planina deposit (East Rhodopes, Bulgaria).

Experimental Methods

Naturally occurring rhyolitic glass (perlite, kindly supplied by Y. Yanev) was used as a starting material (chemical composition in wt. % – 80.44 SiO_2, 11.83Al_2O_3, 5.68 K_2O, 1.60 Fe_2O_3, 0.39 TiO_2, and 0.06 MnO_2). The used perlite was crushed and milled to a fraction less than 0.250 mm.

Merlinoite was reproducibly synthesized from perlite in the presence of 2N KOH solution at different solid /liquid ratios and temperatures from 100 to140°C. At higher temperature (140°C) and solid/liquid ratio = 0.5 and 43 h hydrothermal treatment merlinoite is obtained with the yield of about 85 wt. %.

The SEM and EDS analyses were performed at 20 kV acceleration voltage on a ZEISS EVO 25LS with an EDAX Trident system.

The powder XRD patterns were recorded on diffractometer D2 Phaser (Bruker) with CuK_α radiation (30 kV, 10 mA). The 2θ scanned range was 4–40° with step of 0.05° min^{-1} and 1 sec counting time.

Bruker Advance AV 600 spectrometer was used for the ^{29}Si and ^{27}Al MAS NMR measurements

Results and Discussion

The studied perlite sample is a porous glass-dominated rock with curved or more rarely concentric desiccation cracks. Apart from the glassy material (~75 %), the rock contains quartz (Qz) (prevailing crystalline phase, ~ 10-20 %), sanidine (Sa) (very common phase, ~ 5-15 %), plagioclase (more rare phase, $\leq$5 %) and biotite (sporadically <1 %). The crystalline phases are presented either by hemihedral and euhedral crystals (400-1000 μm in size) or randomly shaped micro grains with size ~20-200 μm (Fig. 1.)

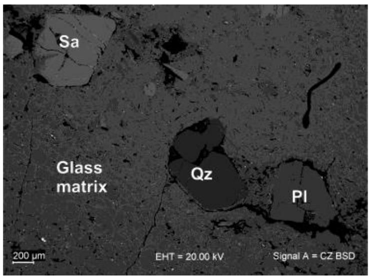
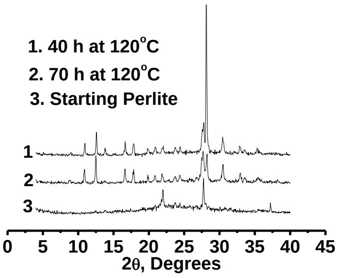


Figure 1. Inclusions of hemihedral crystals (400-600 μm) and micro grains (<200 μm) of sanidine (Sa), quartz (Qz) and plagioclase (Pl) in glass matrix. Perlite. BSE image

The chemical composition of the glassy material as determined in several areas is comparatively uniform and dominated (in wt. %) by SiO_2 – 73-74, Al_2O_3 - ~11, K_2O – 6-7, Na_2O – 1-2. The total sum of other components (Fe_2O_3, MnO, CaO, MgO) is lower- than 1 wt.%. The studied sanidine presents solid solution of potassium feldspar (Ksp) 71-73 mol. % and albite (Ab) 27-29 mol. %. The plagioclase is oligoclase with 72-74 mol. % of albite, 17-18 mol. % of anorthite and ~10 mol. % of potassium feldspar. The synthesized merlinoite is evidenced by the XRD pattern shown on Fig. 2 and the morphology of the crystals is shown on Fig. 3.



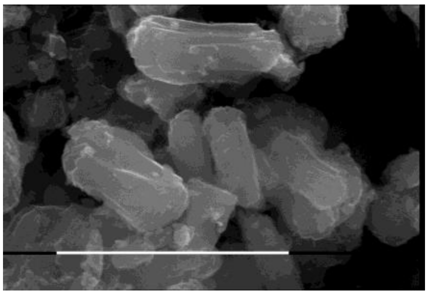
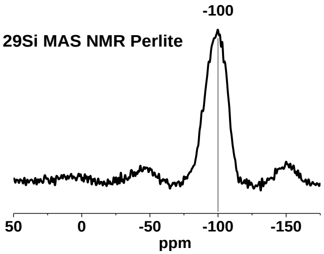


Figure. 2. Powder XRD patterns of perlite and the as-synthesized merlinoite at 120° C for 40 h and 70 h

Figure. 3. SEM photo of merlinoite crystal intergrowths obtained at 120° C for 40 h

The SEM observations (Fig. 3) show that merlinoite forms crystal intergrowths. The Solid-state ^{29}Si MAS NMR spectra of perlite and the obtained merlinoite are shown on Fig. 4 and Fig. 5, respectively and reveal the degree of skeleton structural order in perlite and merlinoite.



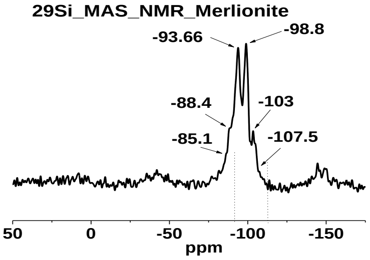


Figure. 4 Solid-state ^{29}Si MAS NMR spectrum of perlite

Figure. 5. Solid-state ^{29}Si MAS NMR spectrum of merlinoite

The peak around 100 ppm (Fig. 4) could be attributed to the presence of Q4(2Al) in perlite (two Al neighbors of Si). Figure 5 present the spectra of merlinoite, which is complex and its deconvolution gives a number of peaks. The most intense peaks are located at around 88 ppm and 94 ppm. The first one denotes the existence of Q4(4Al) aluminosilicate backbone having as structural unit silicon tetrahedron $[SiO_4]^{4-}$ surrounded by four aluminum tetrahedra $[AlO_4]^{5-}$. The peak at 94 ppm denotes the existence of Q4(3Al) aluminosilicate backbone. The peaks at around -99 ppm, -103 ppm and -108 ppm denote the presence of Q4(2Al), Q4(1Al) and Q4(0Al) structural units in the aluminosilicate gel formed during synthesis.

Samples of merlinoite were impregnated with 5 wt. % silver and tested as catalysts for ozone decomposition and CO oxidation to CO_2. It was found that they destroy ozone at room temperatures and possess superior activity in carbon monoxide oxidation to CO_2 in comparison to silver catalyst prepared with silica carrier. It can be concluded that the synthesis of microporous merlinoite is easy, reproducible, and cost-effective. The obtained product has a potential in application also for solving environmental protection problems.

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Structural study of Zn exchanged natural clinoptilolite using powder XRD and positron annihilation data

L. T. Dimowa[1], O. E. Petrov[1], N. I. Djourelov[2] and B. L. Shivachev[1]

[1]*Institute of Mineralogy and Crystallography, Bulgarian Academy of Sciences, Acad. G. Bonchev Street, Block 107, 1113 Sofia, Bulgaria; E-mail: louiza.dimova@gmail.com*
[2]*Institute for Nuclear Research and Nuclear Energy, Bulgarian Academy of Sciences, 7,2 Tzarigradsko Chaussee Blvd., BG-1784 Sofia, Bulgaria*
Nikolay Djourelov

Introduction

The applications of clinoptilolite in industry, ecology, and life as a whole are important and in the last years a new direction of its use with positive effect on human health developed.

Zinc displays antibacterial properties by itself and clinoptilolite can be used as a carrier of zinc ions and as a “buffer” for more gradual release of Zn in the medical preparation (Cerri et al., 2004).

The purpose of the present investigation is to achieve maximal ion exchange with Zn^{2+} ions on clinoptilolite sample starting from water solution of $ZnCl_2$ and to characterize the resultant exchanged form by powder XRD structural analysis and positron annihilation. For this reason the initial clinoptilolite tuff (Ct) was purified by sedimentation and chemical treatment, aiming to obtain a monomineral clinoptilolite fraction (Dimova et al., 2009). The obtained purified sample (Cp) was Zn^{2+} exchanged (Czn).

Experimental Methods

The XRD data for the structural refinement were collected on a Bruker D8 Advance diffractometer (Cu-Ka radiation, 40 kV, 25 mA). The Rietveld refinement was carried out using DiffracPlus TOPAS v. 4.2 (2009). DTA-TG was used to estimate the water content and the thermal behavior of the studied clinoptilolite (STA781 and DTA 675 - Stanton Redcroft). FTIR was used to complement the XRD results for framework stability of sample Cp and to compare samples Cp and Czn. IR transmission spectra were obtained from KBr pellets using a TENSOR 37 Bruker spectrometer. The chemical control was performed using ICP-OES Varian Vista MPX. The positron lifetime spectrometer with resolution of 240 ps was a fast coincidence system. The spectra were recorded in 8192 channels with 12.4 ps width. A source of $^{22}NaCl$ with activity of ~ 30 μCi, sealed between two Kapton foils of thickness of 7.5 μm, was used in sandwich geometry between two identical samples. The measurements were performed at room temperature in air.

Results and Discussion

The derived formulas of samples Cp and Czn (1 and 2) are compared below:

$$(Na_{1.01}\,Ca_{1.66}\,K_{1.10}\,Mg_{0.48})\,Al_{6.39}\,Si_{29.52}\,O_{72}\ 21.20\ H_2O \tag{1}$$
$$(Na_{0.19}\,Ca_{0.39}\,K_{0.40}\,Mg_{0.20}\,Zn_{2.23})\,Al_{6.31}\,Si_{29.61}\,O_{72}\ 22.20\ H_2O \tag{2}$$

Sample Cp contains minimal quantities of quartz, plagioclase, and opal-CT. The sample Czn shows the presence of 6.67 wt. % Zn (starting Zn content of ~0.002 wt. % for the sample Cp).

Zinc cations after the refinement distribute in the unit cell in three sites (Zn1, Zn2, and Zn3) labeled with respect to their lowering occupancy (Fig.1).

Site Zn1 is identical with the Mg position M4 of Koyama and Takeuchi (1977) and is occupied by one Zn ion per unit cell. Six water molecules in three double positions (2´W5, 2´W6, and 2´W7) form octahedral coordination around the Zn ion. The second Zn site (Zn2) is located nearby the calcium position M2, although it is shifted along *a* and *c* axes slightly away of the channel B center. The occupancy refinement suggested that 0.67 zinc atoms per unit cell are located in the Zn2 site coordinated by three water positions and three framework oxygens. The Zn2 coordination remains analogous to the Ca coordination of the natural clinoptilolite. The Zn1 and Zn2 positions account for 1.67 zinc atoms per unit cell. However, the amount of zinc from ICP data for the Zn-form of clinoptilolite is 2.19 atoms. The unaccounted 0.52 Zn couldn’t be refined successfully in Zn1 and Zn2 positions and this allowed us to locate another position (Zn3) situated on the mirror plane in the channel A. Actually, this position is also located near the M1 site but is shifted from the channel center. The distance between Zn1 and Zn3 positions is 1.7 Å and their mutual occupation is forbidden. Only one water molecule (W2 coordinates Zn3). This distribution of Zn^{2+} ions is largely spread in the channels of clinoptilolite, which may, probably, enhance their release in biological media.

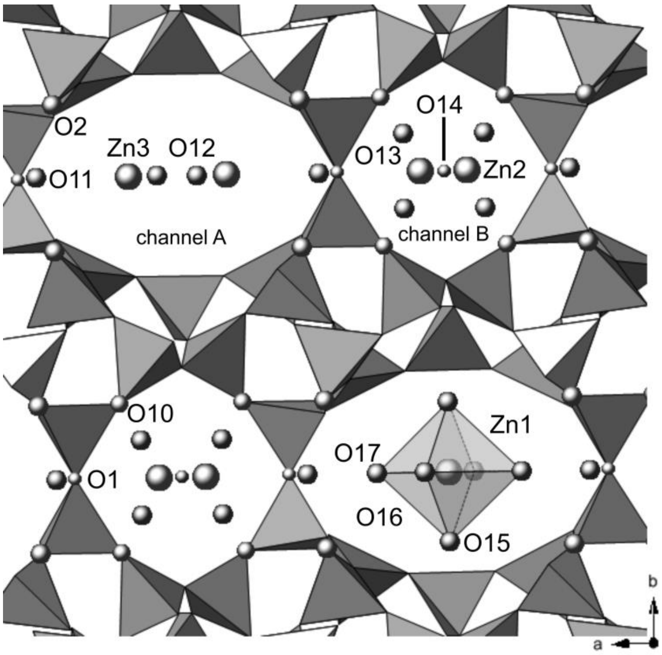

Figure 1. Cations and water molecules positions in sample Czn

The positron annihilation with four components showed positron lifetimes within the ranges: τ_1 = 0.12-0.18 ns; τ_2 = 0.40-0.44 ns, $\tau_3 \approx$ 1.5 ns, and τ_4 = 3.7-5.6 ns. The component association for this type of analysis is as follows: τ_4 and τ_3 are due to pick-off annihilation of *o-Ps* localized into pores (bigger and smaller in size), τ_2 is the lifetime of the positrons not forming *Ps*, and τ_1 is due to *p*-Ps annihilation. Knowledge of τ_3 or τ_4 permits to obtain the average radius R in spherical approximation of the nano-holes where Ps is confined by employing the Tao-Eldrup model (Tao, 1972) and (Eldrup et al., 1981). Having in mind that the samples show two distinct *o-Ps* lifetimes two types of pores can be attributed. This finding correlates well with the clinoptilolite structure, i.e. small β-cage (B channel) and larger α-cage (A channel). The size of the β-cage is the same within the errors for all samples, i.e. it is not disturbed by the different treatment or presences of different elements (cations) in the structure. The samples with presence of Zn show a larger α-cage compared to the rest of the samples.

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Structural changes of natural zeolite from Kralevo deposit (Bulgaria) after thermal treatment

S. Djambazov[1], A. Yoleva[1], O. Petrov[2] and O. Malinov[3]

[1]*University of Chemical Technology and Metallurgy, Sofia; Bulgaria. E-mail: djam@uctm.edu*
[2]*Institute of Mineralogy and Crystallography, BAS, Sofia, Bulgaria*
[3]*GRAVELITA Ltd., Sofia, Bulgaria*

Introduction

Natural zeolites undergo structural changes after heating, which open their possible use in different fields, related to their chemical and physical properties, such as building stone, lightweight aggregate, ceramic membrane, ceramic foam, concrete and ceramic bricks, tiles and porcelain stoneware. Many physical and chemical changes could occur simultaneously during heating of zeolites. Dehydration and dealumination of the zeolite framework are probable processes that will occur on heating. Collapse of the microporous structure of zeolite, melting of product, which has lower melting point and entrapment of gaseous product are some of these phenomena. (Dondi et al. 2004, Şahmaran et al., 2008).

The aim of this work is to study structural changes in natural zeolite from Kralevo deposit (Bulgaria) after thermal treatment at different temperatures.

Experimental Methods

The studied natural zeolite is clinoptilolite tuff from a deposit at the northern part of the area of zeolitized tuffs in Eastern Rhodopes (SW of Kralevo village, Haskovo district). Powder XRD analysis confirmed that the zeolitic rock is composed mainly of clinoptilolite with some anorthoclase and opal-C and is an altered product in the newly mapped poly-phase neck structure in rhyolitic vitroclastic sediments related to the second acidic Paleogene volcanism (Ol_3) (Yoleva et al., 2006. Malinov et al., 2010). In the typical section of Ol_3 in this region, there are two clinoptilolite varieties - Ca-clinoptlolite and high-silica K-Ca clinoptilolite. The chemical composition of this clinoptilolite analyzed by ICP-AES is given in Table 1.

Table 1. The chemical composition of the clinoptilolite

Oxides	SiO_2	Al_2O_3	TiO_2	Fe_2O_3	MgO	CaO	Na_2O	K_2O	ΣH_2O
wt. %	71,35	12,72	0.20	0.90	0.94	2,20	0.94	3,94	12,79

The clinoptilolite sample was thermally treated at temperatures from 300 to 850°C for 4 h at each step. Phase composition changes and structural changes in the studied material after thermal treatment at the different temperatures were followed by powder XRD, DTA/TG analysis (from 20 to 1000°C with step of 10°C/min), IR-spectroscopy (in the range 4000-400 cm^{-1}) and SEM.

Results and Discussion

As seen in Fig. 1 a major part of the studied clinoptilolite is stable up to 800°C. A gradual slight amorphization occurs with temperature, indicated by an increase in the intensity of the broad peak near 4.06 A, which is characteristic for opal C.

DTA/TG analysis shows that at around 100°C a significant endo-thermal effect is registered, which is related with elimination of physically adsorbed water. The total TG loss is about 11.0 wt.%. The IR spectra of natural zeolite before and after thermal treatment at temperatures 300, 550, 750, 800 and 850°C reveal peaks of isolated and H - bonded O-H stretching at 3626 and 3446 cm^{-1}, respectively, and H_2O bending at 1635 cm^{-1}). The peaks at 1070, 792 and 607 cm^{-1} are characteristic for clinoptilolite (Fuentes et al., 1998, Goryanov). The peak at 608 cm^{-1} is related to the amount of clinoptilolite present in the sample. Increasing temperature causes structural collapse of the zeolite above 750°C and this peak disappears. Other vibrations recorded are the Si-O-Si asymmetric stretch at 1072 cm^{-1}, the Si-O-Si symmetric stretch at 792 cm^{-1} and the O-Si-O band at 472 cm^{-1}. SEM micrographs of the natural and heated zeolite are given in Fig. 2. Homogeneous porous structure of natural zeolite with size of pores around 2-3 μm was observed. With increasing the temperature of treatment the pores close and their size decreases.

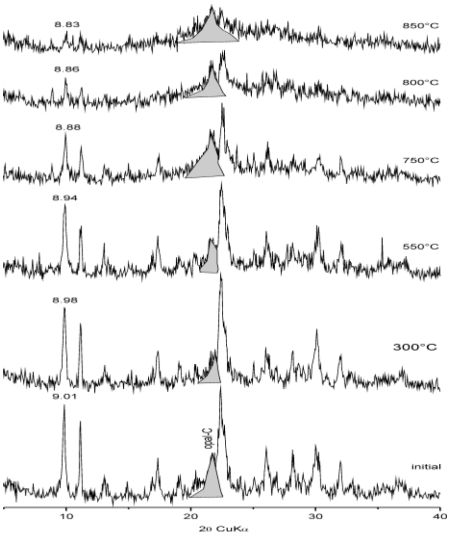

Figure 1. Powder XRD patterns of natural and heat treated clinoptilolite from Kralewo deposit

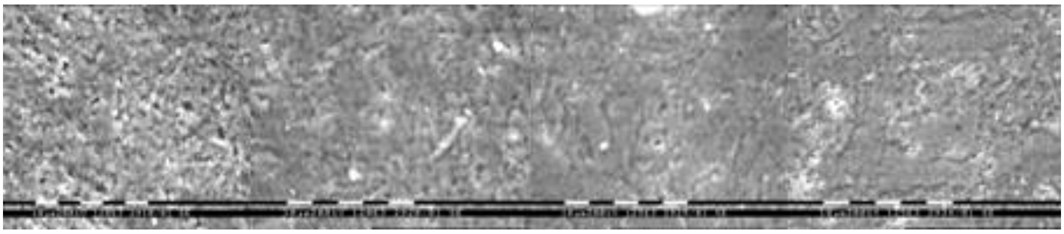

Figure 2. SEM photos of natural and heated at 750, 800 and 850°C clinoptilolite rock (from left to right)

The clinoptilolite from Kralevo deposit has a high content (~85 wt.%) of high-slilica K-Ca clinoptilolite. As secondary phases present in small quantities are plagioclase and opal - CT. The original clinoptilolite structure stays unchanged up to 750°C. Further heating causes complex changes in the structure of the zeolite rock sample characterized by amorphization and closing of pores.

As a result of the performed studies it can be concluded that natural clinoptilolite from Kralevo deposit may be applied for the production of low cost ceramic filtration membranes, lightweight aggregates, ceramic foam, concrete and ceramic bricks, tiles and porcelain stoneware.

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Antagonistic activities of natural zeolite against *Helicobacter pylori* infection

M. Farina[1], C. Juliano[2], G. Rassu[2], A. Brundu[1], M. Cossu[2], M. C. Bonferoni[3], P. Giunchedi[2], E. Gavini[2] and G. Cerri[1]

[1] *Dip. di Scienze della Natura e Territorio, Università di Sassari, Via Piandanna 4, 07100 Sassari, Italy;*
E-mail: gcerri@uniss.it
[2] *Dip. Chimica e Farmacia, Università di Sassari, Via Muroni 23a, 07100 Sassari, Italy*
[3] *Dip. Scienze del Farmaco, Università di Pavia, Viale Taramelli 12, 27100 Pavia, Italy*

Introduction

Helicobacter pylori is a gram-negative microaerophilic human gastric pathogen, which infects more than half of the world's human population and causes chronic gastritis, peptic ulcer disease, and gastric cancer (Lehours and Yilmaz, 2007). This bacteria produces various virulence factors and in particular the vacuolating toxin (VacA), aneutrophil activating protein (HPNAP) and the urease (Montecucco et al., 1999). *Helicobacter* urease is a surface protein component of *H. pylori* that produces ammonia from the host's urea which results in neutralization of the acidic environment in the site of infection (Chen et al., 2012). Ammonia is toxic to cells by itself and after endosomal accumulation of the ion form (NH_4^+), which is isosmotically active, it leads to swelling of vacuoles generated VacA. This process helps to cause damaging of gastric cells (Ricci et al., 1997). In addition, ions such as Fe^{3+} and Ni^{2+} are essential for *H. pylori* growth (Montecucco et al., 1999).

The ion-exchange capacity of clinoptilolite for inorganic cations has been thoroughly investigated by many authors. Moreover, it is known for its high selectivity toward ammonium ion. Furthermore, clinoptilolite is a natural zeolite whose deposits, sometime also of large size, are widespread.

Aim of this work is to investigate if clinoptilolite, due to the its exchange capacity and high selectivity toward ammonium, can show an antagonistic activity against *H. pylori* growth and infection, acting by interfering in the cellular damage induced by the bacterium.

Experimental Methods

A clinoptilolite-rich Sardinian epiclastite, already evaluated for biomedical applications (Cerri et al., 2004; Bonferoni et al., 2007), has been used to prepare a micronized powder with a higher grade of zeolite (obtained by beneficiation process). Later, the material has been modified to in Na-form by ion-exchange. The raw and modified samples have been characterized by XRD and elemental analysis. A NH_4-clinoptilolite has been also prepared for microbiological experiments.

The technological properties of the materials have been determined according to European Pharmacopoeia (7 ed.), evaluating the particle size, the particle size distribution, the true and bulk densities, the flow properties, the compressibility and compatibility, in order to establish their potential suitability as pharmaceutical excipient.

Tests have been also performed to evaluate the resistance of Na-clinoptilolite, its ability to uptake NH_4^+ and release of contaminants (especially heavy metals) in simulated gastrointestinal fluids (European Pharmacopoeia, 7 ed).

Microbiological tests have been carried out. *Helicobacter pylori* ATCC 43504 has been obtained by LGC standards (Milan, Italy). For the entire study bacteria have been grown on Mueller Hinton Agar (Oxoid) supplemented with 10% heat inactivated horse serum (Sigma), at 37°C for 5 days in microaerophilic conditions (CampiGenOxoid, 3.5L). The anti-*H.pylori* activities of samples (zeolite Na- and NH_4-forms) have been evaluated as MIC (Minimum Inhibitory Concentration) by an agar dilution method in duplicate by spot inoculating the plates with about $1x10^5$ microorganisms/mL; plates have been incubated at 37°C in microaerophilic atmosphere and checked for visible growth of bacteria after 5 days. MICs have been defined as the lowest concentration that completely inhibited visible bacterial growth. Amoxicillin has been tested for comparison.

Results and Discussion

The powder prepared has a zeolite grade of about 90 wt. %. The heavy metals content of the unexchanged material is under the limit reported in the European Pharmacopoeia (7 ed.) for smectite (our reference material as zeolite are not reported yet in the Pharmacopeia); the amount of heavy metals in the Na-form is even lower.

For all samples the volume-surface diameter, d_{vs}, and modal diameter, d_m, are 4.96 ± 0.51 and 10.84 ± 0.01 µm, respectively. The true density is 2.18 ± 0.00 g/cm^3. The material shows a scarce flow capacity, at the limit between poor and extremely poor flowability (European Pharmacopoeia, 7 ed). The raw and modified powders can be compressed to form tablet at 20 kN compressional force; at higher forces lamination occurs. The humidity content of materials affects the compactibility: dry powders do not form tablets.

The material is resistant in the gastric environment and able to uptake NH_4^+ releasing Na^+ in simulated gastric juice. Heavy metals release tested in the same conditions is extremely low, comparable or lower than some clay already traded in pharmaceutical field.

Preliminary assays demonstrate that *H. pylori* strain used in our experiments exhibites a very high sensitivity to amoxicillin (MIC 0.035 µg/mL) in our experimental conditions; Na-clinoptilolite does not inhibit bacterial growth at low concentrations. However, this behaviour could be attributed to the inability of zeolite to exchange Na^+ in a solid medium such as the agar used for performing microbiological experiments; besides, clinoptilolite precipitates on the bottom of plates and bacterium is free to grow on the surface where they could not be in contact with zeolite. Thus, further studies are in progress to evaluate different experimental procedures as well as to test higher concentrations by using standard method.

Acknowledgment

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Celtonita: an environmentally friendly product from natural clinoptilolite for high technology agriculture

J. A. Febles[1], F. Borsatto[1], J. P. Ferreira[2] and F. Ferreira[2]

[1]*Industrias Celta Brasil Ltda. Rua Iris Memberg 200, Cotia, SP, Brasil; febles@celtabrasil.com.br*
[2] *Zeocel Rua Chão de Frade, Ameal, Agueda, Portugal*

Introduction

Celtonita is a technical mineral obtained from the Cuban natural clinoptilolite enriched with macro and micro nutrients required for excellent development of different crops.

As its advantages we can mention its capacity to improve soil structure, to promote greater oxygenation of the root, to separate the Na^+ soil avoiding clay dispersion, to decrease the difference of existing osmotic pressure between the root and the environment, to preserve the nutrients and to improve the ability of the plants to assimilate them, its gradual recovery of NH^{+4}, ability to enhance root development and act as accumulator of water and nutrients in the soil.

Usage this mineral have given the excellent results for different crops like vegetables, orchards, forests, ornamental plants, both in seedling development or large production. As a result of its use, it is possible to completely eliminate the need for application of chemical fertilizers, contributing to significant decrease of environmental pollution.

Experimental Methods

The natural zeolite used in the production process of Celtonita is the type of zeolite deposits of San Andrés, Holguín, Cuba, which presents a grain size of 1-3 mm and a chemical composition shown in Table 1.

Table 1. Chemical composition and CEC of zeolite

Percentage (%)											
SiO_2	Al_2O_3	Fe_2O_3	FeO	MgO	CaO	Na_2O	K_2O	P_2O_5	H_2O	TiO_2	CEC meq/g
63.00	11.57	1.87	0.81	0.92	5.78	2.39	1.49	0.09	3.44	0.45	1.57

This mineral is subjected to a modification process through the contact with a chemical solution. Different nutrients are incorporated in the zeolite structure to fulfill the requirements of agricultural cultivation. After this modification process we can identify some nutrients in the zeolite structure analysis by atomic absorption spectrometry like those shown in table 2.

Table 2. Content of nutrients after modification

Nutrient	Content
Ammonium Nitrogen (NH_4^+)	17.0 – 19.0 meq/100 gr
Available Phosphorus (P_2O_5 asimilable)	850 - 900 ppm
Potassium (K^+)	14.0 – 16.0 meq/100 gr
Calcium (Ca^{2+})	24.0 – 25.0 meq/100 gr
Magnesium (Mg^{+2})	10.0 – 11.0 meq/100 gr
Magnesium oxide (MgO)	900 - 950 ppm
Ferrous oxide (FeO)	800 - 830 ppm
Manganese (Mn)	18.4 ppm
Copper (Cu)	0.35 ppm
Zinc (Zn)	0.49 ppm

Results and Discussion

The use of Celtonita in seedlings of greeneries allows total elimination of chemical fertilization traditionally used to significantly improve the growth of plants at this stage. It is also possible to reduce the time of production, as shown in Table 3.

Table 3. Time to raise seedlings in greenhouses

Kind of cultivation	Normal substratum	Substratum with Celtonita
Tomato	30 days	23 days
Lettuce	30 days	24 days
Cucumber	25 days	19 days
Melon	25 days	19 days
Orchards	365 days	275 days

Similar results were obtained by Gonzalez (1999) when adding 5-10 % of Celtonita in substrates for vegetables. In orchards the inclusion of Celtonita was 10 % of the substrate volume enhancing leaf and root development and reducing the time in the greenhouse by more than 90 days in cultures of avocado and guava and resulting also in significant savings in production costs.

Favorable results were also obtained in ornamental plants in the rooting of carnations, roses and chrysanthemums in Bogotá, Colombia. The application of Celtonita increased more than 15 % vegetative growth comparing with plants without Celtonita (Febles, 2003).

The use of Celtonita in different percentages in orchid cultivation conducted in Sao Paulo. Brazil, showed excellent results with the inclusion of 15 to 20 % of Celtonita in the coconut fiber substrate, the elimination of chemical fertilization, significant reduction in the electrical conductivity of coconut fiber substrate and further development of foliar and root, causing enhanced flowering and reduced crop growth time in more than 20 days.

The use of this product obtained through modification of exchangeable ions in a zeolite clinoptilolite, allows the possibility of a safe and profitable rational use of nutrients and water for different soils types and crops, enabling the development of organic farming systems and dramatically reducing environmental pollution

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From wastewater to irrigation water: adsorption of microbial, NH_4^+ and heavy metals pollution through a clinoptilolite bed laminar flux

C. Ferronato, G. Vianello and L. V. Antisari

Department of Agricultural Sciences, Alma Mater Studiorum; viale Fanin 40, 40127, Bologna IT; E-mail: chiara.ferronato2@unibo.it

Introduction

Human pressure on environment is an increasing problem all over the world. Excess of nutrients (P, N), organic contaminants (PAH, PCB, pesticides) and heavy metals (Cu, Ni, Zn, Pb, Cd, etc.) are often affecting water canals because of several discharges form human activities. The monitoring of a “good Ecological Status” of natural waters is required by the European Waterframe Directive (2000/60CE) and some limits concerning organics, metals and microorganisms, are required in order to use water for potable or irrigation purposes or for reusing wastewater in natural water systems.

Natural zeolites are interesting low cost sorbents which have been studied since the last decades because of their high ion exchange capacity between a liquid and a porous phase (Kocaoba et at. 2006) but also for their capacity to entrap microorganisms in their microporous structure (Chen et al. 2005). Among zeolite species, clinoptilolite is a natural zeolite comprising a microporous arrangement of silica and alumina tetrahedral, forming a tabular monoclinic tectosilicate crystals and it has a high attractive selectivity for certain heavy metal cations, such as Pb, Cu, Zn, Cd and it can be used as an ion exchanger for the removal of ammonium ions (Stylianou et al. 2006). In this study clinoptilolite (ECOLIN) has been tested for its capacity to detoxify and depollute the out flow wastewater from an old waste treatment plant.

Experimental Methods

The zeolite used in this study is marketed by ECOLIN srl and it has the following elemental composition: 71.3% SiO_2, 13.1% Al_2O_3, 5.2% CaO, 3.4% K_2O, 1.9% Fe_2O_3, 1.2% MgO, 1.3% Na_2O, 0.3% TiO_2. Wastewater was collected from Calderara di Reno (Bologna, IT) wastewater plant, an old waste treatment plant which discharges water in a reclamation artificial canal whose water is used for irrigation. Two different approach were proposed here to clean and detoxify the wastewater using clinoptilolite.

Method (A) aims to test the efficiency of the zeolites to reduce NH_4^+ content and pathogenic microorganisms (e.g. Faecal coliforms and *Escherichia coli*), while the method (B) aims to test the efficiency of clinoptilolite to depollute the wastewater by heavy metals (As, Cu, Ni, Sn, Se, Zn).

Method (A) was performed in a mesocosm where different amount of zeolite (20, 50, 100g) were put in contact with 500 ml wastewater in a static system for 24 h. Water analysis was performed before and after the treatment during the first 24h. NH_4^+ detection was performed by colorimetric method using Hach-Lange kit with DR3900 spectrometer. Faecal coliform and *Escherichia coli* determination was performed in the first 24 h as described in Ferronato et al. (2013) by filtration membrane method and enumeration of CFU (Colony forming units). Method (B) was performed in an open system by fluxing 50 L wastewater in a clinoptilolite laminar inclined bed (35*35*1 cm of clinoptilolite) for 12 h with a flow rate of 4 L/min. Water were sampled before and after 2 and 12h from the treatment. Samples were first filtrated and acidified with 1:100 HNO_3 suprapure (Carlo Erba) and then processed by Inductive Coupled Plasma – Optical Emission Spectroscopy (ICP-OES - Ametek Spectro Arcos) for heavy metals analysis.

Results and Discussion

Table 1 shows the results obtained from method (A) performed to reduce of both NH_4^+ and microbial forms after 24 h treatment. Organic pollutants load was reduced by 90% when the clinoptilolite was used at water ratio of 1:10. After the cleaning treatment, the lowering of pathogenic microorganisms was lower than the threshold of Italian law and water could be reused for irrigation purposes (D.lgs.152/2006).

Ammonium removal is due to the ion exchange capacity of the zeolite while microorganisms can be entrapped in the zeolite structure by the formation of complexes between microorganisms and the mineral phase, van der Waals interactions, hydrogen bonding or ion bridging (Stotzky, 1985).

Table 1. Effect of different concentration of clinoptilolite on NH_4^+ and microbial community of wastewater, before and after 24 h contact time

		Before tr.	After tr.							
			20	40	50	100	20	40	50	100
			$g_{clinoptilolite}$/500mL				Removal, %			
NH_4^+	mg/L	13.9	1.99	1.58	1.07	1.02	85.68	88.63	92.3	92.66
Faecal coliform	cfu/100mL	177333	17750	10950	9800	9250	89.99	93.83	94.47	94.78
Escherichia coli		120333	11500	7450	6700	5850	90.44	93.81	94.43	95.14

The results of method (B) performed to reduce the heavy metals from wastewater were showed in Table 2. Heavy metals were removed from 80 to 97% after the flushing of wastewater on an inclined plain of zeolites. The removal rate showed that after 12 h high removal rate for all the heavy metals (As>Ni>Sn>Zn>Se>Cu), while after two hours removal efficiency was still low.

Table 2. Effect of flux time on clinoptilolite bed, on Na, P and different heavy metals removal

		Time, h			Removal, %	/time, h
		0	2	12	2	12
As	µg/L	14.93	14.17	0.35	5.09	97.66
Cu		19.12	22.02	4.21	-15.27	77.98
Ni		4.86	4.44	0.2	8.64	95.47
Se		29.31	24.94	5.02	14.91	82.87
Sn		4.33	4.45	0.33	-2.77	92.38
Zn		31.65	32.72	2.54	-3.41	91.97

The differences of efficiency between the heavy metals can be due to the different affinity of metal with the silicate structure and to competition for binding sites of the metals between each other's during time (Srivastava et al., 2009). The study of the prototype to depollute wastewater with laminar beds has been shown to be a good approach to manage water remediation in a rapid and efficiency way. Few studies were found about the interaction of different pollutants whereby the interaction and the competition of metals and organics in zeolite/wastewater must be better understood.

Acknowledgment

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Modification of the lightweight aggregate with the use of spent clinoptilolite after sorption of petroleum substances

M. Franus[1], R. Panek[2], M. Wdowin[3] and W. Franus[2]

[1]*University of Management and Administration in Zamość, Ul. Akademicka 4, 22-400 Zamość, Poland;*
E-mail: m.franus@pollub.pl
[2]*Department of Geotechnics, Lublin University of Technology, Nadbystrzycka 40, 20-618 Lublin, Poland,*
[3]*Division of Geotechnology, The Mineral and Energy Economy Research Institute of the Polish Academy of Sciences, Wybickiego 7, 31-261 Krakow, Poland*

Introduction

A lightweight aggregate can be obtained from raw material modified by clay minerals, zeolites and waste (Franus, 2011). In this experiment, we demonstrate that a lightweight aggregate, with interesting functional properties, was produced using clinoptilolite previously used for the removal of petroleum substances. These substances are widely used in industrial processes, especially as fuels. However, these substances are often dispersed in the environment without any control, thereby causing an ecological risk (Gonzáles-Corrochano et al., 2010 and 2012). The spent sorbent containing petroleum substances constitutes waste, which can be utilized as shown in this study.

Experimental Methods

The spent clinoptilolite-bearing rock (10% of weight) was added to the clay (90% of weight) from the "Budy Mszczonowskie" deposit. The principal mineral components of Budy Mszczonowskie deposit are represented by illite, kaolinite, montmorillonite, along with quartz in minor amounts. Crystalline phases were identified on the basis of their X-ray diffraction patterns. Specific and bulk density of lightweight aggregates were 2.59 g/cm^3 (clay) and 0.572 g/cm^3 (zeolitic rock), respectively. Homogenization process consisted in mixing the ingredients with water until a plastic consistency was formed. Subsequently, the formed beads of coarse fraction of 8-16 mm were dried to air-dry state, and then dried for 2 h in a laboratory oven at 110 °C. The dried samples were calcinated at 1170 °C. The obtained aggregates were tested, following standards protocols, in order to determine their physical and mechanical properties (UNE–EN 1744-3; UNE-EN 1097-3; UNE-EN 1097-6; UNE-EN 13055-1; UNE-EN 12620).

Results and Discussion

Absorbability of the lightweight aggregates, obtained by modifications of the starting composition of the raw mixture with spent clinoptilolite, was 14.6%. This product can be considered as an aggregate with low water absorbability, as the observed value does not exceed 15%. Estimated void percentage of the material (*i.e.*, the relative volume fraction of voids between particles in a unit volume) was 42%.

A frost resistance of a solid is defined as the resistance to low temperatures, expressed by its weight loss. We determined the weight loss of the aggregate under investigation, and its internal changes (cracks) that occur as a result of undergoing cycles of freezing and defrosting. The weight loss of the aggregate sample was 0.3%. According to the standard UNE-EN 12620, the resulting lightweight aggregate can be classified to the F1 category, as for the aggregates used in the production of concrete partially saturated with water containing no salt. This is due to the fact that the weight loss percentage is lower than that required in this category. It does not exceed 4%, therefore complies with the condition of frost resistance. The studies on the resistance to crushing showed limited disintegration of grain.

To describe the morphological and chemical features of the material under investigation, a scanning electron microscope analysis (using a SEM – FEG Quanta 200) was performed. The lightweight aggregate obtained from spent clinoptilolite possesses a compact and porous structure. The pore size varies between 2 and 750 micrometers (Figure 1). Their distribution is quite irregular. Sample fractures are characterized by the presence of a glass phase, *i.e.*, by sintering with a liquid phase.

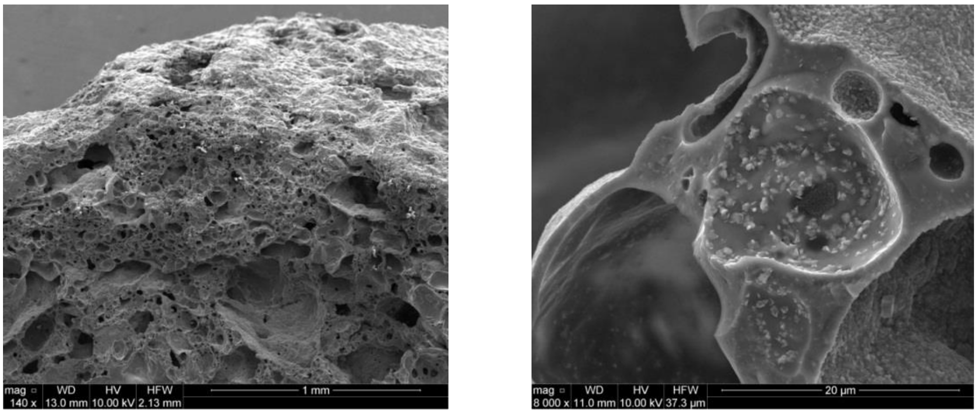

Figure 1. Porous structure of lightweight aggregate modified with the use of spent clinoptilolite, calcinated at 1170 °C, SEM, magnifications 140x (left) and 8000x (right)

In order to describe the thermal behavior and the *T*-induced transformation processes in lightweight aggregate, a further investigation by ThermoVision microscope was performed. The samples – raw material mixtures – after being mixed with water and squeezed in a hand press (to obtain a cylindrical shape sample, 3 mm in diameter and 3 mm high), were subjected to the thermal processing. Temperature gain in the high-temperature microscope was found to be 30 °C/min up to 1100 °C and 10 °C/min over 1100 °C. The experiment was performed in oxidation atmosphere starting from 760 °C up to 1500 °C (maximum temperature of the high temperature microscope). The experimental findings showed that the sintering temperature was 1075 °C, the softening point was 1286 °C, the melting point 1424 °C, and the pouring point 1471 °C. A parameter which discriminates about the suitability of the raw material for the production of lightweight aggregate is the swelling interval between the softening point and the maximum melting temperature of at least 50 °C (Galos and Wyszomirski, 2004).

Our experimental findings indicate that the lightweight aggregate obtained by clay and clinoptilolite (previously used for removal of petroleum compounds) is a valuable building material.

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Compressional behaviour of paulingite - A sub-nanosponge?

G. D. Gatta[1], T. Pippinger[2], R. Miletich[2], R. Skála[3] and Y. Lee[4]

[1]*Università degli Studi di Milano, Dipartimento di Scienze della Terra, Italy; E-mail: diego.gatta@unimi.it*
[2]*Universitaet Wien, Institut fuer Mineralogie und Kristallographie, Austria*
[3]*Institute of Geology, Academy of Sciences of the Czech Republic*
[4]*Department of Earth System Sciences, Yonsei University, Korea*

Introduction

Paulingite is a rare zeolite, found in vesicles in basalt flows, with ideal chemical formula: $(K,Na,Ca_{0.5},Ba_{0.5},)_{10}(Al_{10}Si_{32}O_{84})\cdot 30H_2O$ ($Z = 16$). Its crystal structure was solved and refined by Gordon et al. (1966) in the space group *Im*3*m*, showing the complex framework topology of this zeolite designated with the IZA-code "PAU". A structural re-investigation was carried out later by Lengauer et al. (1997). The tetrahedral framework topology of paulingite is characterized by a connecting double 8-ring (D8R), which links alternatively the α-cage (truncated cuboctahedron) and the γ-cage (gmelinite-type cage). The D8R, the α-cage and the γ-cage represent the building-block units of the PAU framework. The main voids systems of the PAU framework are represented by two parallel (and independent) sets of a three-dimensional channel systems oriented along the principal axes and shifted ½, ½, ½ against each other. Along the threefold axis of the PAU framework, a second type of a channel system exists, which is built up by the α-cage and a modified form of the levyne-cage only observed in the paulingite topology (*i.e.*, π-cage) (Lengauer et al. 1997). The PAU framework type is considered as one of the most complex in the mineral world. In all the structure refinements so far reported, the Si/Al-distribution was modelled as completely disordered. A series of extra-framework sites were located. The long "free diameters" of the channel systems make this zeolite a good candidate to explore the *P*-induced penetration of external molecular species in response to hydrostatic compression (*e.g.*, Gatta 2008, 2010).

Experimental Methods

A sample of paulingite from Vinařická hora Hill near Kladno (Czech Republic) was used for our experiments. A sample from the same locality was previously used by Lengauer et al. (1997) for their chemical and crystallographic study. Electron microprobe analysis (in wavelength dispersive mode) along with thermo-gravimetric data yielded the following chemical formula: $(Ca_{2.57}K_{2.28}Ba_{1.39}Na_{0.38})(Al_{ll.55}Si_{30.59}O_{84})\cdot 27H_2O$ (Lengauer et al. 1997).

A single-crystal of paulingite, free of defects under polarized microscope, was selected for the *in-situ* diffraction experiment with a diamond anvil cell (DAC). Intensity diffraction data were first collected at room-conditions with a Stoe StadiVari diffractometer with an high-brilliance Incoatec Mo Iμs X-ray-source and a Dectris Pilatus 300K pixel detector. The structure refinement was performed in the space group *Im*3*m* using the structural model of Lengauer et al. (1997) to a $R_1 = 0.0802$ for 2477 $Fo > 4\sigma(Fo)$ and 255 refined parameters. The same crystal was used for the high-pressure (H*P*) experiment performed using an ETH-type DAC. The experiment was conducted using a mixture of methanol:ethanol = 4:1 as hydrostatic *P*-transmitting medium, along with a few ruby chips serving as *P*-calibrant. Unit-cell parameters were measured between 0.0001 (crystal in the DAC with no pressure medium) and 3.3(1) GPa.

Two further *in-situ* H*P* synchrotron X-ray powder diffraction experiments were performed at the X7A beamline at the national synchrotron light source (NSLS) at Brookhaven National Laboratory (BNL). A gas-proportional position-sensitive detector was used. The wavelength of the incident beam was 0.60046(1) Å as determined from a CeO_2 standard. A modified Merrill–Bassett DAC was used to generate H*P*-conditions.

Two compression experiments with two different *P*-fluids were performed, *i.e.*, with silicon-oil and a mix of methanol:ethanol:water = 16:3:1. The evolution of the cell parameters with *P* for all three pressure-transmitting media is shown in Fig. 1.

Results and Discussion

The evolution of the unit-cell parameters of paulingite with *P* based on our experiments with different *P*-media show a dramatic role played by the compression-fluid on the behavior of this zeolite (Figure 1). Due to its polymeric nature, silicon-oil can be unambiguously considered as a "non-penetrating" *P*-medium. The compressional pattern obtained with silicon-oil describes the actual elastic behavior of paulingite (*i.e.*, without any interference of the *P*-fluid). The Birch-Murnaghan equation of state truncated to the second-order was used to fit the experimental *P*-*V* data within the *P*-range investigated (*i.e.* 0.0001-2.5(1) GPa), giving the following isothermal bulk modulus: $K_0 = \beta_0^{-1} = V_0(\partial P/\partial V) = 18(1)$ GPa ($\beta_0 = 0.055(3)$ GPa^{-1}). Paulingite appears to be one of the softest crystalline inorganic materials reported so far. The H*P*-data obtained using the mix methanol:ethanol = 4:1 and methanol:ethanol:water = 16:3:1 suggest that these molecules act as "penetrating" media in response to the applied pressure. The *P*-induced penetration of external molecules through the cavities leads to a lower bulk compressibility of paulingite. The different compressibility of paulingite in methanol:ethanol = 4:1 and methanol:ethanol:water = 16:3:1 mix reflects the different penetrability of the media. Water is clearly the most penetrating molecule in response to the applied pressure, and so in general an hydrous medium tends to decrease significantly the compressional pattern of a porous material (Gatta 2008, 2010). Interestingly, the *P*-induced penetration of external molecules in paulingite structure does not lead to spectacular expansion (with a drastic discontinuity in the *P*-*V* behaviour), as observed for example in natrolite (Lee et al. 2002).

The complexity of the paulingite structure did not allow to perform structure refinement at high pressure, hindering a description of the penetration mechanisms at the atomic scale. A series of further experiments are in progress in order to explore: 1) the reversibility of the *P*-induced penetration of aforementioned molecules and 2) the behavior of this zeolite as a "sub-nanosponge" for other small molecules in response to hydrostatic pressure.

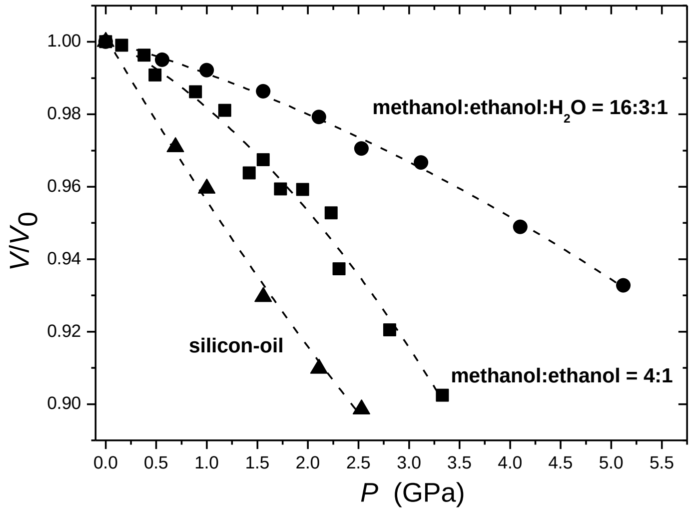

Figure 1. Evolution of the unit-cell volume of paulingite (normalized to the value at 0.0001 GPa) with *P* compressed in three different *P*-media. The polynomial fit shows an anomalous softening when methanol-ethanol or methanol-ethanol-H_2O mix are used as *P*-transmitting fluids

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Effects of low temperature and high pressure on the structure of gobbinsite

G. D. Gatta, P. Lotti and N. Rotiroti

[1]*Università degli Studi di Milano, Dipartimento di Scienze della Terra;Italy; E-mail: diego.gatta@unimi.it*

Introduction

Gobbinsite is a rare zeolite, typically found in amygdaloidal vugs of massive volcanic rocks, where it crystallizes as a hydrothermal post-magmatic product.Gobbinsite typically forms radiating aggregates of sub-microscopic elongated crystals, often associated with phillipsite, gmelinite, natrolite, and calcite. It was first described from the type locality of Co. Antrim, N. Ireland, but other occurrences were later reported from a few other localities. Its ideal formula is $Na_5[Al_5Si_{11}O_{32}]•12H_2O$, but evidence of a Ca,K-enriched form has been reported, so that the general chemical formula can be re-written as: $(Na_{2-2x},Ca_x)_2K_2[Al_6Si_{10}O_{32}]•12H_2O$.
Gobbinsite has a GIS (gismondine) framework type, which can be described as a stacking of two perpendicular double-crankshaft chains, the first running along [100] and the second along [010]. Two secondary building units are present, namely 8- and 4-membered rings, with two perpendicular and interconnecting sets of channels: 8mR[100] and 8mR[010]. The ideal symmetry for the GIS framework type is tetragonal $I4_1/amd$ (idealized unit-cell parameters: a = 9.8 Å, c = 10.2 Å), but zeolites with GIS topology often show a lower symmetry (*e.g.,* gismondine; garronite; amicite; gobbinsite; Na-P1; Na-P2; TMA-gismondine). The lack of crystals large enough (and free of twinning and defects) forced early studies on the crystal structure of gobbinsite to use X-ray powder diffraction techniques. Solution and refinement of the structure led to an orthorhombic unit cell (a = 10.108(1), b = 9.766(1) and c = 10.171(1) Å) and space group $Pmn2_1$. However, such a model showed unusually low coordination for the extra-framework cations (CN = 4 for K and 5 for Na). Discovery of sub-mm crystals from Bundoora, Melbourne, Victoria, Australia, allowed us to re-investigate the gobbinsite crystal structure by X-ray single-crystal methods. The analysis of reflection conditions and statistics of distribution of normalized structure factors suggested the centrosymmetric space group *Pmnb* as highly likely, with unit-cell parameters a = 10.1035(15), b = 9.7819(10) and c = 10.1523(9) Å. Single-crystal structure refinement showed two extra-framework sites partially occupied by Na and Ca, respectively (though inter-site chemical disorder could not be ruled out), five partially occupied sites for H_2O molecules, and a disordered (Si,Al)-distribution in the tetrahedral framework.

In addition to re-investigation of the crystal structure of gobbinsite from Bundoora (Australia), we have investigated the low-temperature (L*T*) and the high-pressure (H*P*) behavior of this zeolite by means of in-situ single-crystal X-ray diffraction. The L*T* experiments were performed in order to minimize the effects of atomic thermal libration and positional disorder. The presence of many centers of motion for a single site (positional disorder) results in large and unusual anisotropic displacement parameters. L*T* conditions were expected to reduce such effects, leading to a clearer picture of the extra-framework configuration. Moreover, comprehension of L*T*-behavior could provide more information about chemical disorder in extra-framework cationic sites. The H*P* experiments were performed following a series of experiments on microporous materials aimed to describe the response of open-framework materials under hydrostatic pressure of the order of GPa.

Experimental Methods

Chemical analysis, by means of electron microprobe in the wavelength dispersive mode and elemental CHN analysis, yielded the following chemical formula:

$$(Na_{4.97}K_{0.07}Ca_{0.48})\Sigma_{5.52}[Al_{5.62}Si_{10.29}]_{\Sigma 15.91}O_{32}•11.9H_2O\ (Z = 1)\ (E(\%) = -6.3)$$

Two single-crystals, free of defects under polarized microscope, were used for the L*T* and H*P* experiments, respectively.
Diffraction intensity data were collected at 293 (room temperature), 250, 200, 150 and 100 K using an Oxford Diffraction Gemini diffractometer operating at 50 kV and 40 mA with Mo*K*α radiation, equipped with a Ruby CCD detector positioned at 50 mm from the sample, and an Enhance X-ray Optics graphite

monochromator. Low-*T* data were collected with the crystal cooled by an Oxford Cryosystems 700 open-flow nitrogen gas system.

The high-pressure experiment was performed using an ETH-type diamond anvil cell (DAC). The experiment was conducted using a mixture of methanol: ethanol = 4:1 as the hydrostatic *P*-transmitting medium along with a few ruby chips as *P*-calibrant. Unit-cell parameters were measured between 0.0001 (crystal in the DAC with no pressure medium) and 4.3(1) GPa, using a list of 36 Bragg peaks centered with a KUMA KM4 point-detector diffractometer, operating at 50 kV and 40 mA, with Mo*K*α radiation (graphite monochromator). Seven intensity data collections were performed at 0.0001, 0.8(1), 1.5(1), 2.5(1), 3.0(1), 3.7(1) and 4.3(1) GPa using an Xcalibur diffractometer equipped with a CCD detector. All datasets showed reflections conditions consistent with space group *Pmnb*. Structure refinements using L*T* and H*P* data were performed with the SHELX-97 program.

Results and Discussion

a) Low Temperature

Reflection conditions confirmed that the space group *Pmnb* is maintained within the *T*-range investigated. At room temperature, the extra-framework population consists of one site partially occupied by Na, one site partially occupied by Ca, and five sites partially occupied by H_2O. At low-*T*, partial dehydration, likely induced by the N_2-flow, was observed, with a significant rearrangement of the extra-framework configuration. Low-*T* induced deformations of the 8- and 4-membered rings were observed

b) High Pressure

No evidence of amorphization was observed within *P*-range investigated. Two changes of the elastic behavior occurred, one at 1.1 - 1.3 GPa and a second at 2.7 - 3.2 GPa. Birch-Murnaghan equations of state truncated to the second order were used to fit the experimental *P*-*V* data within the three *P*-ranges (*i.e.*, 0.0001-1.1, 1.3 - 2.7 and 3.2 - 4.3 GPa), giving the following isothermal bulk moduli: 46.3(9), 52(8) and 28(6) GPa, respectively. The unit-cell compression is significantly anisotropic. In response to the applied pressure, the 8-membered ring channel perpendicular to [100] underwent a significant increase of ellipticity, whereas the channel perpendicular to [010] shrank towards a circular shape at $P \geq 1.3$ GPa. Partial re-organization of the H_2O sites occurred between 1.1 and 1.3 GPa, and new framework deformational modes were observed at $P \geq 3.2$ GPa, coupled with a change in the coordination environment of the extraframework cations.

If we compare the elastic behavior and the H*P* structural evolution of gobbinsite with those so far reported for other zeolites, we can make some generalizations: 1) The range of compressibility among this class of open-framework silicates is large, with bulk moduli ranging between 15 - 70 GPa; 2) Microporosity does not necessarily imply high compressibility – gobbinsite has large channels, compared with other zeolites, but its compressibility is not significantly low; 3) The flexibility observed in zeolites under hydrostatic compression is mainly governed by tilting of rigid tetrahedra around O atoms that behave as hinges within the framework; 4) Deformation mechanisms in response to applied pressure are generally dictated by the topological configuration of the framework rather than the Si/Al-distribution or the extra-framework content. The channel content governs the compressibility of the cavities.

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Efficient technology for the development of agrofertilizer based on raw material of high-potassium tuff (HPT) from Tashir, Lory region, Armenia

R. G. Gevorgyan, A. R. Demirchyan, A. V.Galstyan and M. R. Gevorkyan

Faculty of Geography and Geology, Yerevan State University, Armenia; E -mail: rgev@ysu.am

Introduction

Traditionally different chemical fertilizers (potassium chlorine, nitrogenous saltpeter, phosphates) are used in agriculture; however 30-50% of their initial volume is washed away by water and removed from lands. As a result we see the ecological balance to be perturbed to the negative side and significant amount of fertilizers lost. Thus, to solve the problem of food in Armenia we need new types of fertilizers whose production technology obtaining end product and application will increase the harvest and will keep the ecological balance. For more than 20 years Armenia does not import traditional potassium chlorine fertilizers. Currently there are all conditions for Armenia to produce and export non-chlorine potassium (potassium-silicate) and ecological clean fertilizers.

Experimental Methods

Modified HPT is slowly acting fertilizer which can be put into soil once in high dozes for 3-4 years. HPT fertilizer is ecologically clean which is extremely important for the people of Armenia and for export. For instance, the use of 400kg/ha will relatively increase harvest by 50 ts/ha and will allow to get additional 450 thousands AMD in earnings. In addition, HPT reduces accumulation of heavy metals in the soil for about 18.5-20kg/ha which is an important mean of preventing pollution of lands. It was also established that HPT, as potassium fertilizer, is safe to use.

Thus, Tashir modified HPT proposed above can be guaranteed as non- chlorine potassium (potassium-silicate) fertilizer which can find wide and efficient use (application) in agriculture of Armenia and foreign countries, Демирчян А.Р. и др., (2008).

Let us note that potassium salt mines are located in northern latitudes of earth (Russian Federation, Belarus, USA, Canada,) and the demand of potassium fertilizers is so great that it must be obtained at least 5 years ago and paid a deposit (prepayment). Such conditions give us thought that Armenia and neighboring countries also will not import potassium fertilizers in coming decades which prices are actively growing every year. We are sure that local raw materials received from ecologically clean potassium fertilizers will be a wonderful alternation for getting out of existing situation.

Unlike previously developed technologies, new optimal conditions are proposed for potassium concentrates modification: air stream crushing, *t*hermo chemical, microwave development. Crushing degree of HPT provides 75% up to 0.007 mm; volume of autoclave (chamber) downloads up to 0.6 parts and synthesis's period provides 1.5 hours. From the enrichment of HPT to tailings dump, unshipping caudal materials can serve as additional feedstock raw materials for other productions.

- Fertilizer was overwhelmed with unwanted elements, and the percent of the potassium oxide reached maximum 7.6

Our working group has developed a technology, and some experiments allow:

- To reduce the power consumption of the fertilizer for 3-4 times
- To get concentrate enriching the mineral (ore)
- The content of oxide in potassium up to 12%
- To have production without waste

In contrast to previously obtained fertilizers, the following indicators differ from:

- As a result of significant reduction in power consumption, the cost and the selling price also will be reduced which is very important for farmers
- By the enrichment of mineral (ore), affecting substances of fertilizer will increase by around 40%
- Instead of former powder fertilizer, it will be granular which will make it possible to turn to the soil through traditional agro-techniques
- New product also will contain other additives necessary for plants
- The product will be without waste, and the impact will be minimal on the environment and etc.

Results and Discussion

The potassium-silicate fertilizer positively affects plants growth, improves the water regime and reduces the loss of nitrogen from soil. This fact also contributes to the improvement of the ecological balance (especially in Lake Sevan for keeping waters away from pollution) Демирчян А. Р. (2008).

Taking into account the present market of potassium fertilizers, we are confident that our initiative, connected with new technologies and licensing, will have a developed product which after successful completion will be in demand for many years.

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Extraction of rhenium and sulfur dioxide using natural zeolites from Armenia during molybdenite concentrate roasting

R. G. Gevorgyan, A. V. Galstyan and Sh. E. Sarkisyan

Faculty of Geography and Geology, Yerevan State University, Armenia; E-mail: rgev@ysu.am

Introduction

Extraction of rhenium and sorption of sulfur dioxide will solve a number of problems simultaneously, *e.g.* to protect the environment and to avoid irretrievable loss of valuable raw materials that can be used in the future for the production of stainless steel, sulfuric acid and other mineral components.

Zeolitic tuffs from Noemberyan deposits, Armenia, show high clinoptilolite content (70-85 wt. %) along with high silica content. The adsorption of SO_2 is proportional to the zeolite content. Noemberyan deposits are exposed and can be mined opencast. Estimated reserves of zeolite-bearing rocks in Armenia are 400 - 500 million tons, thus making these rocks as suitable materials for the adsorption of sulfur dioxide and extraction of rhenium during roasting of molybdenite concentrate.

Experimental Methods

Extraction of rhenium and sulfur dioxide recycle could be performed by the use of solid adsorbents, one of which is represented by zeolite-bearing rocks. The adsorption properties of natural zeolites-bearing rocks are strongly governed by: the zeolite content of the rock, silica content, and adsorption temperature.

The use of zeolite in this contest is based on its ability to absorb rhenium heptoxide from the gaseous phase at 350-400°C. Measurement of dynamic activity of clinoptilolite showed that increasing the adsorption temperature from 100 to 500 °C, the activity of zeolite increases by 3-6 times. The activity is observed to decrease by 10-12 % only after the first 5-10 cycles, and it is kept constant in subsequent cycles.

In Armenia, non-ferrous metals occupy an important place in the industrial production and have a huge tendency of growth (compared to 1990 increased from 8 to 31% [2nd National Messages, 2010]). The neutralization of sulfur dioxide in non-ferrous metallurgy is a difficult task, due to the large volume, high temperature and low concentration of sulfur dioxide in the flue gas emissions into the atmosphere.

Currently, there are two directions in the utilization of sulfur dioxide: wet process related to SO_2 absorption by various solutions and processes of dry or adsorption purification, based on availability of cheap sorbents that have significant SO_2 activity, (Anurov S.A. et al., 1999).

The utilization of sulphurous anhydride should be organized with the use of natural sorbents, one of which are zeolites. At present there are more than 40 types of zeolite minerals, of which only six are of industrial importance (clinoptilolite, mordenite, erionite, chabazite, ferberit, philipsite), and among these, the most significant role is of clinoptilolite, Chelishchev N.F. et al. (1986). Zeolites are water aluminosilicates, with infinite openwork frame structure, formed by the junction of common vertices of SiO_4 and AlO_4 tetrahedra, where are interconnected cavities occupied by large ions and water molecules. The term "molecular sieve" is applied, as dehydrated zeolite crystals, due to the system of channels and cavities penetrating crystals have well developed internal surface, accessible to the adsorbed molecules, (Alietti A. 1972).

Results and Discussion

The adsorption properties of natural zeolites by SO_2 are caused by: clinoptilolite content in the rock, the silicon oxide, the temperature of adsorption and the type of zeolite modification. At the same time the adsorption capacity for SO_2 is directly dependent on the clinoptilolite content in the breed, (Tsitsishvili G.V. et al., 1985).

The very important factor to arrange SO_2 recovery is in the formation of kremen content as lawflint zeolites are characterized by a high adsorption capacity and low acid resistance, while the High-silicons - have a low adsorbability to SO_2 and high acid resistance.

Thus lawflint zeolits can be used for the extraction of the SO_2 from pre-dehydrated systems, high-silicones - for catching SO_2 from wet environments, since the action to them of acids even slightly improves their absorption capacity (Tamboli J.K. et al., 1970). Acid stayability is a very important factor in the organization of SO_2 recycling, as in the regeneration process, due to high acidicy the SO_2 zeolitic structures collapse and, therefore, can not be used for multicycle processes.

Table 1. Adsorption capacity for SO_2 due to the clinoptilolite content

Deposite	Clinoptilolite content in the breed, %	Adsorption capacity for SO_2, g/100g
Sokirnitsa	75	6,3
Noyemberyan	65	4.1
Akhaltcikhe	50	2.6
Ay-Dag	75	6.2
Hot Spring	80	6.0
Beretianskoe	40	2.4

The sorption of SO_2 on clinoptilolite at low SO_2 concentrations and with temperature up to 200 °C remains high. This allows you to recommend the clinoptilolite as an efficient absorber of SO_2 at low concentrations of SO_2 and of high temperatures, which is important for the production (Liang P.M., 1989). The adsorption capacity for SO_2 largely depends on the ion exchange shape of the modified zeolite, thus the exchange of Na^+ to Ca^{2+} and Mg^{2+} ions in the zeolite structure significantly increases the adsorption capacity. Obviously in exchange of ions two sodium cations are replaced by a cation of calcium, and the input window expands, and this facilitates the penetration of SO_2 molecules in the cavity of the zeolite structure, (Barrer R. M., 1956). Widespread use of zeolites in the industrial scale is due to the possibility of complete and SO_2 desorption at 350-400^{O}C. Desorption of SO_2 and appropriate regeneration of the "spent" zeolite is one of the important steps that basically define the technical and economic value of the adsorption process.

In order to obtain by desorption concentrated gas various variants of zeolites' regeneration were investigated:

1) the use of hot air as heat carrier and stripping gas leads to the dilution of desorbed gas;
2) uniformly intense heating of the sorbent layer (5, 10, 20 deg/min) with simultaneous stripping, SO_2 evolvment forms gas with a maximum concentration of about 24%;
3) the desorption by gas, circulating in a special closed circuit with 300-35 ^{O}C allows to extract SO_2 with the concentration of about 30%;
4) purging of the spent layer by the superheated steam (220-260 °C) the SO_2 may be allocated in a concentrated form after the condensation:

Three last ways of the regeneration of natural zeolites can allow to utilities SO_2 by next using it in the sulfuric acid production, or in the production of liquid sulfur dioxide Tsitsishvili G.V. et al, (1985). When using zeolites in many cycles its activity decreases only for the first 5-10 cycles and only for 10-12%, but in subsequent cycles this capability remains unchanged. The main conditions for the use of zeolites for the neutralization of non-ferrous metallurgy's waste gases are:

- the ability to light thermo-chemical modification of the zeolite, which is very important for the selective adsorption;
- the adsorptive properties of zeolites depend little on up to 200 ° C flue gas temperature and therefore a wide temperature range without changing the adsorption capacity applies;

Therefore, the Armenian zeolites are an indispensable raw material for the organization of recycling waste sulfuric gases of ferrous metallurgy.

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Bio-fertilizer MM on the basis of microorganisms and modified according to the new technology of Mineral composites - Association of microbes with natural modified minerals

R. G. Gevorgyan, R. A. Madoyan and A. O. Sargsyan

Faculty of Geography and Geology, Yerevan State University, Armenia; E -mail: rgev@ysu.am

Introduction

Intensive cultivation (manifold cultivation of soil, melioration, applying mineral and organic fertilizers, pesticides etc.) influences valuably on the ratio of nutrients in soil solution and results in disorders in steady biological balance, causing shifts in soil biodynamic in natural conditions. Using too much mineral fertilizers leads to their accumulation in soil, then in plants, adversely influences in technological qualities and nutritive value of agricultural project. The world community faced problems with growing rates of mineral fertilizers' utilization, which like other chemicals, is toxic and cause damage to biosphere and to people through nutrition products and water.

Experimental Methods

Opening of nitrogen fixers led to the creation of so-called microbial fertilizers. Already in 1895 Nabbe and Hiltner patented a preparation of germ culture Nitragin. It was produced in 17 different ways for different plants. The preparation is a group of nitrogen-fixing microorganisms' cultures. Applying Nitragin to the soil or the treatment of seeds was called inoculation and enabled the farmers to enhance the quality and quantity of the product, Hakob Sargsyan et al. (2008).

After the Second World War the period of chemization of agricultural production began, and the works on research of microbiological preparations terminated. Huge possibilities of Chemistry, and their usability shifted to the second plan the microbial preparations. Nevertheless, it became clear, that intensive and multiple applications of synthetic nitrogen fertilizers aside to positive effects (growth of productivity) are very dangerous, because the nitrogen-bearing substances pollute the soil, subsoil waters, rivers and lakes. The mineral fertilizers wash out from the soil, leach out and turn into dangerous for humans substances: nitrites, nitrosamines etc., and, that is why, recently the microbial preparations, bio-fertilizers, are again preferred.

There are a number of microbial fertilizers. In soil there are not one, but several associations of microorganisms, having better stimulating effect, than homogeneous strains of microbes. It is possible to state for sure: associations give better result compared with pure cultures, which was time and again proved in practice. Synthesis of new compounds and decomposition of organic remains in soil take place at impact of ferments, assignable from different associations of microorganisms, and continuously one association of microbes is changed by another. There are a great number of microorganisms in soil. According to M. Gilyarov, in each gram of chernozem there are 2-2.5 billion bacteria. Microorganisms not only decompose organic remains into more common mineral and organic compounds, but also take part actively in synthesis of high-molecular compounds - compost acids, which form the reserve of nutrition substances in the soil. Thus, taking care of the soil productivity, it is necessary to take care of the nutrition of microorganisms. The essence of soil productivity is in "nutrition of bacteria and other animate beings", living in soil. It is necessary first to "feed" microbes and worms, which, on their turn, will feed the plants. This function is performed by the inhabitants of the soil, and for these inhabitants it is necessary to take care first. This aspect of the soil problem requires change of traditional thinking of agronomists.

Intensive chemization of the fields has destroyed the micro flora and organisms of the soil family, which are the main reproducers of soil productivity. Old technologies are replaced now with microbiology, which solves ecological, energy and nutrition problems that the mankind faces.

Results and Discussion

Complex microbial preparations are the result of microbiological achievement. Exposure to soil micro flora, which provides predominance of useful microorganisms in it, can stimulate the enhancement and provision of chemical and physical qualities of the soil.

In nature the micro-organisms symbiosis by groups, forming rather long nutritional, protective and other chains. Break of one of the links or enrichment of the soil by one type of microorganisms only gives a short-time effect, because the balance between the soil culture families, providing their normal vital functions is destroyed, and thus, the microorganisms die or go to anabiosis bastardizing the soil productivity. Besides, the efficiency of monocultural fertilizers is limited by such factors like: drought, surplus humidity of the soil, strong frost, spontaneous fires, anthropogenic emissions etc.

Development of the new technology of acquisition of complex ecologically pure biofertlizers, combining useful qualities of nitrogen-fixing microorganisms, probiotics, photosynthetic and other bacteria and modified natural composites (volcanic aches, clay, tripoli, zeolites, diatomite etc.), by their effectiveness exceeding the existing bio fertilizers, is the most actual problem nowadays. Nevertheless, the plants for their normal growth need not only potassium, nitrogen and phosphor; they also need microelements cerium, selenium, lanthanum etc. In known fertilizers the microelements are presented as chemical additives. In suggested fertilizers the suppliers of microelements are natural mineral composites. A special group of microbes-destructors decompose mineral composites and turn a great number of microelements and silicon dioxide into a condition digestible for plants. Because of the combination of naturally modified mineral composites with a complex of bacteria this fertilizer guarantees active vital functions of composites in soil despite of any negative external effect. In the basis of the offered preparation lays the development of the method of getting a new complex bio fertilizer of wide specter, including the use of two most important components for agriculture:

– bio preparation on the basis of the association of microorganisms and natural zeolite of Armenia modified according to the new technologies, (Саргсян А. О., и др., 2011).

Applying the new bio fertilizer to the soil will give double effect: long-term effect of the applied fertilizer and prevention of washing out nutrition substances. Thus, we suggest a new, ecologically clean, high-productive complex bio fertilizer of long-term and multi-sectoral effect. Such bio fertilizer at lower cost can be an effective substitution of mineral chemical fertilizers, and, besides, it will promote the growth of agricultural productivity by 50-60% and more. Its application with ratio: 7-8 liters for 1 ha saves 250-300 kg ammonia saltpeter (i.e. about 40000 AMD), which is 3 times more expensive, than the offered bio fertilizer. And the most important thing is that it valuably increases not only the productivity, but also the ecological compatibility of the agricultural products.

The use of MM enables to reduce the terms of ripening of the crop by 7-10 days, extend the terms of fruiting of the plants by 1-2 weeks and increase the productivity by 50% and more. Besides, in fruits and vegetables the content of sugar, vitamins and dry substance increases, and valuably falls the quantity of nitrates. The fruits and vegetables grown in greenhouses using MM have practically the same taste and flavor as the ones grown in natural environment. The terms of crop preservation increase almost 2 times. It is vital to mention, that MM has long-term effect for 1.5-2 years after applying it to the soil. MM fastens the growth and development of decorative plants, enhances rich flowering, promotes better establishment of grafts and stimulates rhizogenic process.

In laboratory and field experiments it was shown, that MM valuably suppresses the following plant pathogens: Verticillium family (wilt, dry mould), Phomopsis family (black blotch), Sphaerotheca family (powdery mildew), *Uncinula necator* (powdery mildew), Pythium family (blackleg), Phytophthora family (late blight) and Fusarium family (seedling blight).

The main group of modern bio preparations (Epine or Ideal) contains only ferments which increase their vital functions but not particular living micro-organisms. It is obvious, that long-term live symbiosis created with their help is impossible, thus, their effect is also short-term.

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Treatment of nuclear power plant radioactive wastes by immobilization into a stable crystallized glass-ceramic matrix (pyroceram sitall) based on natural minerals

R. G. Gevorgyan and A. O. Sargsyan

Faculty of Geography and Geology, Yerevan State University, Armenia; E -mail: rgev@ysu.am

Introduction

The purpose of the project was the development of an innovative resource-saving technology for the conditioning (sitallization) of radwastes (slurries, sorbents, etc.) by immobilization into stable Crystallized Glass-Ceramics materials (GCM) such as special sitalls (pyrocerams) prepared on the basis of natural minerals and rocks of Armenia.

Experimental Methods

The risk of the increased levels of radioactive radiation necessitates the adoption of special cardinal and operative measures for the isolation of radwastes (RW) from the population. Based on the analysis of the incidents at the Nuclear Power Plants (NPP) and other nuclear facilities, one can determine three basic trends on RW management:

- RW processing by the extraction of the radioactive nuclides for further use,
- transformation of the liquid radwastes (LRW) to hard form and their storage,
- RW entombment in geological formations.

However, the most actual (and not optimally solved) problem is the minimization of the concentrated liquid radwastes (CLRW) by their transformation into the stable form. The distillation or Deep Evaporation producing middle active and highly-saline CLRW is frequently applied to the reduction of LRW volumes.

The CLRW immobilization technology using matrices such as glass or cement is wildly spread everywhere for the provision of safe storage. The matrix blocks with the immobilized radioactive nuclides are usually packed into metal or concrete capacities, and the products from the Deep Evaporation Machine (DEM) are placed into the special containers for the subsequent long storage.

The construction of storehouses, the adoption of special waterproofing measures, and the storage of the DEM products containers at the NPP are technologically difficult problems which demand significant expenses and do not provide the safe storage of CLRW. As regards the glass matrixes, they allow the reduction the conditioned waste volume but at the same time have, because of their amorphous nature, a number of disadvantages such as high fragility, presence of numerous structural defects, low homogeneity and density as well as rather low radiation resistance.

Within the frame of the ISTC project A-485 “Efficient treatment of radioactive liquid waste by zeolites modified through chemical and radiation methods” research on the development of treatment technology for Armenian Nuclear Power Plant LRW using various natural sorbents has been successfully performed at Yerevan State University. During the last stage of this project, the optimal conditions of the extraction of radioactive nuclides by zeolites have been specified on a pilot facility. Thus, under static and dynamic conditions a significant reduction of LRW volumes (up to 400-600 times) by transformation into a hard phase has been achieved. At the same time, the reduction of LRW volumes was considered by the participants of the above mentioned project as a provisional measure until the development of the sitallization technology of sorbents with high concentration of radioactive nuclides and slurries obtained from the Deep Evaporation equipment. This direction of works, on which the preliminary work has already been carried out, is more time and additional budget demanding, Петросов И.Х. и др., (1999).

Concerning the mentioned project, highly competent personnel made the following steps:

- distillation and Deep Evaporation technology have been introduced for the minimization of Armenian NPP LRW concentration;
- a pilot plant (experimental-industrial technological setup) for the LRW treatment using chemically and radiation modified zeolites has been developed and tested in NPP;
- decontamination of radioactive effluents by sorption (also using natural sorbents) has been developed;
- the chemical and physical properties and structure of minerals and rocks taken into consideration for the separation of health endangering radionuclides from the biosphere have been investigated.

The participants of the project accumulated great experience in:

- the research of the aluminosilicate and other systems for formation of GCM matrices, the compound of which includes analogues of the soil-forming minerals;
- the development and implementation of the new technology of special sitalls production;
- the development of the treatment of natural sorbents;
- the development of the technology of thermo-chemical and microwave modification of natural sorbents.

Results and Discussion

This project was devoted to the development of an innovative sitallization technology of the exhausted CLRW (evaporation slurries of the liquid radioactive outlets and zeolites loaded with the radioactive nuclides).

Armenia natural and technogenic materials (volcanic glass, perlite, tuff, slag, litoid pumice, bor-containing travertine, barite and etc., and also alkaline and soil- alkaline magmatic rocks of sienit, phonolits, trakhitits, nepheline-sienits, etc. type) will be used as an initial raw material for sitalls formation.

For the effective and long-term isolation of the exhausted sorbents and the slurries (the oozy formations accumulated in settling tanks) from the biosphere, the authors of the project proposed the sitallization technology, a method incorporating the radwastes into stable (against cataclysms) and durable crystalline glass – ceramics materials (sitalls).

The end product of the researches will be homogeneous, recrystallized microcrystalline GCM compound in which the granules of the radioactive sorbents and the particles of slurries will be homogeneously distributed. The ingredients of the silicate GCM will create a matrix, isolating the radioactive sorbents from the environment for a long time due to its high stability of the silica-alumina sorbents to the external conditions. New phases formed in the silicate matrix material will include in their structure radioactive nuclides, particularly cesium and strontium, as a result of isomorphic replacement. At high concentrations they will form independent isostructural phases distinguished by thermodynamic stability and high resistance to the environment, Gevorkyan R.G. et al., (2002), Арутюнян Р.С. и др. (2012).

Thus, within the framework of this project the following primary objectives will be achieved:

- the reduction of LRW volumes stored at operating NPPs will be achieved, i.e. the special storehouses' creation expenses will be decreased;
- safer storage for RW will be provided, i.e. their migration into the environment will be extremely reduced, as they will be incorporated in more hard crystalline matrix;
- the durability of GCM containing radioactive nuclides will be increased, due to their modification and formation of new mineral-like compounds;
- the conditioning technology of the radioactive sorbents and slurries will be simplified and made cost effective due to the use of inexpensive and radiation resistant Armenian rocks and minerals.

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Results of trials of obtained lactobacterial preparations based on modified zeolites

M. R. Gevorkyan, R. A. Madoyan and H. Sargsyan

Department of Geography and Geology, YSU, Armenia; E -mail: rgev@ysu.am

Introduction

At the Department of Mineralogy, Petrology and Geochemistry of Yerevan State University some new modified zeolites of gel-like structure have been obtained. These zeolites are perspective for creation of complex preparations for medical-biological purposes. Taking into account the promising data of using of such zeolites for the development of effective and long acting pharmaceutical, as well as fertilizing preparations of nitrogen-fixing bacteria, a problem of development of complex immobilized forms of modified zeolites with lactobacteria has been set. For these purposes a strain of acidophilic lactobacteriahas been used; these strains are used for making of “Narine” - medical-prophylactic sour-milk product.

The main goal of our work was the study of viability of cells of lactobacteria and conservation of their enzymatic activity after including into the modified zeolite. The work has been carried out on the basis of RCDM, Sargsyan H. et al., (2008).

Experimental Methods

Two strains of lactobacteria are used: the strain – producer of “Narine” and the culture.
Used to 2 strain of lactic acid bacteria- producer of "Narine" and L.acidophilus - str. H-10.
For obtaining the cells biomass the cultures were grown on liquid (MRC medium) and solid (tryptose agar) nutrient mediums. The cultures were grown at 37°C during 20 hours.

Composition of mediums (g/l):

<u>*MRC medium*</u>
Yeast extract -5,0
Meat extract – 1,0
Peptone – 1,0
Glucose – 2,0
NH_3 – citric acid – 2,0
Na-acetous – 5,0
Twin 80 -1,0
K_2HPO_4 – 2,0
$MgSO_4 .7H_2O$ – 0,2
$MnSO_4 .4H_2O$ – 0,05
Distilled water up to 1000,0
pH 6,5

<u>*Tryptose agar*</u>
Yeast extract -3,0
Glucose – 10,0
Twin 80 – 1,0
Tryptose agar – 39,0
$CaCO_3$ – 5,0
Distilled water up to 1000,0
pH 7,2

The biomass of bacteria has been obtained by centrifugation of their suspension with further cleaning by distilled water (10 min., 5000 revo). The number of viable bacterial cells was determined in Goryaev’s counting chamber and sifter of their suspension on the tryptose agar in Petri dishes. The biochemical activity of obtained preparations with included cells was determined by specific enzymatic reaction proper to this group of bacteria. The lactase activity was determined by quantity of reducing substances formed as a result of enzymatic reaction. 20 mg of biomass was incubated 60 min. with 1 ml 1% lactose solution at t-37º. After centrifugation (10 min., 5000 revo) in supernatant was determined the quantity of reducing substances. The lactase activity was expressed in M/g of raw cells per hour. K_m and V_{max} was determined using the diagram of dependence of reaction rate on concentration of substrate.
The lactase activity was determined both for intact and immobilized in zeolite bacteria. At that for determination of activity of immobilized bacterial cells recount with residue of zeolite mass has been done; it was done for education of pure lactase reaction of immobilized cells biomass.

Results and Discussion

During the reporting period the activity of immobilized preparations of tested strains of lactobacteria on zeolites of different modification with using of different methods of immobilization (impregnation of cells into gel, covering with film, etc.) has been studied As a result of this work and corresponding workup certain methodical approaches for obtaining on the base of modified zeolites the effective immobilized complex preparation of lactobacteria with long activity have been established, Butorac A. I. et al (2002).
The table shows summarized results of study of lactase activity of one complex preparation on modified zeolite with application of two lactobacteria strains.

Table 1.Lactase activity of cells strains *Lactobacillus acidophilus* in immobilized preparations modified by zeolites (lactase activity M/g hour)

Strains	Initial lactase activity	Lactase activity of immobilized cells	
		Recount to biomass	In per cent from initial
INMIA – (317/402)	1.86	0.08	13.0
H-10	1.53	0.133	26.1

Based on the negative results obtained with abovementioned strain a new methodological approach has been applied for immobilization of lactobacteria, namely *Lactobacillus rhamnosus.* For testings has been used solution of 1% rhamnose. The data obtained have shown that incubation in 37^{o}C of the strain for 24 hours in rhamnose suspension resulted in fermentation of 50% of rhamnose used.
So, we may conclude that we have rather efficient method for obtaining of immobilized lactobacteria with zeolite gel.

One can see from represented data that the enzymatic activity of bacterial cells in the complex with zeolite is essentially weak, although in recount to pure mass of immobilized cells it remains on rather high level and can be used in the practice of sour milk products production, Щурубикова А.А. и др., (2003).
Generalizing the data obtained the following conclusions may be done:
- Clinoptilolite of Armenia is rich source of obtaining the modified mineral derived gels and high-sorption materials for creation of complex biopreparations for medical, agricultural and industrial purposes;
- Inclusion of microbe cells into zeolites is accompanied by decrease of mass exchange and correspondingly,
- biocatalytic activity of bacterial cells;
- As an effective way and methodological approach for obtaining the complex of modified zeolites and microorganisms with high mass exchange may be the non-carrier immobilization of cells with using of filamentous globules.

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Occurrence, properties and uses of mordenite-bearing tuffs from Milos-Kimolos-Polyegos volcanic field (Greece): A review

A. Godelitsas[1], G. Stamatakis[2], P. Gamaletsos[1] and M. Stamatakis[1]

[1]*Faculty of Geology and Geoenvironment, University of Athens, GR-15784 Athens, Greece;*
E-mail: agodel@geol.uoa.gr
[2]*Faculty of Chemistry, University of Athens, GR-15784 Athens, Greece*

The Milos-Kimolos-Polyegos volcanic field belongs to the Hellenic Volcanic Arc that is located 120-250 km north of the Hellenic subduction trench and is characterised by Pliocene to present-day volcanic activity (mainly high-K calc-alkaline to calc-alkaline magmatic rocks) related to subduction of the African plate beneath the overriding Eurasian plate (Francalanci et al., 2007). The altered pyroclastic rocks –tuffs- of the above volcanic islands are rich in **MOR**-type natural zeolites, constituting significant industrial mineral deposits which are currently exploited in the island of Kimolos (Fig. 1).

Figure 1. Left: Mordenite in tuffs of SW Milos island. Right: View of the Bentomine Kimolian Enterprises S.A. quarry in the NE part of Kimolos island

The mordenite-bearing tuffs in Kimolos are characterised by a relatively low SiO_2 component (av. 70 wt. %) compared to surrounding volcanic rocks. Mordenite crystals are alkali- (Na- and moreover K-) rich and coexist with K-feldspars, opal-CT and clays (Christidis et al., 2001; Godelitsas et al., 2010; Stamatakis et al., 2010). According to trace-element discrimination diagrams (Zr/TiO_2–Nb/Y), the protoliths could be trachyandesites, whereas Ti/Al–Eu/Eu* diagrams indicated a clear felsic affinity. Normalised REE patterns confirmed an expected negative Eu anomaly and a relative HREE depletion, whereas relevant multi-element diagrams indicated positive Cs, Rb, Th, Pb, U and Ta, negative Ba, P and Ti and compatible elements anomalies (Godelitsas et al., 2010). It should be noted that zeolite deposits of Kimolos (Greece), together with those of Mudhills (CA, USA), appear to contain the highest Cs concentrations in the world, due to alkaline fluids and mineralogical selectivity factors (Godelitsas et al., 2010; Campbell et al., 2012). Similar zeolitised tuffs occur on the island of Polyegos. These materials have been studied in terms of their mineralogy (Kitsopoulos, 1997; Kitsopoulos and Dunham 1998), while their detailed geochemistry remains rather unknown.

Zeolitic rocks of Kimolos and Polyegos have been studied with regard to industrial potential as pozzolanas in the cement industry (Kitsopoulos and Dunham 1996; Fragoulis et al., 1997; Stamatakis et al., 2010). Laboratory cements produced with Kimolos materials indicated that the reactive silica of the samples was linearly correlated to total silica whereas the compressive strength was not correlated to either reactive silica content or Blaine alone (Fig. 2). On the other hand, concerning the sorptive properties, the SSA_{BET} of the rocks reached a value of 63 m^2/g (Godelitsas et al., 2010). In that case, the CEC was measured to be 98 meq/100 g. The above data suggest that the mordenite-bearing tuffs from Milos-Kimolos-Polyegos volcanic field show good capabilities for the development of new products for innovative industrial and daily uses, including the possibility for treatment of olive mill wastes (Stamatakis 2010).

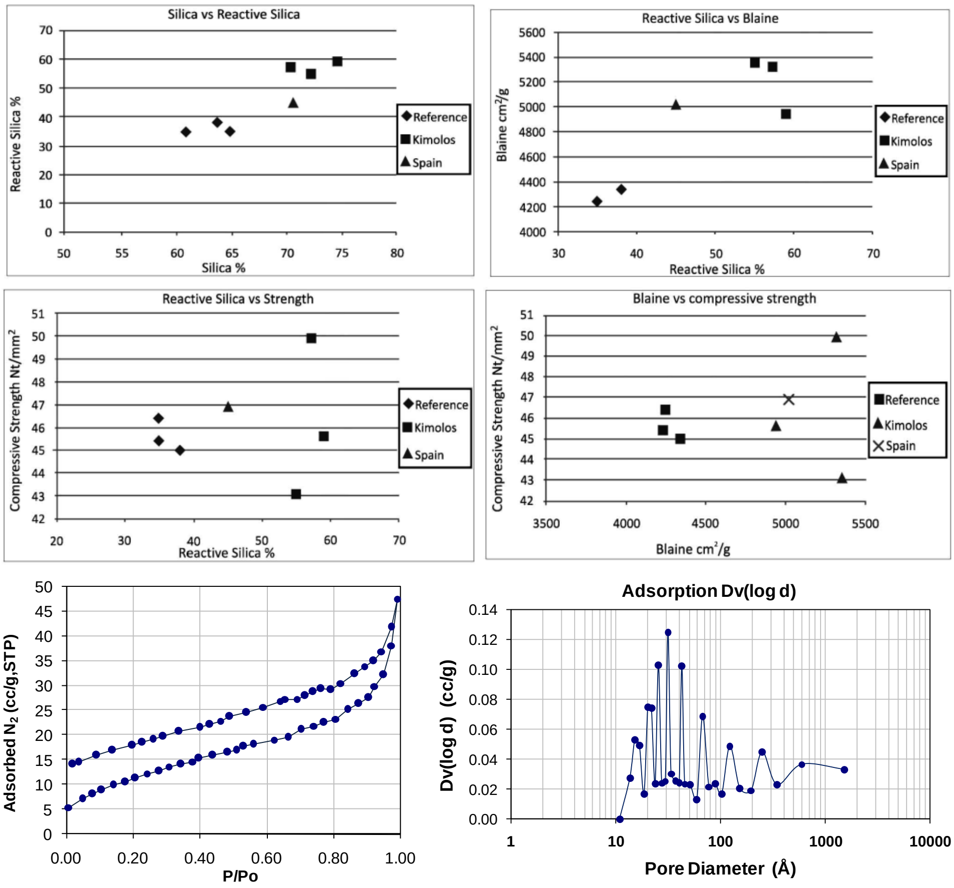

Figure 2. Laboratory cement data (upper, Stamatakis et al., 2010) and N_2-BET data (lower, Godelitsas et al., 2010) concerning mordenite-bearing tuffs from Kimolos island

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Defluoridation of drinking water using a composite based on stilbite from Ethiopia

L. Gomez-Hortigüela[1], E. Agudo[1], J. Pérez-Pariente[1], T. Sani[2], Y. Chebude[2] and I. Diaz[1, 2]

[1]*Instituto de Catálisis y Petroleoquímica, CSIC, Madrid, Spain; E-mail: idiaz@icp.csic.es*
[2]*Chemistry Department, Addis Ababa University, Addis Ababa, Ethiopia*

Introduction

The presence of fluoride in drinking water can be beneficial or harmful for human health depending on the concentration. At concentrations in water ranging between 1.0 and 1.5 mg/L, fluoride is beneficial, especially for children, for the calcification of the dental enamel. In contrast, a too high ingestion of fluoride can lead to dental and/or skeletal fluorosis (Fawell et al., 2006). The World Health Organisation (WHO) predicted in 1984 that more than 260 million people consume water with a concentration of fluoride higher than 1.0 mg/L. Hence, the development of technologies, preferably low-cost and environmentally-friendly, capable of reducing the fluoride concentration below the limit established by WHO (1.5 mg/L) represents nowadays a world-wide crucial target. Various defluoridation methods have been applied to remove excessive fluoride from drinking water and prevent the associated health problems (Jagtap et al., 2012). Among them, adsorption processes are generally considered attractive in terms of their effectiveness, convenience, accessibility, availability of a wide range of adsorbents, ease of operation, simplicity of design, and for economic and environmental reasons (Loganathan et al., 2013). Natural zeolites have potential for defluoridation; however they have rarely shown acceptable defluoridation capacity as raw materials (Gómez-Hortigüela et al., 2013). In this study we have grown nanohydroxyapatite (nHAp) crystals on the surface of natural stilbite from Ethiopia to further evaluate its defluoridation capacity.

Experimental Methods

We describe here the preparation of high-performing nHAp for fluoride removal, using a natural zeolite, stilbite, as a source of calcium ions and as a release-controlling agent for the growth of HAp, thus producing a composite stilbite-nHAp material (Gómez-Hortigüela et al., 2014). This natural stilbite releases the Ca^{2+} present within its cavities by ion exchange in a very slow and controlled way (Gómez-Hortigüela et al., 2014 submitted). Ca^{2+} ions are first ion-exchanged by NH_4^+, thus being released to the solution which, in the presence of PO_4^{3-} and at an adequate pH, leads to a precipitation of HAp on the zeolite surface. By carefully controlling the Ca-NH_4 exchange through variations of temperature and time during the HAp crystallization, we manage to produce decreasingly smaller nHAp crystals with increasingly higher F uptake capacities. The chemical composition, structure and morphology of the synthesized STI/HAp composites have been characterized by ICP, XRD, ^{31}P NMR and Electron Microscopy. For the defluoridation essays, lab-made F-containing solutions have been prepared according to real polluted water compositions obtained from Ethiopia. The conditions for the general initial defluoridation tests were: room temperature, initial concentration of fluoride ($[F]_o$) around 5 mg/L, and 20 h of contact time under continuous agitation. In particular cases, different initial fluoride concentrations and adsorbent doses were studied; the adsorption kinetics was also investigated. Fluoride concentrations were measured by means of ISE (ion selective electrodes) technique, using a pH&Ion-meter GLP 22 CRYSON device.

Results and Discussion

The natural zeolite stilbite mineral coming from Ethiopia, which has a STI framework type (Baerlocher et al., 2007) has a remarkably high content on Ca^{2+} of 5.23 weight % (Table 1). In the final composite material crystallized at different temperatures and times, the amount of HAp (evidenced by ^{31}P NMR) is quantified by the content of P (measured by ICP). The behaviour of these STI/HAp composites has been analysed on a demanding process of removal of fluoride from water with initial fluoride concentrations of about 5 mg/L (at autogeneous pH of 8-8.5). A clear relationship between the amount of HAp crystallized (as a function of the crystallization temperature and time) and its associated F^- removal intrinsic capacity is found: the higher the amount of HAp crystallized, the lower its associated defluoridation capacity (Figure 1A). Such behaviour is due to the smaller crystal size of HAp crystallized at lower temperatures, as suggested by ^{31}P NMR and SEM.

Table 1. Composition of the natural zeolite stilbite (measured by ICP, in weight %)

Al	B	Ca	Mg	Fe	K	Li	Mn	Na	Nb	Si	Ti
8.67	0.81	5.23	0.16	0.43	0.10	0.51	0.01	0.80	0.01	29.50	0.11

STI/HAp composites obtained at higher temperatures reduced less efficiently the fluoride concentration, despite having a larger amount of the fluoride-removal active HAp phase. This represents a clear evidence that nHAp of decreasing crystal size is more efficient for F^- exchange, possibly due to a less restricted diffusion (shorter diffusion pathway) through the 6-ring channels. Figure 1B shows the defluoridation of a solution with 5.0 mg/L of fluoride initial concentration as a function of the HAp dose (excluding the zeolite mass), and the associated intrinsic HAp defluoridation capacity. The limit imposed by the WHO of 1.5 mg/L is reached with a dose of 0.5 g of HAp per liter. It should be noted that the intrinsic defluoridation capacity of HAp remains constant at very high values between 7-9 mg of fluoride per g of HAp in the demanding process of adsorbing F^- in such low concentrations (5 mg/L). To our knowledge, such intrinsic HAp defluoridation capacities are the highest ones found so far for removing F^- from solutions with such low initial concentrations (~ 5 mg/L). Finally, the presence of the zeolite as a support for a high capacity material such as the nanohydroxyapatite grown under the conditions described in this work reduces the engineering and toxicity problems related to the use of small particle sizes.

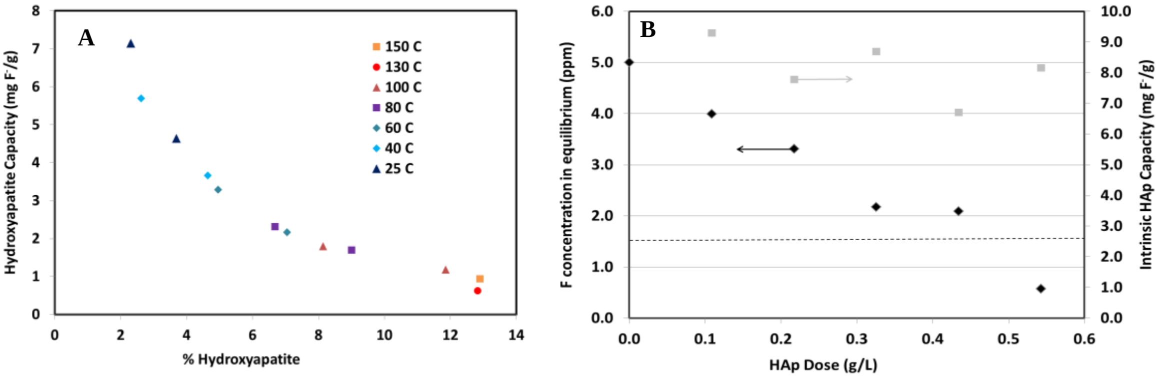

Figure 1. (A) Intrinsic HAp capacity (in mg of F- per gram of HAp) as a function of the amount of HAp (in wt percentage, crystallized at different temperatures and times, see legend), using a dose of 25 g/L of the composite and an initial fluoride concentration of 4.3 mg/L; (B) Concentration of fluoride in equilibrium (in mg/L) (left axis, black dots) and intrinsic fluoride removal HAp capacity (in mg of F- per g of HAp) (right axis, grey dots) as a function of the HAp dose; initial F concentration: 5 mg/L

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Phytonutritional efficiency of zeolitized tuff in pedotechnologies for functional recovery of degraded lands.

E. Grilli[1], G. F. Capra[2] and R. C. Vigliotti[1]

[1]*Seconda Università degli Studi di Napoli, Via Vivaldi n° 43, 81100 Caserta, Italy;*
E-mail: grillieleonora@hotmail.it
[2]*Università degli Studi di Sassari, Via Colombo n° 1, 08100 Nuoro, Italy*

Introduction

In damaged areas, the most affected environmental compartment is the pedosphere (Bradshaw, 2002). Soil features alteration by human activities is often severe and irreversible, leading to the loss of physical, chemical and biological fertility (Bell, 2006) in extreme cases, obliteration of soil occurs (Séré et al., 2008). In order to restore degraded lands for their possible re-use, soil functionality must be first recovered, through appropriate pedotechnical interventions. The *ex novo* soil building is a new good approach (Séré et al., 2010), and, in some cases, the only possible solution. The soil can be built by co-utilizing several organic and inorganic matrices, such as building materials, industrial by-products, amendment and compost (Buondonno et al., 2013), also, in case, in addition to earthy materials taken from "*in situ*" or surrounding soils.

Zeolitized tuffs have been shown to be adequate materials for reconstructive pedotechniques to *ex-novo* built soils, also designed as "*proto-horizons*" or "*embryonic*" soils (Buondonno *et al.*, 2002, 2007, 2013; Bucci et al., 2005).

Our study aims at evaluating the phytonutritional efficiency of *proto-horizons* made up by co-utilizing the Phlegraean Yellow Tuff (PYT), the zeolitized yellow facies of Campanian Ignimbrite, with phillipsite > chabazite (Grilli et al., 2011).

Experimental Methods

We considered the following three model proto-horizons for the possible establishment and stabilization of pasture/grass as a starting step for damaged lands restoration: (i) straight zeolitized tuff (PYT), with no organic or mineral nutrient supply; (ii) PYT + commercial compost (CC); (iii) PYT + phosphorite (PH) + poultry manure (PM). All models were assembled and monitored for nine months under controlled (pot) conditions. One gram of pasture/grass for pot was sowed (Buondonno et al., 2013).

The physionutritional efficiency of such pedotechnosystems (proto-horizons + pasture/grass) was assessed on the basis of agronomic performance, plant quality and residual soil fertility. In order to weight the key-components of the proto-horizons, and the possible interactions among them, conventional as well as experimental indices were proposed. In particular: i) the Soil/Plant Translocation Index (SPTI) evaluates the pedotechnosystems efficiency in transferring nutrients from substrate stock to plant, estimating both substrate capability to releasing available nutrients and plant metabolic aptitude to assimilate them, and, ii) the Physiological Efficiency Index (PEI), allows to assess the plant capability to use a specific nutrients.

Results and Discussion

All the investigated proto-horizons were characterized by a good crop production, following the order PYT < PYT+CC < PYT+PH+PM (data not showed). Beside an overall good performance, the experimental indices were quite differentiated (Fig. 1). On the whole, the amendment pedotechnosystem (PYT+CC), notwithstanding its initial remarkable organic matter and nitrogen contents, showed unsatisfying results: exiguous production, low utilization of N stock, and a significant cut of phosphorous and potassium fertility. On the other hand, the less expensive pedotechnosystems, *i.e.* straight zeolitized tuff (PYT) and fertilized-zeolitized tuff (PYT+PH+PM), provided the best phytonutritional performances, in terms of both nutrients release by substrates and plant assimilation capability. Indeed, the available phosphorus content was larger than amendment pedotechnosystem, and, on the other hand, in PYT+PH+PM the high rizosphere activity, due to a remarkable grass growth, etched the zeolitized substrate, leading to mobilization and subsequent availability of potassium.

These outcomes, along with previous data (Buondonno et al., 2013), suggest that zeolitized tuff is capable to sustain plant growth in stressed conditions, like those found in degraded lands where inert and infertile soils frequently occur. Further, in the experimental conditions, the growth of pasture-grass contributed in turn to improve and stabilize soil fertility thank to i) accumulation of organic matter by vegetal residues, ii) nitrogen production through legumes components, iii) physical stabilization by root systems, and iv) transformation of organic and inorganic components of substrate by rizosphere activity and linked pedomicrobiota, with subsequent increase of available nutrients.

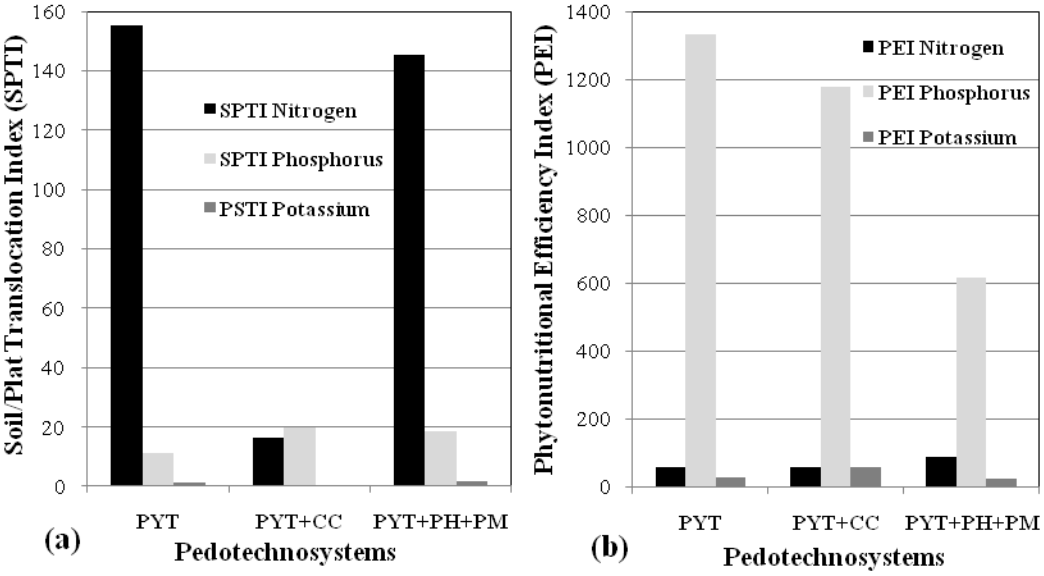

Figure 1. (a) Soil/Plant Translocation Index (SPTI) and (b) Phytonutritional Efficiency Index (PEI) in pedotechnosystems at the end of experiment

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Elements release from zeolitized tuff: kinetic aspects

E. Grilli[1], S. Salvestrini[1] and G. F. Capra[2]

[1]Seconda Università degli Studi di Napoli, Via Vivaldi n° 43, 81100 Caserta, Italy;
E-mail: grillieleonora@hotmail.it
[2]Università degli Studi di Sassari, Via Colombo n° 1, 08100 Nuoro, Italy

Introduction

The knowledge of weathering processes and dissolution patterns under different conditions are important to understand the rock evolution toward the soil formation (Grilli et al., 2011). With special reference to zeolitized tuff that were historically and widely used as soil amendment, natural fertilizer and media growth, the characterization of native nutrients release is of great interest in evaluating the fertility potential of them (Buondonno et al., 2000).

The present paper reports the preliminary kinetic results of an experimental pedology research project aimed at simulating the chemical weathering of zeolitized tuff (Grilli et al., 2011). Our attention was focused on the application of kinetics models to explain the release dynamics of elements and to attempt to identify the distinct mineral sources.

Experimental Methods

The zeolitized tuff used is the yellow facies of Campanian Ignimbrite formation, named Lithified Yellow Tuff (Cappelletti et al., 2003). The rock sample investigated was collected in the Phlegraean Fields District (Naples, Italy), and we have named it Phlegraean Yellow Tuff (PYT) (Grilli et al., 2011). The PYT sample had the following chemical composition (wt. %): SiO_2 = 54.46, TiO_2 = 0.43, Al_2O_3 = 13.96, Fe_2O_3 = 3.56, MnO = 0.13, MgO = 1.12, CaO = 4.56, K_2O = 6.63, Na_2O = 1.31, P_2O_5 = 0.11, H_2O = 13.73, and a total zeolite content, equal to 47% (30% phillipsite, 17% chabazite). Other tuff components were feldspars 39%, amorphous phases 13% and biotite 1%. Cation Exchange Capacity (CEC) was 2.12 $\text{mmol}_c\ g^{-1}$. The weathering of PYT was carried out by a ‘‘discontinuous equilibrium’’ batch through 23 Weathering Treatment Cycles (WTCs) to simulate natural soil wetting/drying cycles. Each WTC lasted seven days. The weathering solutions (WS) used were deionized water (W) and tannic acid (TA) solutions ($C_{76}H_{52}O_{46}$, FW 1.702 kD, Fluka) to reproduce respectively mild hydrolysis and subsequent leaching of meteoric water, and complexation of polyvalent cations by low molecular- weight organic acids. TA solutions were used at different concentrations, i.e. $[3{\cdot}10^1]$, $[3{\cdot}10^2]$, $[1{\cdot}10^3]$, $[3{\cdot}10^3]$, $[1{\cdot}10^4]$, $[3{\cdot}10^4]$, where square brackets indicate $\mu\text{mol}\ l^{-1}$. After each WTC the supernatants carefully removed and quantitatively replaced by fresh weathering solutions. Supernatants were filtered and element contents were determined by Flame Atomic Absorption Spectroscopy with a Perkin Elmer Analyst 100 Spectrometer (Grilli et al., 2011).

Results and Discussion

As expected, the cumulative final amounts of elements released from PYT increased in proportion to the TA concentration in the weathering solutions (Zhang and Bloom, 1999) following the order Si > K > Al > Ca ≈ Na > Mg > Fe and Si > Al > K> Ca > Fe > Na > Mg respectively for W and TA supernatants.

The dissolution release was particularly rapid during the early period, and it was likely to be dominated by ion exchange reactions and dissolution of fine particles together with high-energy sites such as crystal imperfections (Zhang et al., 1996).

In particular, in W supernatants (Fig. 1) the release was almost linear during all the experimental period for Mg, Fe, Na and, to a lesser extent, for K. For such elements, pseudo-constant first derivative values were estimated (data not shown), suggesting a quasi-zero order dissolution kinetics. It is interesting to note that Buondonno et al. (2000) showed that potassium release from campanian zeolitized tuff (phillipsite > cabazite), by Electro-UltraFiltration (EUF) under mild conditions follows a zero-order reaction. Further, as reported by previous research (Buondonno et al., 2000), also in our experimental conditions, potassium release is directly linked to abundance of phillipste as zeolitic phase. Indeed even if phillipsite and chabasite are K-selective exchangers, phillipsite is more selective than chabazite (Buondonno et al., 2000). On the contrary, the trends for Ca, Al and Si were neither linear nor monotonic.

In $[3{\cdot}10^4]$ TA supernatants (Fig. 2) the release trends of Mg, Fe and Na were to a certain degree similar to the respective values observed in W, but K, Ca, Al and Si exhibited even more composite patterns.

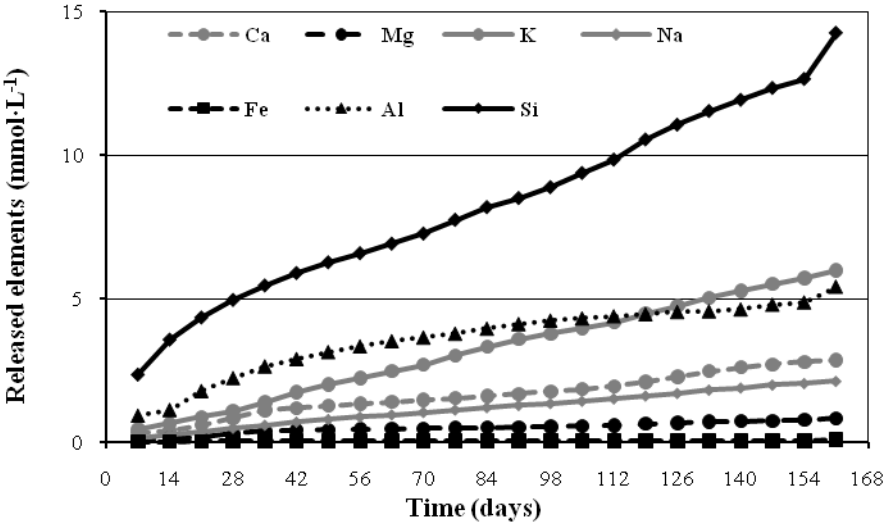

Figure 1. Element releases from PYT in W *vs.* time (days).

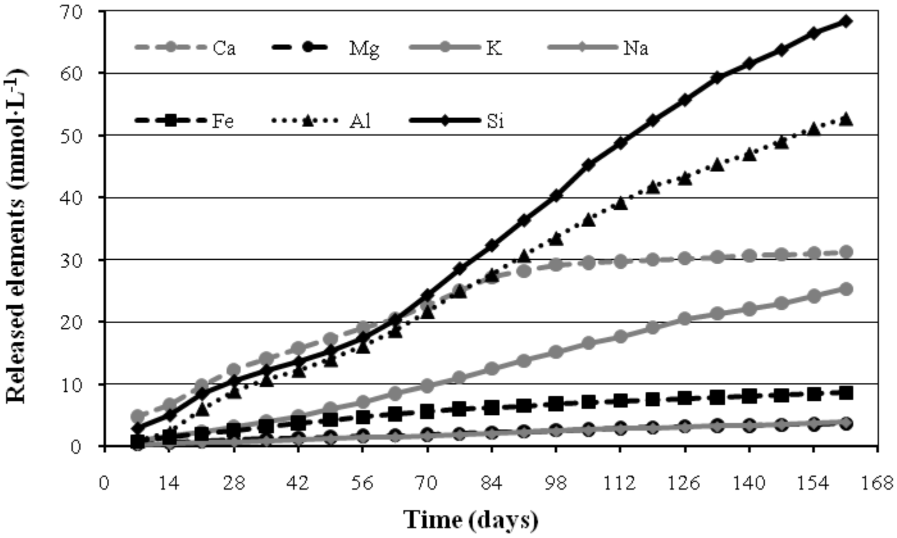

Figure 2. Element releases from PYT in TA solution at the maximum concentration ($3 \cdot 10^4$ mmol l^{-1}) *vs.* time (days).

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Nanoporosity and Dealuminated Zeolites from Mexico

M. A. Hernández[1], F. Rojas[2], R. Portillo[3], M. A. Salgado[3] and L. Corona[1]

[1]*Depto de Investigación en Zeolitas, Instituto de Ciencias de la Universidad Autónoma de Puebla, México;*
E-mail: vaga1957@gmail.com
[2]*Depto de Química, Universidad Autónoma Metropolitana-Iztapalapa, México 09340 D.F.*
[3]*Facultad de Ciencias Químicas, Universidad Autónoma de Puebla. México*

Introduction

There is a large amount of deposits of natural zeolites in Mexico. These deposits consist mainly of mordenite (MOR), erionite (ERI), epistilbite (EPI), heulandite (HEU) and clinoptilolite (CLI) zeolites. It is essential that your knowledge of porosity. Zeolites are microporous materials with voids smaller than 2 nm. Micropores can be subdivided in ultramicropores (pore width smaller than 0.7 nm) and supermicropores (pore width between 0.7 nm and 2 nm) (Hernandez et al., 2014). The presence of pores larger than supermicropores in natural and modified zeolites can be attributed to the existence of impurities or to the partial destruction of supermicropores in the matrix during dealumination or desilication. The pore space of a zeolite is filled in a volumetric fashion rather than through a layer-by-layer mechanism due to the close proximity of the surrounding pore walls to the adsorbate molecules. Sorption uptake increases with pressure and saturation of each pore domain with adsorbate molecules depends not only on size and shape of the microporous channels and cavities, but also on size and geometry of the adsorptive molecule. Therefore, the structure of the adsorbed phase within micropores is rather different than that occurring within mesopores. All zeolites have high internal surface area (microporosity) available for adsorption due to channels which are uniformly distributed through the entire volume of the solid. Microporosity results from the specific crystalline structure of the zeolite which in turn depends on its composition. Moreover, the external surface area (mesopores) contributes only to a small extent of the total available surface area. However, the distinction between external and internal surfaces is not always clear. External surface area (A_E) can be define as the available area for multilayer physical adsorption; *i.e.*, the overall BET surface area without taking into account any contribution of micropores. The porosity of these solids can be determined by adsorption studies as well as by other methods (Sing et al., 1985). In addition to their microporosity, natural zeolites are characterized by a system of secondary pores formed by mesopores and macropores. Secondary pores permit adsorption of relatively large molecules and play an important role in some sorptive and catalytic processes. However, the effects of secondary porosity on such sorptive and catalytic properties have not been studied in depth. In this work, natural zeolite samples mined from diverse locations in Mexico, are studied with respect to their adsorption behavior toward N_2 uptake. Determination of primary porosity and external surface area is carried out utilizing the Dubinin-Astakhov Theory, αs-plot and BET equation obtained from volumetric N_2 adsorption (at 77 K).

Experimental Methods

The zeolites used in this work are Mexican natural zeolites proceeding from different locations (see location and mineralogy in Table 1). There is one natural (N) and one modified (H1 and H2; Table 2). X-Ray Diffraction Analysis. Samples were characterised by X-ray diffraction analysis using a Siemens D 500 apparatus. The zeolite specimens were classified according to recognised zeolitic types from the diffractograms obtained. Identification results are shown in Table 1. All N_2 adsorption isotherms were measured at the boiling point of liquid N_2 (77 K) using an automatic volumetric adsorption system (Quantachrome AutoSorb-1LC).

Table 1. Source and mineralogy of natural zeolites

Localization: town, state	Natural zeolite sample	X-ray characterization
Chalma, Edo de México	MORN	Mordenite
San Gabriel, Puebla	CLIN	Clinoptilolite
San Juan, Puebla	HEUN	Heulandite
Zapopan, Jalisco	EPIN	Epistilbite
Agua Prieta, Sonora	ERIN	Erionite

Results and Discussion

The zeolite samples were classified according to recognised zeolitic types from the diffractograms obtained, Fig.1. In Fig. 2, the pore size distribution of the chemically modified mordenite (calculated according to the DA model and assuming cylindrical pores) are showed. Tables 2 lists a series of values corresponding to some important adsorption parameters obtained from the analysis of the N_2 isotherms (*i.e.*, surface areas calculated from the BET model; Langmuir equation; micropore volume, W_0, calculated by the α_S plots). In the same table, other important parameters are summarised: the constant, C_B, of the BET equation and total pore volume, V_Σ, calculated according to the Gurvitsch rule (applied at $p/p^0 = 0.95$).

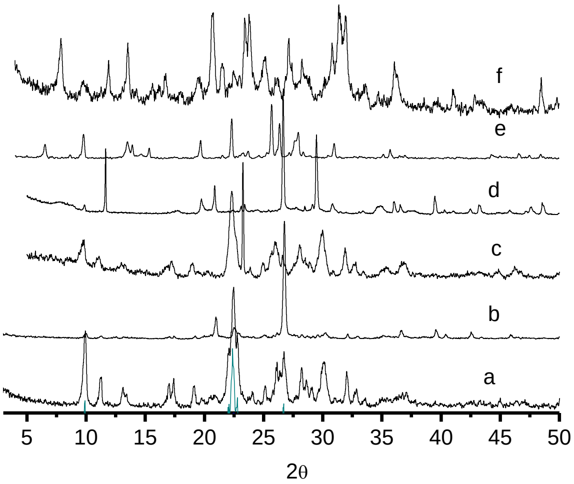

Figure 1. XRD patterns of natural zeolites, a) CLIN, b) quartz, c) EPIN, d) HEUN, e) MORN and f) ERIN

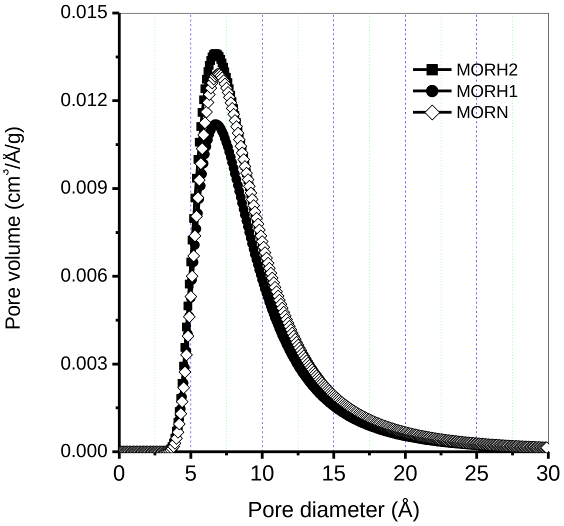

Figure 2. Nanopore size distribution (NSDTP) mordenite zeolite, Dubinin-Astakhov approach

Table 2. Some sorption parameters of natural (N), and modified zeolites (H)

Zeolite	As_L $m^2\ g^{-1}$	As_B $m^2\ g^{-1}$	V_Σ $cm^3\ g^{-1}$	C_B	PD_{DA} nm	$W_{0\alpha s}$
EPIN	45.48	62.69	0.048	-111	0.878	0.009
EPIH1	42.5	20.90	0.020	203	0.881	0.001
EPIH2	415	306	0.045	32	0.740	0.072
MORN	211.1	137.5	0.106	-120.9	0.680	0.070
MORH1	158.7	109.2	0.111	-62.08	0.680	0.040
MORH2	205.8	139.6	0.111	-99.46	0.670	0.053
ERIN	604.5	417.8	0.169	-79.98	0.520	0.14
ERIH1	424.3	320	0.170	-59.03	0.540	0.15
ERIH2	296.8	248.2	0.153	-152.3	0.615	0.11

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N_2, NO_2 and CO_2 adsorption on Epistilbite exchanged with H^+

M. A. Hernández[1], F. Rojas[2], M. A. Salgado[3], R. Portillo[3], L. Corona[1] and A. De la Cruz[4]

[1]*Depto de Investigación en Zeolitas, Instituto de Ciencias de la Universidad Autónoma de Puebla, México; E-mail: vaga1957@gmail.com*
[2]*Depto de Química, Universidad Autónoma Metropolitana-Iztapalapa, México 09340 D.F.*
[3]*Facultad de Ciencias Químicas, Universidad Autónoma de Puebla. México*
[4] *Facultad de Ingeniería Química, Universidad Autónoma de Puebla. México*

Introduction

The epistilbite (EPI) zeolite belong to the shabazite and have the following chemical composition: Ca_3 $(Si_{18}Al_6)$ $O_{48}\cdot 16H_2O$ with a Si/Al ratio = 3. In this work, epistilbites, natural and modified ionically from Zapopan, Jalisco in Mexico were used to adsorb CO_2 and NO_2. The adsorption isotherms for the various substrates were determined at temperatures of 473-623 K by means of a gas chromatograph at zero degrees of coverage. The data obtained at these temperatures were conveniently analyzed using the Langmuir and Dubinin-Astakhov adsorption equations. The interaction between the molecules of CO_2 and NO_2 and the substrates was measured in terms of the isosteric heats of adsorption. Most energy of interaction with the natural substrate occurred and other lightly treated with dilute HCl. Also, the isosteric heat of adsorption increased with the amount adsorbed NO_2 and CO_2 as a consequence of the cohesive interactions between the adsorbate molecules. Zeolites exchanged homogenized micropore surface and consequently the values of isosteric heat of adsorption of NO_2 and CO_2.

Experimental Methods

*(i)*X-ray Powder Diffraction. In situ X-ray powder diffraction of zeolite EPI samples were collected at various temperatures using PHILIPS X'pertMPD system equipped with Anton Paar high-temperature reaction chamber XRK900. The diffractions in the 2θ ranges of 5-65 are collected using CuKα radiation. The temperature was increased from room temperature to 973 K at a heating rate of 10 K min^{-1}, and the X-ray diffraction was measured at different measurement temperatures in the range 298-973 K. The temperature elected was maintained for 1 h before collecting the diffraction pattern. Percentage crystallinity of the EPI samples was determined from the X-ray diffraction pattern by considering the peaks at 2θ values 9.86, 22.48, 25.96, 28.06, 32.19, 39.74, 46.13 and 60.02.
(ii) SEM and EDX. Microscopic analysis of zeolite EPI samples were obtained using *LEO 1430 VP* variable pressure scanning electron microscope equipped with *INCA Oxford* EDX facility.
(iii) N_2 adsorption. The N_2 sorption isotherms were measured at the temperature of 77 K in an automatic volumetric sorption instrument Quantachrome Autosorb-AS1. The saturation pressure was recorded continuously during the course of the adsorption measurements. Before the adsorption, the substrates of 60-80 mesh were degassed at 623 K for 20 h at a pressure lower than 10^{-6} Torr which was provided by the instrument turbopump. Textural results (surface areas and pore volumes) obtained from analysis of the nitrogen isotherms at 77 K have been evaluated by means of: i) BET equation, ii) Langmuir equation, iii) *t* method and iv) Gurvitsch rule. The pore size distribution of the samples under study was evaluated from the data of the curve limit descending or desorption using the approximation of Density Functional Nonlocal (NLDFT).
(*iv*) Adsorption of NO_2 and CO_2. Isotherms of NO_2 and CO_2 on epistilbites were measured at temperatures of 258 and 298 K in a volumetric apparatus adsorption of high vacuum equipped with valves free from grease; a thermostatic bath (298 K) or a mixture of ice and NaCl (258 K) was used to control the temperature of the experiment of adsorption.

Results and discussion

Adsorption isotherms of NO_2 and CO_2 on Natural (EPIN) and dealuminated epistilbite zeolites (EPIH1 and EPIH2) were measured by the inverse gas chromatography method at zero-coverage. This type of microporous solids such as EPIN and EPIH1and EPIH2 zeolites were conditioned by means of acid treatment of the natural zeolitic precursor (EPIN) with HCl at different concentrations. Adsorption of selected gases

(NO_2 and CO_2) on EPI zeolites were studied in the temperature range from 463 to 583 K. The Freundlich and Langmuir adsorption models were found to approximately fit the gases adsorption data, within the selected temperature range. The uptake amount of these gases by the diverse adsorbents was temperature dependent. Additionally, the energies of interaction between these gases with EPI microporous walls were realized from the evaluation of the internal energies of adsorption (ΔU_0) and isosteric heats of adsorption (*qst*). The Nanopores Size Distribution Functions (NSDF) of epistilbites under study was obtained by the Dubinin - Astakhov method (DA). This zeolite is composed of 8 member rings with dimensions of 0.37 x 0.44 nm. The filling of the epistilbite supercavities with dimensions of 0.37 x 0.84 nm and interconnected is the main contribution to the adsorbed volume. The porous structure of epistilbite can be assumed simply as an array of cylindrical pores, the width of the supercavities is 0.84 nm. The results shows the curves NSDF of some epistilbites obtained according to the DA method assuming a cylindrical shape of the microporous channels with n=3; the NSDF provide very similar value to the width of the porous cavities of the average diameters epistilbite. The results indicate that the chemical treatment to these zeolites favors the appearance of nanopores and the collapse of a large group of them, distributions are described with pore sizes near 0.74 nm.

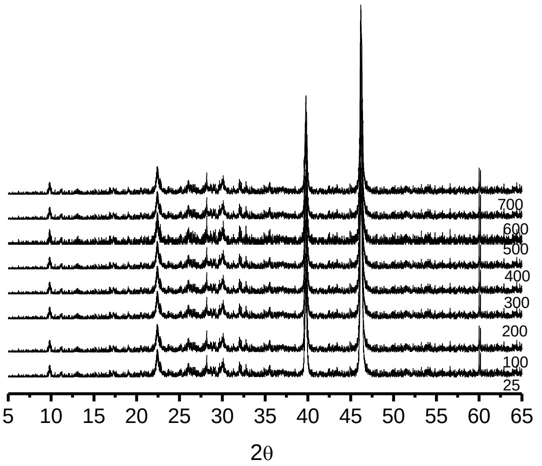

Figure. 1. X-ray difracction patterns of Epistilbite

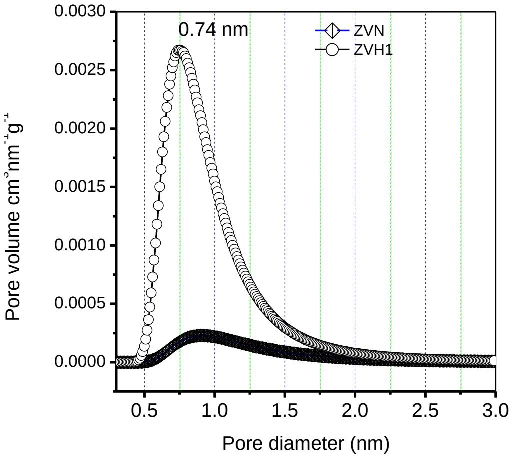

Figure. 2 . NSDF curves of Epistilbite, D-A

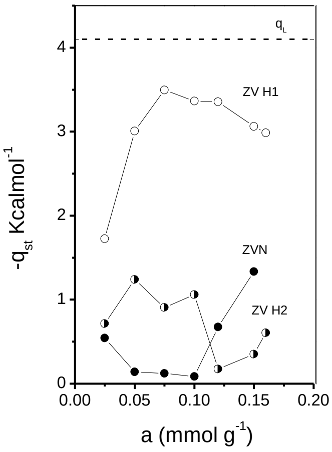

Figure. 3. Adsorption heat of CO_2

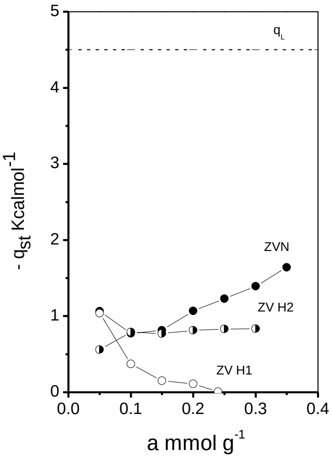

Figure. 4. Adsorption heat of NO_2

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Zeolitization of 2nd Rupelian acid phase pyroclastics near Kostino village, Kardzhali District (E. Rhodopes, S. Bulgaria)

R. Ivanova[1], I. Peytcheva[1], M. Kadiyski[2], A. Vlahov[1] and N. Vuković[3]

[1]*Geological Institute, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria; E-mail: rossiv@geology.bas.bg*
[2]*Institute of Mineralogy and Crystallography, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria*
[3]*Faculty of Mining and Geology, University of Belgrade, 11000 Belgrade, Serbia*

Introduction

The most important Bulgarian zeolite deposits as well as many zeolite occurrences are genetically related to the Paleogene volcanic activity in the Eastern Rhodopes, Southern Bulgaria (Yanev et al., 2006). The volcanism is bimodal in composition and cyclic in character: four intermediate phases alternate in time with five acidic ones. All established zeolite deposits are hosted in the explosive products of the first two Rupelian acid phases. According to the currently accepted ideas, the zeolitization of pyroclastic sections in the Eastern Rhodopes results from the existence of a low-temperature hydrothermal system, operating within still hot pyroclastic deposits when deposited in shallow marine environment (Yanev et al., 2006).

This study concerns the zeolitized (clinoptilolitized) acid pyroclastics, erupted during 2nd Rupelian acid phase from a volcanic source located in the area of Borovitsa caldera (Fig. 1a). These rocks currently occupy the highest parts of the landscape in the region to SE of the caldera and NW of Kardzhali. Their zeolitization has been mentioned before (Djourova and Aleksiev, 1989) but none of their exposures have been studied.

The section studied builds the topmost parts of a hill rising near Kostino village, located 10 km NW of the town of Kardzhali (Fig. 1b). It lies over the products of the earlier volcanic phases (Yanev, 2007): acid pyroclastics of 1st Rupelian acid phase - Dazhdovnitsa Formation (also clinoptilolitized, Djourova and Ivchinova, 1987, Yanev et al., 2006) and volcano-terrigeneous formation (2nd intermediate volcanic phase). The section is about 80 m thick and can be interpreted as consisting of six pyroclastic flow units, most of them associated with ash-cloud units, and one ash-fall in origin layer (Fig. 1c).

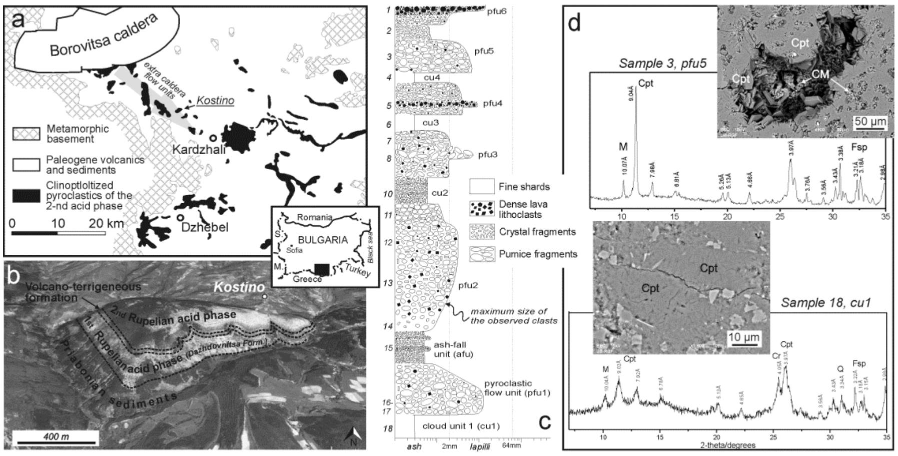

Figure 1. (a) Distribution of the 2nd phase acid volcaniclastics in part of the E. Rhodopes (Yanev et al., 2006), (b) "Google Earth" view of the studied area with the local geology (Yanev, 2007), (c) out-of-scale lithology column with the sample position, (d) BSE images and XRD patterns (samples 3 and 18) showing differences in grain-size and crystallinity of clinoptilolite in fine- and coarse-grained rocks. Cpt-clinoptilolite, Fsp-feldspars, Cr-cristobalite, Q-quartz, M-mica

Experimental Methods

All of the exposed rocks varieties and all of the identified depositional units were sampled. The rock textures were studied in 14 thin sections. The bulk mineralogy was studied by XRD using TUR-M-61 diffractometer (CoKα, 30 kV, 20 mA). Chemical analyses of clinoptilolite were made in 6 carbon coated polished slabs using JEOL JSM-6610LV (15 kV, 100 s live time) connected with an Oxford Instruments EDS unit (INCA software).

Results and Discussion

Optical microscope observations revealed that the section consists of shards and pumice-dominated rocks. Ash-sized shards build ash-fall and cloud units while pumice, also mainly ash-sized, is more typical of flow units. Thin levels rich in dense lithics appear in the uppermost parts of the section. Crystal fragments of quartz, feldspars, biotite, and amphibole are present in all of the units. Marine fossils are common (Fig. 2a).

Clinoptilolite replaces pseudomorphically all glassy particles larger than about 0.01×0.05 mm. Finer-grained particles have not been observed. The rocks that presumably contain large amount of finest (like rod-shaped pumice-derived particles as in co-ignimbrite ash-cloud units) are in fact composed by fine-grained aggregates of secondary minerals. Respectively, clinoptilolite in these rocks seems poorly crystalline and does not form well-shaped crystals (Fig. 1d, sample 18). Platy clinoptilolite crystals as large as 30-40 µm in diameter can form in central hollows of the largest shards in the coarser-grained rocks (Fig. 1d, sample 3).

Clinoptilolite composition varies slightly throughout the section studied: Na is present only in its lower parts (samples 18 and 15) and its highest values (average 0.17 apfu) are registered in the lowermost unit (sample 18). Ca contents decrease slightly upward (from 2.15 to 1.7 apfu). The lowest values of Mg are measured in the cloud units (< 0.3 apfu), the highest (0.58 apfu) – in the topmost analyzed level (sample 2). Although it is not well expressed in the studied section (Fig. 2c), similar distribution of the extra framework cations has been described in other zeolitized sections in the Eastern Rhodopes, regardless the volcanic source they are related to (Djourova and Ivchinova, 1987). Si/Al ratio varies between 4.44 and 4.71.

Clinoptilolite is accompanied by small amounts of opal-CT, clay minerals and secondary feldspar. In the fine-grained varieties they appear as tiny grains scattered in the space between clinoptilolitized particles. Pumice-dominated rocks are enriched in larger aggregates of green clay minerals that seem closely attached to the surface of pumice clasts (Fig. 2b).

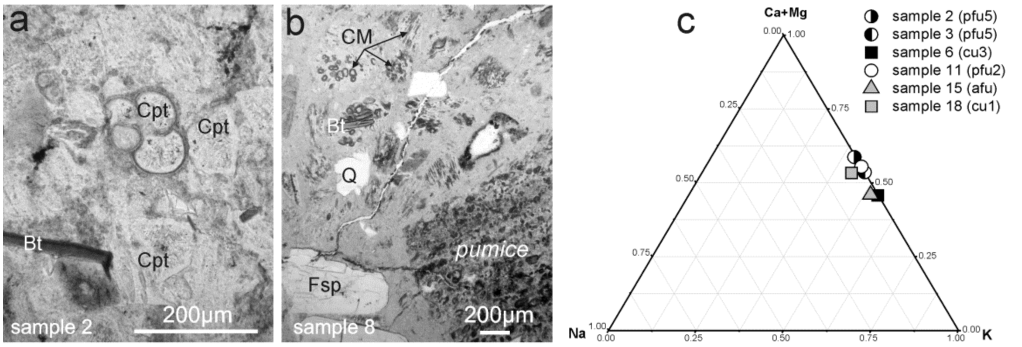

Figure 2. Microphotographs (plane-polarized light) of samples 2, with a marine fossil skeleton (a), and 8 (b), (c) plot of the main extra framework cation ratio in the studied clinoptilolite. Bt-biotite, for the other abbreviations see Fig. 1.

Summarizing some of our results, we can conclude that distribution of the secondary phases in the studied pyroclastic section near Kostino village seems very much controlled by the shape of the glass particles, while their grain-size might have had an impact on the size of the glass-replacing clinoptilolite individuals as well as on the degree of its crystallinity. Regarding clinoptilolite composition, it seems mainly depending on position of the clinoptilolite in the section.

Acknowledgment
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Characteristics and formation of phillipsite crystals in a sediment core from the Central Indian Ocean Basin

S. D. Iyer[1] and S. M. Pinto[2]

[1]CSIR-National Institute of Oceanography, Dona Paula, Goa 403 004, India; E-mail: iyer@nio.org
[2]Geological Survey of India Training Institute, Bandlaguda, Hydrabad-500 068, Andra Pradesh, India;
E-mail shannonmeryl@gmail.com

A study of authigenic minerals present in deep-sea sediments would not only provide an insight to the marine geochemical cycle of many elements but also the history of the physico-chemical processes that have operated and/or operating on the seafloor and within the sediments. Hence, zeolites are important minerals in pelagic sediments and of these, phillipsite and clinoptilolite, the two most abundant zeolites, constitute as much as 80% of the weight of the sediments (Czyscinski, 1973).

Phillipsite occurs as cemented/consolidated slabs (Morgenstein, 1967), as cavity filling of tuff as in Sylvania Guyot, Pacific Ocean (Rex, 1967), as fracture filling in basalts of Leg 17 (Bass et al., 1973) and in dredged volcanic debris altered to ~50% phillipsite. Plagioclase crystals replaced by phillipsite (Bass et al., 1973) and phillipsite in the nucleus of ferromanganese nodules have also been reported (Bonatti, 1963). Although phillipsite, clinoptilolite and natrolite occur in the Indian Ocean (Kastner and Stonecipher, 1978) these have not been detailed for the Central Indian Ocean Basin (CIOB). In the CIOB, phillipsite and harmotome occur near seamounts and fracture zones.

We investigated the characteristics and formation of the ubiquitously present authigenic phillipsite crystals in a Van Veen grab sediment that was collected near a seamount and lifted from the siliceous ooze domain from a water depth of 5190 m at latitude 13° 58.773' S and longitude 75° 57.990' E. The sediment hosted 15 buried ferromanganese nodules that have a rough surface feature. The sediment coarse fraction (1% to 1.25%) also consists of ferromanganese micronodules, glass shards, Fe-rich fragments, microtektites, pumice pieces, mineral fragments, palagonite and biogenic matter (radiolarians, foraminifera, fish teeth).

Phillipsite occurs as colorless to yellowish prismatic crystals (130 to 300 μm), rarely as single crystals, mostly as typical cruciform twinned forms, several multiple twinned crystals and sometimes as spherical ball-shaped mass of phillipsite. Most of the crystals are either fresh and show no pores or pits while a few have dissolution features. Microprobe analysis of the phillipsite crystals reveals the following composition (wt %): SiO_2 (52-61), Al_2O_3 (18-21), FeO (1-4.5), MgO (0.10-1.4), Na_2O (1-4.5), K_2O (4.8-12.5) and very low CaO (<0.3) and BaO (<0.6). Some crystals have traces of TiO_2, P_2O_5 and MnO. The Si/Al and Na/K range from 2.4 to 2.8 and 0.12 to 0.4, respectively. The phillipsite compositions are on a par with those reported by Goldberg (1961), Sheppard et al. (1970) and Stonecipher (1976).

Deep-sea authigenic minerals form by: diagenesis, metamorphism, hydrothermal and halmyrolysis processes. The distribution and chemistry of phillipsite depends on: compositions of the precursors and of the host sediments, sedimentation rate, Eh-pH conditions, temperature, thermodynamic stability and time taken to form. The Si/Al ratio indicates the phillipsite crystals to be intermediate in composition between those formed from mafic rocks and silicic tuffs. The phillipsite crystals probably formed by the following mechanism from the surrounding weathered basic and acidic volcanic under the influence of low-temperature hydrothermal conditions (Iyer and Sudkhakar, 1993, Iyer et al., 2007).

Precursor	Intermediate product	End product
A. Volcanic glass	$\xrightarrow{\text{palagonite}}$	clay minerals (typically montmorillonite, Fe-rich montmorillonite + zeolites
B. Volcanic glass (silicic/mafic)	$\longrightarrow$	zeolites

Hence, other than the ferromanganese nodules (macro and micro), glass shards etc. it is equally important to study the other authigenic phases that occur in a sediment core. In this respect, phillipsite crystals being common in volcanogenic sediments and relatively resistant to alteration could be used to understand the formational processes and the rates of sediment accumulation.

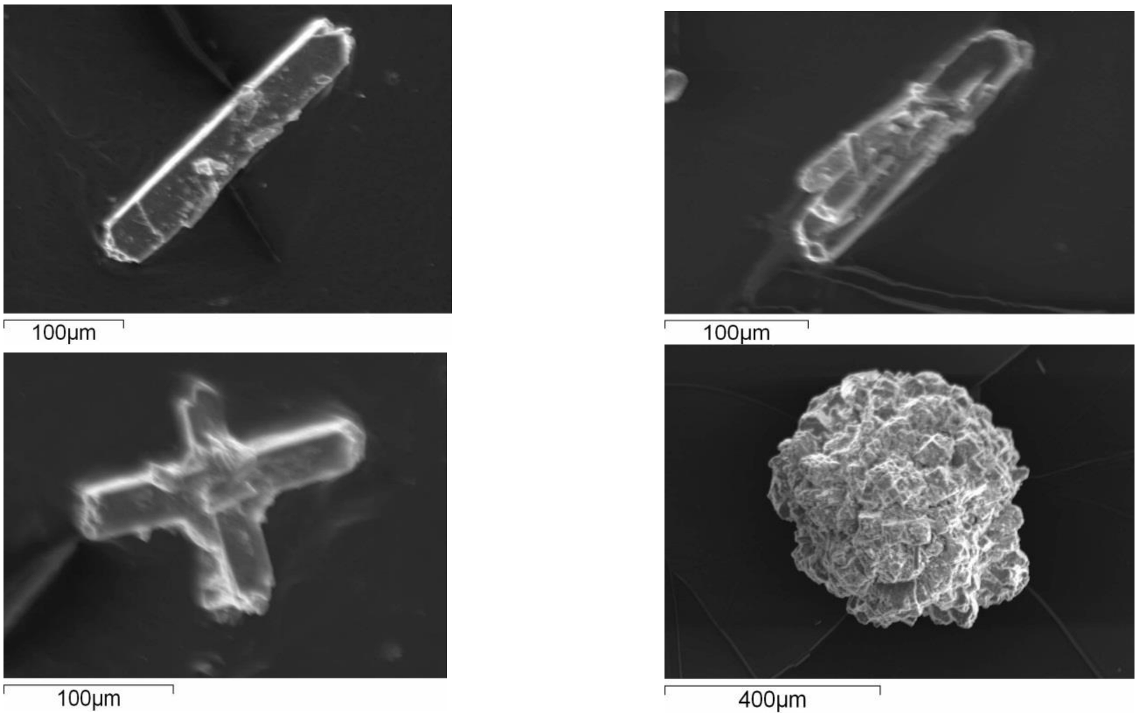

Figure 1. Scanning electron micrographs of phillipsite crystals. Top left: Single crystal, Top right: Single crystal with over growths. Bottom left: Typical cruciform crystals with overgrowths. Bottom right: A spherical ball of phillipsite crystals

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Equilibrium and Kinetic Study for Removal of Acid Fuchsin dye by Natural Zeolite

E. Kalkan[1], H. Nadaroglu[2] and N. Celebi[2]

[1]Ataturk University, Oltu Erath Sciences Faculty, Geological Engineering Department, 25240 Oltu-Erzurum, Turkey; E-mail: ekalkan@atauni.edu.tr
[2]Ataturk University, Erzurum Vocational Training School, Chemistry Department, 25400 Erzurum, Turkey

Introduction

Some dyes contain heavy metals like: copper, nickel, mercury, chromium and cobalt as the functional group of dyes or by-products. In addition, bacterial growth in water and the photosynthesis of aquatic plants may be disrupted by discharged dyes because of the inhibition of sunlight penetration into the water (Rahman et al., 2013, Nadaroglu et al., 2014). To solve the problem related to the colored dye effluent adsorption technologies receive much attention in the recent year owing to their efficiency in color removal treatment. In adsorption treatment, material called adsorbent plays an important role for pollutants removal from water stream (Kalkan et al., 2013, Rahman et al., 2013). The adsorption is considered to be superior in comparison with the other techniques of waste water treatment in terms of low cost, easy availability, simplicity of design, high efficiency, ease of operation, biodegradability and the ability to treat dyes in more concentrated form (El-Said et al., 2012). Among natural materials zeolites resulted to be effective adsorbents for the removal of various heavy metals and other environmental pollutants because of their selectivity, ion exchange capacity, and low-cost (Ahmaruzzaman, 2008, Wang et al., 2008, Han et al., 2010, Baskan and Pala, 2011). In this study, Acid Fuchsin dye was absorbed by natural zeolite from aqueous solutions. Adsorption isotherms and kinetic studies have been performed to describe the adsorption process.

Experimental Methods

Acid Fuchsin dye was purchased from Sigma-Aldrich Co. Ltd. The natural zeolite was collected from an open pit mine in Gördes-Manisa (Turkey). This material was ground and passed through a 200-mesh standard sieve. After washing with distilled water, it was heated at 100±5 °C for 24 h. The solid fraction was washed five times with distilled water following the sequence of mixing, settling, and decanting. The last suspension was filtered and the residual solid was then dried at 105ºC, ground in a mortar, and sieved through a 200-mesh sieve. The product was used in the study. Synthetic wastewater was prepared by dissolving Acid Fuchsin dye. The absorbance of the solutions was measured at 547 nm with a spectrophotometer (PG Instrument T80 Spectrophotometer). A calibration curve was prepared in the range 0-40 ngmL^{-1} of Acid Fuchsin dye according to the general procedure.

Results and Discussion

Effect of pH, contact time, temperature and adsorbent dosage on the removal of Acid Fuchsin dye by natural zeolite was illustrated in Figure 1. Removal of dye was decreased at increasing solution pH values from 3 to 8 (Figure 1a). At low pH, the H^+ ions are predominant in solution and the surface of zeolite will be charged with those ions (Samarghandi et al., 2012). The removal increased quickly within the initial 30 min (Figure 1b). Rapid absorption and equilibrium in a short period of time is related to the efficacy of the adsorbent, especially for wastewater treatment (Pereira de Sa et al., 2013). The rapid removal of the adsorbate has significant practical importance because it will facilitate smaller reactor volume ensuring efficiency and economy (Dhabab, 2011). The adsorption increases with increasing temperature, and maximum adsorption of Acid Fuchsin dye is obtained at 60ºC (Figure 1c). An increase in temperature involves an increased mobility of the metal ions and a decrease in the retarding forces acting on the diffusing ions (Elouear et al., 2008). An increase of adsorption capacity was observed from 0.25 to 1 mg/mL of adsorbent dosage (Figure 1d). The increasing of dye removal with adsorbent dosage can be attributed to an increase of adsorbent surface and the consequent availability of more adsorption sites (Mahmoodi, 2013).

In this study, the suitability of the Langmuir and Freundlich adsorption isotherm models to the equilibrium data was investigated for removal of Acid Fuchsin dye by natural zeolite and the results were summarized in Table 1. It has been deduced that Langmuir adsorption isotherm model better fitted to the experimental data. Also, experimental data generated from Acid Fuchsin dye adsorption tests were evaluated by using pseudo-first-order kinetic and pseudo-second-order kinetic models and the results were summarized in Table 2. It was seen that kinetic data was best fitted onto pseudo-second-order model.

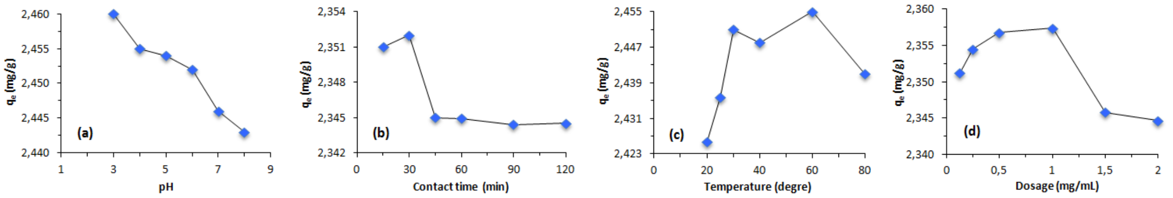

Figure 1. Effect of pH (a), contact time (b), temperature (c) and adsorbent dosage (d) on the removal of Acid Fuchsin dye by natural zeolite

Table 1. Values of the Langmuir and Freundlich adsorption isotherms

Langmuir constants		Freundlich constants	
q_{max}(mg/g)	333.33	K_F	0.062
b (L/mg)	106.67	n	0.654
R^2	0.9897	R^2	0.9881

Table 2. Comparison between the estimated adsorption rate constants, q_e and correlation coefficients associated with the pseudo-first-order and the pseudo-second-order rate equations

		Pseudo-first-order rate equation			Pseudo-second-order rate equation		
Initial dye concentration (mg/L)	q_e expected (mg/g)	k_1	q_e calculated (mg/g)	R^2	k_2	q_e calculated (mg/g)	R^2
5	2.48	0.022	1.71	0.9418	0.41	2.56	0.9950
25	15.76	0.032	16.52	0.9991	0.0025	32.79	0.9951
50	22.30	0.045	22.86	0.9681	0.000109	30.12	0.9663

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Geology of the Slanci zeolitic tuff deposit near Belgrade (Serbia)

V. Kašić[1], D. Životić[2], V. Simić[2], J. Stojanović[1], A. Radosavljević-Mihajlović[3], Ž. Sekulić[1] and S. Mihajlović[1]

[1]*Institute for Technology of Nuclear and Other Raw Mineral Materials, P. O. Box 390, Belgrade, Serbia;*
Email: v.kasic@itnms.ac.rs
[2]*Mining and Geology faculty, Djusina 7, 11000 Belgrade, Serbia*
[3]*Institute for Nuclear Science Vinča, University of Belgrade, Belgrade, Serbia*

Introduction

The wide area of the "Beogradski dunavski kljuc" was studied in order to realize the geological map of Belgrade (1:25000). The most recent research was carried out during 2002 within the project of obtaining geological map of the "Beogradski dunavski kljuc" (Kondzulović et al., 2003). Within this investigation, presence of tuffs on the Tapino brdo locality was noticed. Administratively, the exploration area belongs to the Palilula municipality, city of Belgrade. According to mineralogical and crystallographic research these layers are considered as zeolitic tuffs of the very good quality (Kasic et al., 2004). Intensive exploration of these tuffs began in 2004 (ITNMS) on the Tapino brdo locality and the results of these explorations are shown in this paper.

Geological characteristics of the exploration area

Miocene and Quarternary sediments are represented on the Tapino brdo and Zapis localities (Obradovic and Dimitrijevic, (1978). Miocene layers have been discovered on the higher parts of heights of Tapino brdo and Zapis. They are constituted by Lower Miocene lacustrine and Badenian marine sediments. Lacustrine sediments rise on the surface right beneath the peak heights. They are composed by grey and greenish grey claystones, intercalations of sandstones and tuff and tuffite layers. Recent Miocene sediments are represented by layers of Badenian age (mostly conglomerates, marly and sandy limestones), which are situated on the very top of heights of Tapino brdo and Zapis.

Results and Discussion

Geological operations embraced processing of up-to-date results, mineral prospecting, mapping and sampling of exploration digs and drill holes (five drill holes with total driling length 110m), interpretation and guiding of further exploration operations. On the basis of exploration operations and analyses of obtained results, zeolitic tuff layers are about 2.5m in thicknes (from 1 to 3.9m), with a dip angle of about 20º N-NE. Laboratory examinations were performed at ITNMS (Institute for Nuclear and Other Mineral Raw Materials) in Belgrade. Zeolitic tuffs samples were examined both by stereomicroscope and by polarizing observations (in transmitted light), and by X-ray powder diffraction (XRPD) method. Macroscopically, these samples are white-grey to yellowish, sometimes significantly coated by limonite, without distinctly visible minerals. Mineralogical composition is: *quartz, feldspars, micas, zeolite minerals, limonite-goethite, clay minerals, zircon, rutile, volcanic glass; plant fossils were also present.* XRPD analyses yielded the following mineral composition: *clinoptilolite-heulandite group zeolite minerals*, *quartz, plagioclases, amorphous material* (Stojanovic et al., 2003).
Chemical analyses: On the basis of complete silicate (SiO_2, Al_2O_3, Fe_2O_3, CaO, MgO, MgO, K_2O, Na_2O, heating loss-H.L.) and heavy metal analyses (Pb, Zn, Cd, Cr, Ni, Sb, Cu, Mn) the obtained chemical composition of investigated samples is presented in Tables 1 and 2. Physicochemical investigations, such as moisture content, specific volume, DTA and TG analysis, acid stability, and cation exchange capacity (CEC) were also performed. The type and content of exchangeable cations in the starting clinoptilolite-rich tuff from Slanci deposit is shown in Table 3. The total capacity of cationic change is defined as the sum of exchangeable cations content.

According to the laboratory results, the zeolitic tuff from Slanci deposit displayed very good quality. It may fulfils demands for industrial application in agriculture, stock farming, and environmental protection.

Table 1. Chemical analyses of samples from Slanci deposit (in % wt).

Mark	Sample	Oxides								
		SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	TiO_2	Na_2O	K_2O	I.L.
B_1-P_5	Zeolitic tuff	69.28	12.76	1.18	2.80	0.484	0.333	0.972	1.04	11.07
B_6-P_6	Zeolitic tuff	68.00	12.28	1.14	3.85	0.726	0.250	0.554	1.05	12.08
B_7-P_7	Zeolitic tuff	69.32	13.23	1.07	2.45	0.448	0.167	0.904	1.07	11.24
B_8-P_8	Zeolitic tuff	68.62	12.70	1.29	3.50	0.501	0.190	0.338	1.08	11.73
B_1-P_9	Tuffite	25.78	6.14	2.47	21.03	12.45	0.300	0.392	0.94	30.47

Table 2. Heavy metal content of samples from the Slanci deposit (in ppm)

Mark	Sample	Heavy metals							
		Cd	Cr	Ni	Pb	Sb	Cu	Zn	Mn
B_1-P_5	Zeolitic tuff	1	10	35	45	30	12	33	35
B_6-P_6	Zeolitic tuff	1.5	13	40	40	25	11	34	49
B_7-P_7	Zeolitic tuff	1	11	25	45	25	11	31	22
B_8-P_8	Zeolitic tuff	2	12	40	45	25	9	22	42

Table. 3. Content of exchangeable cations in zeolitic tuff from the „Slanci” deposit

Ca^{2+} mmolM$^+$/100g	Mg^{2+} mmolM$^+$/100g	Na^+ mmolM$^+$/100g	K^+ mmolM$^+$/100g	CEC mmolM$^+$/100g
145.0	3.0	4.1	8.0	160.0

Acknowledgements

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Embedment of Methylene Blue in natural and synthetic phillipsite

S. Kowalak, M. Szyld and A. Jankowska

A. Mickiewicz University, Faculty of Chemistry, Poznań, Poland; E-mail:skowalak@amu.edu.pl

Introduction

The uniform porous system of zeolites and other molecular sieves is widely applied for selective adsorption and separation of molecules with respective size. The intracrystalline voids of zeolites can be also utilized for encapsulation (*ship in a bottle*) of chosen compound molecules. The encapsulation provides a very well dispersion of guest molecules, protect the unstable compounds against aggressive agents or physical conditions (light, temperature). The geometry of pore system provides an ordered arrangement of entrapped molecules which can evoke their novel properties. The entrapped dye molecules can form fast pigments (e.g. Maya Blue) (Kowalak and Zywert 2011). Zeolites can be also utilized for adsorption of dyes from waste water. Methylene Blue (M.B.) is a cationic dye which can be introduced into zeolites by means of ion-exchange provided that pore opening of zeolite is large enough to allow the guest entering into the inner voids (Schultz-Ekloff et al., (2002), (Simoncic and Armbruster 2005).

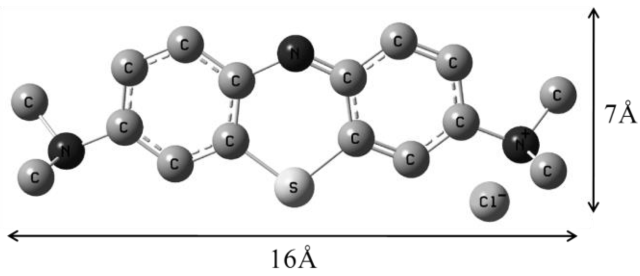

Figure 1. Model of Methylene Blue molecule

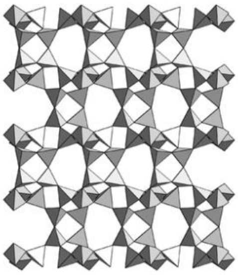

Figure 2. Model of PHI structure

Phillipsite is one of common natural zeolites occurring in various environments (Wise, 2013). As illustrated in the above Figures the aperture of phillipsite (~0.38 nm)is smaller than the diameter of a Methylene Blue molecule (0.7 nm) and therefore a high efficiency of ion exchange cannot be expected. The encapsulation of chosen molecules can be also attained by crystallization of zeolite from the initial mixture supplemented by the guest compound. It was demonstrated (Hoppe et al., 1995) that Methylene Blue can be introduced into faujasite either by ion-exchange procedure or by crystallization of zeolite in the presence of dye. It was found that localization of dye is different in products prepared by either way. The chemical structure of Methylene Blue, particularly the contribution of alkylamino groups in the molecule suggests a potential ability to act as potential template agent directing the crystallization of the starting mixture.

Here we attempted to crystallize zeolite from the mixture supplemented with Methylene Blue in order to check its influence on the direction of the crystallization course. Our earlier syntheses of faujasite, zeolite L did not indicate such influence and the expected structure of zeolite was always attained. We noticed some directing influence of Methylene Blue on crystallization of zincophoshate molecular sieves and therefore we prepared the initial crystallization mixtures containing not only silicon and aluminum sources but also some admixture of zinc source. The resulted products appeared to show the PHI structure and it was reasonable to compare the properties of them with natural phillipsite, particularly in terms of their capacity to entrap Methylene Blue.

Experimental Methods

Synthesis of zeolite was conducted in hydrothermal conditions. Water glass, potassium aluminate, $Zn(NO_3)_2$, were principal substrates of initial gel, which was supplemented with Methylene Blue. The molar proportions of the components were following: Si/Al/Zn/Na/K/M.B = 15/1/0.1/15/0.2/0.01. The resulting (blue) gel was crystallized in an autoclave at 160 ^oC for 45 hours.

A similar mixture without any Methylene Blue was crystallized at the same conditions. The resulting products were washed with distilled water as long as filtrate turned colorless. The samples were characterized by means of XRD, IR, diffuse reflectance UV-Vis, SEM, and elemental analysis. The sample prepared without any Methylene Blue were treated with the dye aqueous solution three times and then washed extensively with water until the filtrate became colorless. The same procedure was employed for natural zeolites (phillipsite, mordenite and clinoptilolite) in order to compare their ability to adsorb M.B. with that of the obtained synthetic zeolite.

Results and Discussion

The prepared samples showed high crystallinity and a PHI structure which is indicated in Fig.3. The high Si/Al framework ratio is reflected in the IR stretching T-O band at ~1080cm^{-1}. The samples prepared with admitted M.B. blue showed intense blue coloration, which was maintained after extensive washing with water (Fig. 4).

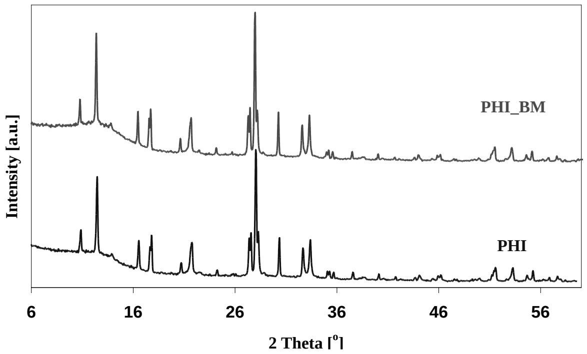

Figure 3. XRD of samples prepared with and without M.B.

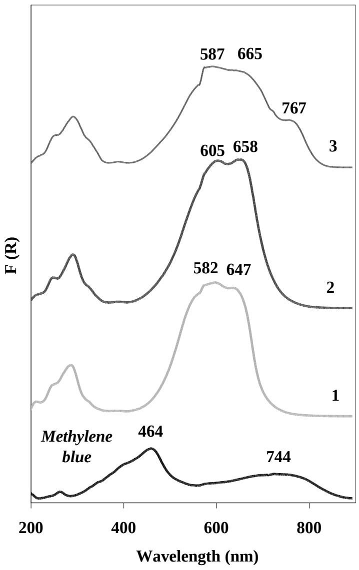

Figure 4. Typical UV-vis spectra of M.B entrapped in crystallized phlillipsite (1), in ion-exchanged PHI (2), in natural zeolites (3)

The samples prepared without contribution of Methylene Blue show also the same PHI structure. It indicates that M.B does not affect markedly the crystallization neither plays a role of structure directing agent. The samples of prepared M.B. - free phillipsite and natural zeolites treated with M.B aqueous solution are blue and remain colored after washing. The dye content in samples crystallized with M.B. higher than those modified with M. B. by ion-exchange. Nevertheless, it is rather surprising that the PHI structure (natural and synthetic) with narrow aperture enables to accommodate considerable amount of M.B. The UV-Vis spectra of zeolite entrapped M.B. do not resemble that of solid M.B. but rather of its aqueous solution. The absorption bands in range 550 - 670 nm correspond to monomeric and oligomeric Methylene Blue molecules combined with zeolite. An additional band at ~770 nm is seen in modified natural zeolite. Such bands are always assigned to the protonic form of M.B.

Acknowledgment
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Kinetics of Pb(II) ions removal from aqueous solution using the natural and Fe(III)-modified zeolite

M. Kragović[1], Ž. Sekulić[1], M. Stojanović[1], M. Petrović[1], V. Dondur[2], Lj. Damjanović[2] and A. Jović[2]

[1] *Institute for Technology of Nuclear and Other Mineral Raw Materials, P. O. Box 390, 11000 Belgrade, Serbia; E-mail: m.kragovic@itnms.ac.rs*
[2] *Faculty of Physical Chemistry, University of Belgrade, Studentski trg 12-16, P.O. Box 137, Belgrade, Serbia*

Introduction

The removal of heavy metal ions from aqueous solutions plays an important role in wastewater treatment and includes different methods such as oxidation, reduction, precipitation, and ion exchange/adsorption. Among all the methods ion exchange and adsorption on natural materials (zeolite, bentonite, cellulose, etc.) are highly effective and economical (Zhu et al., 2008). Due to their unique properties zeolites have great potential as inexpensive and efficient adsorbent for heavy metals from aqueous solutions. In previous paper (Kragovic et al., 2012) we reported that the natural zeolite from Zlatokop deposit, Serbia, is an efficient adsorbent for lead ions with adsorption capacity of 66 mg/g, but, its modification with Fe(III) ions in 0.1 M KOH solution significantly increased lead adsorption capacity up to 133 mg/g. Also, we indicated that removal of lead ions by using the natural and Fe(III)-modified zeolite takes place through two mechanisms, ion exchange and chemisorption. For a better understanding of the adsorption mechanism, it was important to examine the kinetics of lead removal by both adsorbents. Experimental data were fitted according to different kinetics models, and an intra-particle diffusion model is described in this paper.

Experimental Methods

The starting material was the natural zeolitic tuff from the Zlatokop deposit, Vranjska Banja, Serbia, with the particle size below 0.043 mm. The Fe(III)-modified zeolite was prepared according to procedure given elsewhere (Kragović et al., 2012). The kinetics of Pb(II) ions adsorption on the natural and Fe(III)-modified zeolite was studied by adding 50 cm^3 of 4000 mg Pb^{2+}/dm^3 solution to 1 g of both adsorbents at 303, 313, 323 and 333 K and at time interval 0-2880 min. Initial pH in all experiments was 4.2. Each point of the adsorption isotherm was collected in a separate experiment: in sealed flask continuous stirring was performed at constant temperature and at particular time interval solution and each adsorbent were separated through standard filter, and concentrations of non adsorbed lead ions in supernatants were determined by atomic absorption spectrophotometry (AAS) using an “Analytic Jena Spekol 300”.

Results and Discussion

The experimental data were fitted using pseudo-first and pseudo-second order model and the best fit was obtained with pseudo-second order model indicating that the chemical adsorption could be the rate-determining step controlling lead ions adsorption process by the natural (NZ) and Fe(III)-modified zeolite (FeZ) (Kragović et al., 2013). In order to examine the role of diffusion in the adsorption process, the kinetics of removal of Pb(II) ions using both adsorbents, at various temperatures, was analyzed by intra-particle diffusion model. According to this model adsorption process generally involves three stages: 1) migration of the adsorbate from the solution to the surface and the formation of film on the surface of the adsorbent; 2) adsorption at active sites on the surface, and 3) intra-particle diffusion (Yousef et al., 2011).

The plots of q_t vs. $t^{1/2}$ (where q_t (mg/g) represents the amount of adsorbed Pb(II) ions at time t (min)), shown in Figure 1, for the natural (a) and Fe(III)- modified zeolite (b) at various temperatures show nonlinear curves consisting of three linear segments. The first segment of each plot, for both adsorbents, was related to the diffusion of Pb(II) ions through the solution to the external surface of adsorbent, as well as adsorption at surface and ion exchange of Pb(II) ions with easily removable and weakest bounded cations (Ca^{2+}, Mg^{2+}, K^+, Na^+) from the most accessible places at surface of adsorbents. The second segment was attributed to the intra-particle diffusion of the Pb(II) ions into clinoptilolite channels and vacancies, while third segment described final equilibrium stage when the intra-particle diffusion started to slow down due to the low lead concentration left in the solution (Cheung et al., 2007). Thus, from these plots, for both adsorbents, boundary layer diffusion (segment 1) and intra-particle diffusion (segment 2) affect the rate of Pb(II) ions adsorption.

The slope of each linear portion indicates the rate of the corresponding process, and a lower slope describing a slower adsorption process. Calculated diffusion rate constants, k_d, for both adsorbents are shown in Table 1. Based on obtained results, it can be concluded that for both adsorbents at all investigated temperatures, boundary layer diffusion is much faster than the intra-particle diffusion. According to intra-particle diffusion model, if curves $q_t=f(t^{1/2})$ are linear in whole time interval and passing through the origin point, the rate limiting process is only intra-particle diffusion. If that is not the case, as in this study, the intra-particle diffusion, although important over long contact time period, was not the rate-limiting step. Thus, it can be concluded that adsorption processes at surface as well as diffusion process have controlled the rate of the removal of Pb(II) ions from solution by both adsorbents.

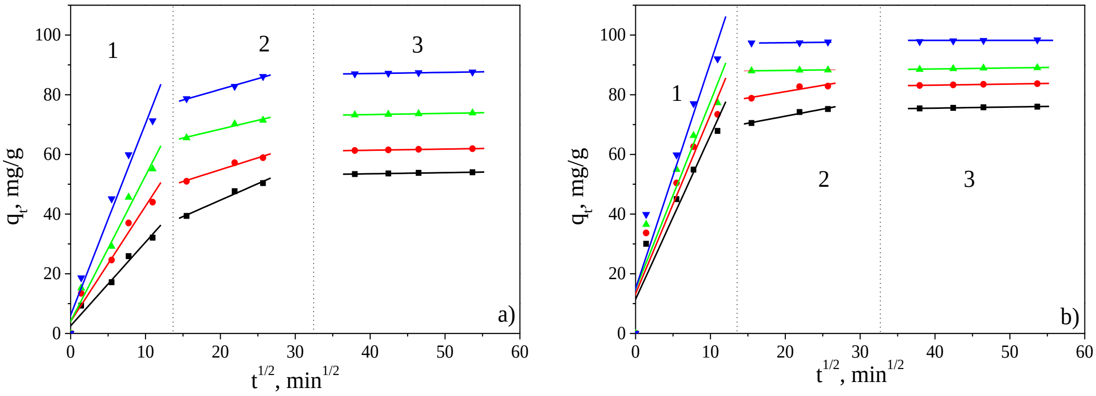

Figure 1. Intra-particle diffusion model of removal of Pb(II) ions from water solution using a) natural and b) Fe(III)-modified zeolite at four different temperatures: T=303 K(-■-), T=313 K (-●-), T=323 K (-▲-) and T=333 K (-▼-)

Table 1. Calculated values of diffusion rate constants for removal of Pb(II) ions using NZ and FeZ

		Temperature, K			
		303	313	323	333
k_d (NZ), mg/(min$^{1/2}$g)	1	2.80	3.86	4.88	6.42
	2	1.01	0.79	0.59	0.72
	3	0.04	0.04	0.04	0.16
k_d (FeZ), mg/(min$^{1/2}$g)	1	5.50	8.10	6.29	7.57
	2	0.47	0.43	0.03	0.03
	3	0.04	0.04	0.03	0.08

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Ibuprofen sorption and release by modified natural zeolites as prospective drug carriers

D. Krajišnik[1], A. Daković[2] and J. Milić[1]

[1] *Department of Pharmaceutical Technology and Cosmetology, University of Belgrade–Faculty of Pharmacy, Vojvode Stepe 450, 11000 Belgrade, Serbia; E-mail: danina@pharmacy.bg.ac.rs*
[2]*Institute for the Technology of Nuclear and Other Mineral Raw Materials, Franše d' Epere 86, P.O. Box 390, 11000 Belgrade, Serbia*

Introduction

It has been demonstrated that natural and modified clinoptilolite-rich materials, due to their ion exchange and adsorption capabilities could have various biomedical application in recent years (Colella, 2011). Modification of zeolitic surface with cationic surfactant leads to an increase in adsorption capacity for organic i.e. drug molecules. The mineral–organic interaction can be used to control the release of active ingredients (drugs) with improved therapeutic properties (Aguzzi et al., 2007).

The aim of this work was to carry out a study of cationic surfactant type and level effect on sorption properties of natural zeolite for an anti-inflammatory drug, ibuprofen. Furthermore, pharmaceutical performance of the modified zeolites-drug composites was evaluated by *in vitro* dissolution experiments in order to evaluate the potential use of these materials as prospective drug carriers.

Experimental Methods

Two cationic surfactants, benzalkonium chloride (BC) (Fluka) and cetylpyridinium chloride (CP) (Sigma-Aldrich), were used for the preparation of modified zeolites (composites). In experiments, 10% aqueous suspension of the initial zeolitic tuff from Zlatokop deposit (Vranje, southern Serbia) (ZVB) was treated with surfactant amounts equivalent to 100, 200 and 300% of its external cation exchange capacity *ECEC* (denoted as ZBC-10, ZBC-20 and ZBC-30, i.e. ZCP-10, ZCP-20 and ZCP-30, respectively).

Sorption of ibuprofen (IB) (Ph. Eur. Grade, pKa 4.55) on the prepared composites was carried out in batch experiments at room temperature. Stock solutions of the testing drug (50 to 500 mg/l) were prepared in phosphate buffer at pH 7.4 (USP 30). Details of the preparation and characterization of the composites and the subsequent drug adsorption are given elsewhere (Krajišnik et al., 2010; Krajišnik et al., 2011).

The comprimates (200 mg) of the tested powders were prepared by compression on an eccentric tablet machine (EKO Korsch, Germany) using flat-faced punches with a diameter of 9 mm. Drug release from the comprimates consisting of surfactant modified zeolite-drug composites was performed on a rotating paddle apparatus (Erweka DT70, Germany) in phosphate buffer (pH 7.2)(USP 30) at 37 °C during 8 h.

Results and Discussion

Sorption of IB by ZBC and ZCP composites followed a nonlinear Langmiur type of isotherm (Fig. 1). IB sorbed amounts for ZBC 10-30 composites increased with increasing the amount of surfactant used for modification, while for ZCP 10-30 composites the highest drug sorbed amount was achieved for ZCP-20 composite (Table 1).

Table 1. Fitted Langmuir parameters for IB adsorption by ZBC 10-30 and ZCP 10-30 composites

	Sample					
	ZBC-10	ZBC-20	ZBC-30	ZCP-10	ZCP-20	ZCP-30
Q_m (mg/g)	5.40	13.35	20.04	9.01	20.20	19.27
K (l/mg)	0.032	0.018	0.012	0.068	0.190	0.365
R^2	0.990	0.996	0.985	0.998	0.999	0.999

To determine the contribution of adsorption and partition to the total IB sorbed amount the adsorption/partition model (Zhu et al., 2000) was used. With exception of ZCP-30 composite, adsorption was more pronounced than partition for all the investigated samples (Fig. 1). Furthermore, for ZCPs composites contribution of adsorption was ≥ 90 %, while for ZBCs composites it was in range 40 – 64 %.

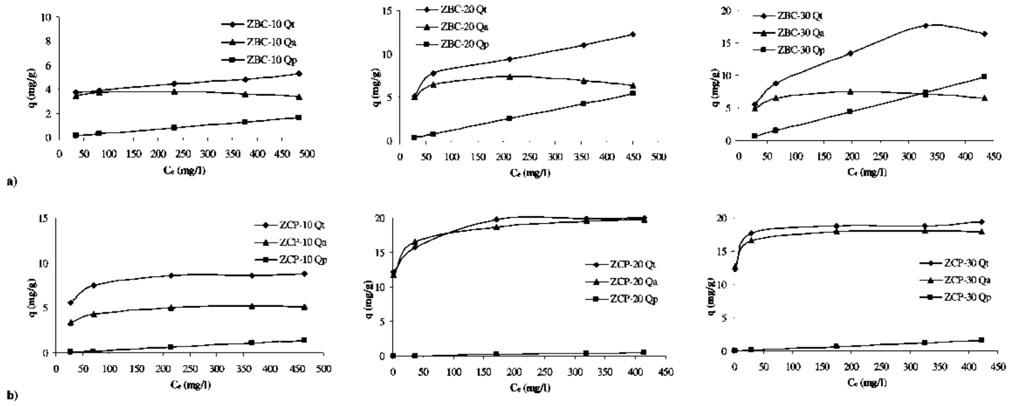

Figure 1. Partition (Qp) and adsorption (Qa) contributions for the total sorption amount (Qt) of IB onto: (a) ZBC 10-30 composites and (b) ZCP 10-30 composites

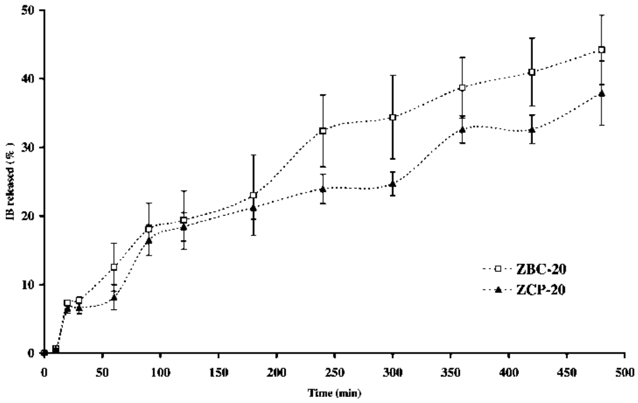

Figure 2. *In vitro* dissolution profiles of IB from ZBC-20 and ZCP-20 composites

Results of IB release from modified zeolite-drug composites revealed that 44 % of the drug was released from ZBC-20 and 38 % from ZCP-20 composite during 8 h in a sustained manner (Fig. 1) and that the distinction in dissolution rates was in agreement with the drug sorption findings.

The presented results of drug uptake by surfactant/zeolite composites revealed that sorption properties of ibuprofen are closely related to overall hydrophilic/hydrophobic interaction of ionizable drug molecule with modified zeolitic surfaces and that it can be well described with adsorption/partition model. The non-toxic nature of these material accompanied with a minimum of surfactant desorption support further researches exploring the potential use of these low cost and abundant materials as prospective drug carriers.

Acknowledgment

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Removal of Pb(II) and Cd(II) ions by natural zeolite in phosphoric acid media

M. Zh. Kussainova[1], R. M. Chernyakova[2], U. Zh. Jussipbekov[2], G. Sh. Sultanbayeva[2] and A. A. Agatayeva[1]

[1]*Kazakh- British Technical University, Almaty, Kazakhstan; E-mail: chem@kbtu.kz*
[2] *Institute of Chemical substances named after A.B.Bekturov, Almaty, Kazakhstan; E-mail: ics_rk@mail.ru*

Introduction

Heavy metals in the biosphere lead to accumulation in the soil greater than background reasons in many times and cause the reducing of soil productivity and also negatively affect the flora and fauna and ultimately in humans (Jovanovic et al., 2012, Motsi et al., 2011).

The main sources of heavy metals that coming into the soil are from energy companies, industrial corporations, aviation, road and rail transportations, fertilizers and chemicals used for fertilizers, pesticides, irrigation water etc. (Burton et al., 2006, Förstnern et al., 1979).

To solve or find a usable and durable solution of all problems mentioned above, the preliminary purification of phosphoric acid with sorbents is a kind of method to reduce the concentration of heavy metals.

In the present work, Shankanaj deposits of Kazakhstan used as a sorbent which has a high sorption characteristics with phosphoric acid has used for the subject of extensive study. In previous studies carried out by our research team Alykov (2009, 2010) described itself that the mineral treated with acid has a good sorption capability for cations such iron, copper, lead especially in concentrated phosphoric acid.

Experimental Methods

Study of the sorption capacity of natural zeolite with respect to cations of lead (II) and cadmium (II) in phosphoric acid medium was performed in a model system " H_3PO_4-Pb^{2+}-Cd^{2+}-zeolite".

Sorption process in this system was carried out with stirring at a constant ratio zeolite:H_3PO_4 (S:L)=10:100 at 25°C. The concentration of phosphoric acid was 20 % P_2O_5. Selection of the acid concentration was made due to the fact that in the production of phosphorite Karatau extraction method was used, the extractive phosphoric acid with a concentration of 18-23 % P_2O_5.

Cadmium nitrate $Cd(NO_3)_2 \cdot 4H_2O$, lead nitrate $Pb(NO_3)_2$ were supplied from Sigma Aldrich and Fluka Chemical Corporations. To study adsorption have been prepared phosphoric aid solutions with concentration of heavy metals ($C_{Cd}{}^{2+}$ and $C_{Pb}{}^{2+}$) = 0.0505 g/l.

In order to determine the effect of time on the process of sorption of Pb^{2+} and Cd^{2+} cations in 20% H_3PO_4, experiments were performed in the range of 5-60 minutes. For determination of concentrations of lead and cadmium was used atomic absorption spectrophotometer AAS-400(model: PerkinElmer).

Results and Discussion

Shankanaj deposit zeolite of the following composition, wt. % : K_2O – 1.38; Na_2O – 0.95; Fe_2O_3 – 0.16; Al_2O_3 – 10.81; CaO – 2.32; MgO – 0.93; SiO_2 – 65.28, p.p.p - 18.15 is used.

Analysis of the data presented in Table 1 have shown that in diluted phosphoric acid (20% H_3PO_4) by increasing the process time to 30-40 minutes, the degree of sorption of heavy metal cations increases. The optimum time was obtained about 30 min for cadmium and lead in the adsorption process. The maximum degree of removal of Pb^{2+} was 89.24%, and of Cd^{2+} 71.25 % respectively.(Figure 1).

Table 1. Concentration of heavy metal ions in 20% phosphoric acid after sorption process by natural zeolite

Sorption time, min	Concentration of metals, g/l	
	Pb^{2+}	Cd^{2+}
	C_{P2O5}=20.0%	
5	189.9	355.9
10	135.3	323.9
20	117.9	283.1
30	98.1	238.9
40	98.1	224.1
60	102.3	268.1

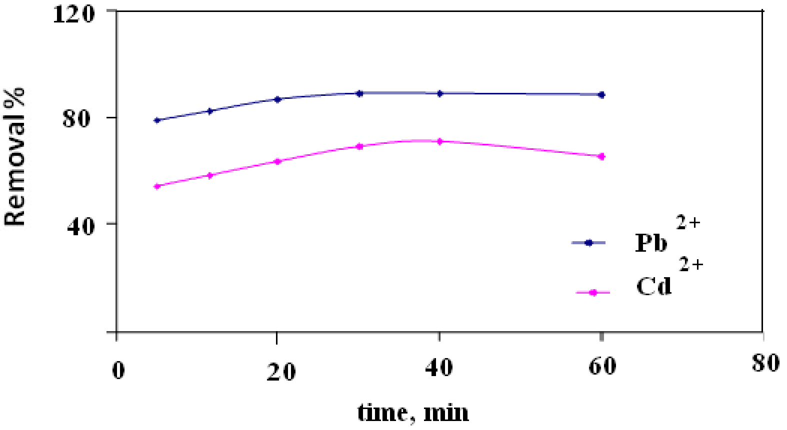

Figure 1. The removal percentage of Pb (II) and Cd (II) by natural zeolite from 20 % solution of H_3PO_4

The appearance of a small maximum at the sorption curves of lead and cadmium, due to their desorption process from the phosphoric acid that occurs during prolonged contact of the cleaning solution with the sorbent. Comparison of the degree of sorption of lead and cadmium found that in the studied conditions Pb^{2+} cations were more adsorbed than Cd^{2+}. Comparative analysis of the sorption of Pb (II) and Cd (II) cations by natural zeolite in a model system " H_3PO_4-Pb^{2+}-Cd^{2+}-zeolite " showed preferred sorption capacity of the sorbent to lead. Sorption capacity of natural zeolite to cations increases till 30 minute. Decrease of Cd (II) and Pb (II) sorption after 30-40 minute suggested that sorption-desorption hysteresis occurred in the system.

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The organo-zeolitic-soil system: a comprehensive fertilizer

P. J. Leggo

Department of Earth Sciences, University of Cambridge, UK; E-mai: pjl46@cam.ac.uk

Highly contaminated mine and refinery metal waste sites can remain barren of vegetation for many years. In some cases the only solution has been to bury it in a landfill sites, but it is more desirable to regenerate the land. A new strategy of soil amendment to greatly enhance the scope of plant growth on damaged and marginal soils has been developed. A critical factor is how to supply sufficient plant nutrients to sustain growth. Organo-zeolitic biofertilizer answers this question as unlike synthetic chemicals, it provides a natural source of plant nutrients by greatly increasing the population of soil nitrifying micro-organisms.

The use of chemical fertilizers, over the last sixty or more years, has been of great benefit in keeping world food crop supply ahead of population growth. However, this achievement has not been without a cost to soil health and the environment as it is now known that without a regular input of organic matter (OM) the over use of nitrogen, phosphorus, potassium (NPK) fertilizers causes nutrient limited microbes to rapidly decomposes the soil OM which, in time, can lead to a structure-less soil with less capacity to hold water; causing greater runoff and groundwater pollution (Ball, 2006). In addition to the high energy costs of the Haber–Bosch process for producing ammonia from atmospheric nitrogen the source of natural phosphate is becoming less readily available. The organo-zeolitic biofertilizer do not suffer the disadvantages of the conventional NPK fertilizers in being potentially less expensive, particularly in countries that have zeolitic tuff resources, easier to produce in terms of energy costs and of greater benefit to soil health.

In earlier work it was discovered that zeolitic tuff, containing an abundance of clinoptilolite, was very effective in the removal of ammonium ions from secondary effluent and the application to water and wastewater treatment has been studied in considerable detail (Kalló, 2001). This work focuses attention on the highly selective ion-exchange behaviour of natural zeolites for ammonium ions. Further, work on the removal of ammonium ions from municipal wastewater showed that an increase in nitrate occurred in the treated water which was indicative of biological activity. (Semmens et al., 1977, Murphy et al., 1978). This earlier work has lead to a working hypothesis based on new empirical date, which proposes that by mixing crushed zeolitic tuff with organic waste ammonium ions from the decomposing organic matter are ion-exchanged into the zeolite lattice. When this mixture (the biofertilizer) is added to a plant substrate, contaminated or otherwise, it would appear that the ammonium ions are slowly back exchanged by soil potassium after which ammonium oxidizing micro-organisms initiate nitrification with the effect of producing luxuriant growth and high plant quality.

What limited work that has been done on the analysis of plant shoots has shown that the uptake of an adequate supply of major, minor and beneficial trace elements occurs (Leggo, et al., 2010). The analytical results of this study show large differences in uptake between plants grown in substrates with and without the biofertilizer amendment. Both *Brassica napus* (Oil Seed Rape) and *Salix viminalis* (Osier Willow) showed these differences. As a very large growth enhancement is always seen in those plants grown in substrates amended with the biofertilizer it would appear logical to conclude that homeostasis is playing a major role and that the nutrient uptake is controlled by this behaviour.

Recent research in the Cambridge laboratory has been directed towards the identification of the microbial organisms that cause the nitrification in the biofertilizer amended substrates. A time-course experiment was made to observe populations of ammonium oxidizing bacteria and/or archaeal prokaryotes using *B. napus* in plant pots. A local sandy soil low in plant nutrents was used as a substrate. This substrate was amended with the biofertilizer and manure was used as a control in the same ratio of amendment to soil. Using molecular biological methods three species of ammonium oxidizing Crenarchaeota have been discovered. Dilutions of the extracted soil DNA were used as templates in polymerase chain reactions (PCR) using primers targeted to conserve portions of the ammonia oxidizing genes (Hansel, et al., 2008). It is interesting to note that no bacterial nitrifiers have so far been found. This feature is consistent with other work that finds that prokaryotes from the kingdom Archea, the Crenarchae, are now known to be commonly occurring soil nitrifying micro-organisms.

It is now clear that use of the biofertilizer will allow marginal land to be cultivated in many parts of the World. Those countries that have suitable zeolitic tuff resources will be in a position to make the biofertilizer at far less expense than importing chemical fertilizers. The application rate of the biofertilizer depends on the soil and plant type involved and this, at present, is still undergoing development.

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Sorption of organic pollutants onto natural zeolites: isosteric and standard enthalpy

V. Leone, P. Iovino, S. Salvestrini and S. Capasso

Department of Environmental, Biological and Pharmaceutical Sciences and Technologies, Second University of Naples, Via Vivaldi 43, 81100 Caserta, Italy; E-mail: sante.capasso@unina2.it

Introduction

Thermodynamic parameters of sorption processes, such as equilibrium constants, maximum sorption capacity and changes in entropies and enthalpies provide fundamental information on the mechanisms involved and are an essential requisite for the design and management of sorption/desorption plants. Here, we report a study of equilibrium sorption of some non-ionic organic pollutants onto a zeolitic tuff, rich in phyllipsite and chabazite (PCT).

Experimental Methods

Materials: Analytical-grade benzyl alcohol, toluene, phenol, cyclohexanol and cyclohexane were purchased from Fluka (Germany). PCT was obtained from a quarry near Naples (Italy), its detailed chemical and mineralogical composition is reported in a previous work (Capasso et al., 2007).

Adsorption experiments in batch: The selected compounds were dissolved in water (10-150 mg L^{-1}) containing $1.0 \cdot 10^{-3}$ mol dm^{-3} TrisHCl/Tris buffer, pH 6.0, and $1.0 \cdot 10^{-2}$ mol dm^{-3} KCl. For cyclohexane, because of its lower solubility in water, the highest concentration tested was 50 mg L^{-1}. Two hundred-mL aliquots of each solution were mixed with 50 mg of FCT in glass containers (of the type usually used for head space analyses) and kept in a thermostat at 4 °C, 14 °C, 24 °C or 34 °C and were periodically shaken. After seven days, 1.0 μL of solution was removed through the cap and analyzed by gas-chromatography. Analyses carried out after longer periods of time gave similar results to the seven-day incubation, so this was adopted as the protocol procedure.

Results and Discussion

The sorption isotherms for the hydrocarbon sorbate analyzed (toluene and cyclohexane) showed that FCT is an effective adsorbent for these compounds; while the adsorbitity efficiency is very low for the hydroxylated compounds (phenol, cyclohexanol and benzyl alcohol) where the amount adsorbed was of the same order of magnitude of the experimental errors. As an example, Fig.1 (a) presents the sorption isotherms for toluene recorded at four temperatures.

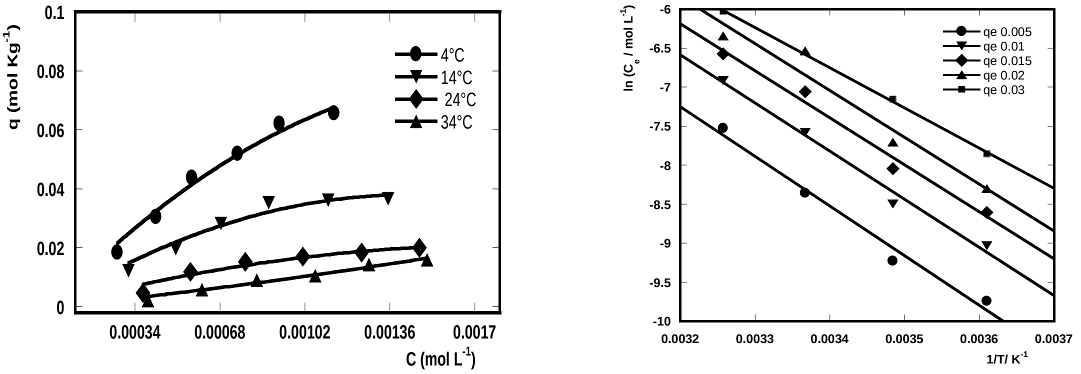

Figure 1. (a) Sorption isotherms for toluene onto the zeolitic tuff at the temperatures indicated; (b) plots of logarithms of the equilibrium concentrations (C_e) of toluene against the reciprocal of temperature

The isosteric enthalpy of adsorption (H_{ist}), that is the enthalpy change for sorption at constant amount of solute adsorbed, is given by

$$H_{ist} = -RT^2 \frac{d \ln C_e}{dT}$$

where R and T are respectively the gas constant and absolute temperature.

Integration of this equation, assuming that H_{ist} does not change over the temperature range analyzed, gives:

$$\ln C_e = \frac{H_{ist}}{R} \frac{1}{T} + Con$$

where *Con* is an integration constant.

Accordingly, plots of the logarithm of the equilibrium concentrations in solution against *1/T* at constant amount adsorbed [Fig.1 (b)] give the isosteric enthalpies of sorption (Salvestrini et al., 2014). Estrapolation at zero amount adsorbed gives the Standard enthalpy or the adsorption. The values for the adsorption onto PCT are reported in table 1.

Table 1 Isosteric enthalpy of adsorption (H_{ist}) and Standard enthalpy ($\Delta_{ads}H°$) for the sorption of toluene and cyclohexane onto PCT

Sorbate	Sorption degree (mol kg^{-1})	$\Delta_{ist}H$ (kJ mol^{-1})	$\Delta_{ads}H°$ (kJ mol^{-1})
toluene	0.005	-53.0	- 55.6
	0.01	-51.3	
	0.015	-50.1	
	0.02	-50.0	
	0.03	-42.8	
cyclohexane	0.0075	-32.2	-36.7
	0.01	-30.5	
	0.0125	-28.9	
	0.015	-27.5	
	0.0175	-26.1	

The values reported refer to the transfer of 1 mol of solute (A_l) from the solution to the solid adsorbent (S) to form the adduct (AS): $A_l + S \rightleftarrows AS$.

It is worth noting that the standard states for the Standard enthalpy reported in Table1 are 1 mol dm^{-3}, adsorbent without A and adsorbent containing 1 mol kg^{-1}, for A_l, S and AS, respectively.
The data in the table show that for the adsorbate analyzed the adsorption is exothermic and the interaction energy between the adsorbate and the tuff decreases with the amount adsorbed.

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Modeling adsorption rate of cadmium(II) from aqueous solution onto clinoptilolite

R. Leyva-Ramos, P. Coronado-Oyarvide, R. Ocampo-Perez and J. Mendoza-Barron

Centro de Investigacion y Estudios de Posgrado, Facultad de Ciencias Químicas, UASLP, Mexico
Av. Dr. Manuel Nava No.6, San Luis Potosí, S. L. P. 78210; E-mail: rlr@uaslp.mx

Introduction

The discharge of toxic heavy metals in municipal and industrial wastewaters has been posing a serious hazard to human health as well as environment. Heavy metal pollution is mainly due to residues and wastewater generated from industrial activities such as mining, metallurgy, metal refining, smelting and finishing. Removal of metals from wastewater is achieved principally by the application of separation processes such as adsorption, reverse osmosis, chemical precipitation/sedimentation, ion exchange on polymeric resins, filtration, electrodialysis and flotation.

Several studies in the adsorption of heavy metals from aqueous solution on natural zeolites have been reported in the last 30 years (Blanchard et al., 1984; Ćurković et al., 1997). It has been shown that the overall rate of adsorption of heavy metals on various adsorbents is predominantly controlled by intraparticle diffusion. Thus, it is important to know the overall rate of adsorption of Cd(II) on clinoptilolite and the controlling step.

The rate of adsorption in liquid solutions has been interpreted using kinetic and diffusional models. Normally, the kinetic models are extensively used to examine the rate of adsorption of heavy metals on natural zeolites, but these models disregard the intraparticle diffusion of the metal ions in the porous structure of the natural zeolite. On the other hand, the diffusional models based upon the intraparticle diffusion have not been very frequently applied to interpret the rate of adsorption of metals on natural zeolites. In the diffusional models, the overall rate of adsorption of Cd(II) from aqueous solution is assumed to happen by the following steps: external mass transport, intraparticle diffusion and adsorption rate at an adsorption site.

The main objective of this work was to interpret the rate of adsorption of Cd(II) using kinetic and diffusional models. Furthermore, the characterization of the natural zeolite was carried out, and the adsorption isotherm was obtained.

Experimental Methods

The zeolitic mineral used in this work was from a deposit located in San Luis Potosi, Mexico. The clinoptilolite was modified into its sodium homoionic form. Identification of the crystal species present in the zeolitic mineral was done by X-ray diffraction analysis. The natural zeolite was characterized to assess their surface area and chemical composition.

The concentration of Cd(II) in a water solution was quantified by atomic absorption spectroscopy. The experimental adsorption equilibrium data of Cd(II) on clinoptilolite were obtained by the following procedure. A mass of 0.2 g of clinoptilolite and 40 mL of a solution with a known initial concentration of Cd(II) at an initial pH of 2, 4, 5 and 7, were added into a batch adsorber. The Cd(II) solution remained in contact with the clinoptilolite particles until equilibrium was reached. The solution pH was measured periodically and kept constant by adding 0.01 and 0.1 M solutions of HCl and NaOH, as needed. After reaching equilibrium, the Cd(II) concentration in the solution was determined and the mass of Cd(II) adsorbed at equilibrium was calculated by performing a mass balance of Cd(II).

A rotating basket batch adsorber was used to obtain the experimental concentration decay curves for the Cd(II) adsorption on clinoptilolite. This adsorber was stirred by an impeller with its two blades replaced by two stainless steel mesh baskets, and was partially immersed in a constant temperature water bath.

A given mass of clinoptilolite was added to the baskets and then the baskets were attached to the stirrer in the adsorber. Soon afterwards, 980 mL of a solution of known pH is poured into the adsorber to completely cover the baskets. A given volume of a Cd(II) solution of known concentration is added very rapidly, and the timer and motor of the stirrer are turned on immediately. At a certain time, a sample of the solution is taken out. The volume of the system is maintained constant by adding to the adsorber and equal volume of make-up solution right after the sample is taken. The concentration of the make-up solution is between the initial and equilibrium concentrations of the adsorber solution. The samples are analyzed and the sample concentration is plotted against time to obtain the concentration decay curve.

Results and Discussion

X-ray diffraction analysis revealed that the zeolitic mineral was mostly composed of clinoptilolite. The surface area and pore volume of the clinoptilolite were 26 m^2/g and 0.06 cm^3/g, respectively. The Langmuir adsorption isotherm fitted reasonably well the experimental adsorption equilibrium data and the Langmuir constants were evaluated by a least-squares method based on an optimization algorithm.

The behavior of the concentration decay curves is shown in Figure 1. It can be observed that the concentration decay curves present a very fast adsorption rate regime at the beginning (less than 2 hours) followed by a slow adsorption rate. The rate of adsorption data were interpreted with diffusional models as well as kinetic models. The kinetic models did not fit the experimental concentration data due to the fact that the rate of adsorption data presented these two adsorption rate regimes.

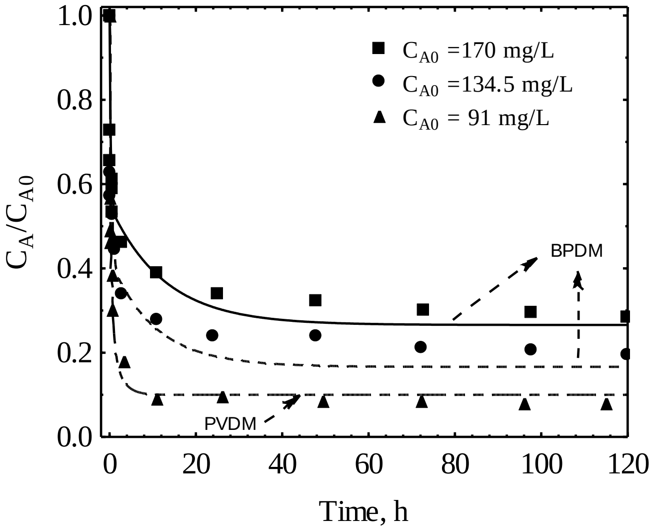

Figure 1. Concentration decay curve for Cd(II) adsorption on clinoptilolite. The lines represent the prediction of the diffusional models BPDM and PVDM

The experimental concentration decay data were matched to the pore volume diffusion model (PVDM) and the branched pore diffusional model (BPDM). In the PVDM it is assumed that intraparticle diffusion is controlling and Fick diffusion is the only mechanism of intraparticle diffusion. The BPDM was developed by supposing that intraparticle diffusion is fast in the macropores, but it is slow in the micropores because of restricted diffusion. The PVDM predicted reasonably well the concentration decay data for low concentrations of Cd(II), whereas the BPDM adjusted quite the kinetic data for high concentrations of Cd(II).

The porous structure of the natural zeolite can be better represented by BPDM because the natural zeolite has micropores due to the zeolite framework and macropores formed by the disordered arrangement of the zeolite crystals.

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Natural zeolite application to the stabilization of concrete produced using fly ash

Y. Li

Beijing Concrete Association, Admixture Expert Committee, China; E-mail: lysail@126.com

Introduction

The coal-fired power stations are the largest fly ash discharging units. The fly ash, after collection, is used for the production of concrete. Recently, because of environmental protection reasons, the power stations usually use lime or limestone as an additive in order to reduce the emission of the poisonous gas SO_2. During this process, CaO originating from lime or limestone reacts with the sulfur dioxide and forms calcium sulfate:

$$2CaO + 2SO_2 + O_2 \rightarrow 2CaSO_4 \qquad (1)$$

However, a quantity of CaO may be overburnt and aged causing the expansion and splitting of the fly ash containing concrete. This is due to the fact that the CaO reacts with H_2O to form $Ca(OH)_2$ and its volume increases very fast

$$CaO + H_2O \rightarrow Ca(OH)_2 \qquad (2)$$

The decomposition of limestone blocks begins at 600 ^oC

$$CaCO_3 \rightarrow CaO + CO_2 \qquad (3)$$

The CO_2 release continues up to temperature of 900 to 925 °C yielding a porous and light quick lime (Yaling, 1990). At temperatures higher than 1000 °C an overburning of the limestone takes place leading to the formation of aged lime. Presence of aged lime causes a decrease of the hydration rate lowering the quality of the concrete. As an example of this quality deterioration one could mention the plastering of the walls with lime slurry. Although the wall surface is hard at the beginning, it will split or fall away at last, because of the slow hydration and expansion of the free aged CaO particles in the humid environment leading to convex formation on the wall surface. If the fly ash additionally contains grains of free aged CaO a further decrease of the strength of the concrete will be expected during the delayed hydration and expansion period. For this reason the quantity of the free aged CaO in the fly ash must be limited and measures should be adopted to ensure the stability of the concrete.

Recently a number of works (Li, 1990; Guo, 1980; Li, 2002) cconfirmed that SiO_2 (up to 70%) from the naturul zeolite can react with free aged CaO and form the hydrated calcium silicate (HCS) under alkaline conditions. This will mitigate the expansion damages during the hardending of concrete. Furthermore, according to the Guo (Guo, 1980), when 100g of zeolite powder (clinoptilolite with cation exchange capacity (CEC) 130 mmol/100g and specific surface area 400 m^2/kg) react with 44.3g free aged CaO improvement of concrete properties can be achieved.

During this work the effect of the addition of zeolite in the fly ash in order to achieve stabilized concrete was investigated.

Experimental methods

The conditions used for the experimental work were similar to those applied by Guo (Guo, 1980). These conditions were used to investigate the stability of fly ash, namely the concrete stability. The stabilization of fly ash was studied by the preparing and boiling the cake samples described in Table 1. The results of the splitting tests are also given in the same Table.

Table 1. Components of cakes 1 and 2 and Results of splitting test

Sample	Cement (g)	Fly ash (g)	Free aged CaO (g)	Zeolite (g)	Water (g)	Splitting test
Cake 1	200	60	10	0	105	Split
Cake 2	200	60	10	20	115	No split

Cake 1 contained cement, fly ash and free aged CaO while Cake 2 contained the same components with addition of zeolite powder. The components in Cakes 1 and 2 were mixed, and then water was added. The mixtures were stired for 2 minutes to form slurries and cylindrical cakes (diameter: 70-80 mm, center thickness at the center ca. 10 mm) were prepared on a glass plate from each slurry. The cakes were kept under the humidity of >95%, at 20 ± 2ºC for 24 hours. Finally, cakes were immersed into boiling water for 3 hours and dried.

Results and discussion

The zeolite-containing cake showed no splitting. Based on the fact that SiO_2 from zeolite instantaneously reacts with free aged CaO, the delayed expanding and splitting of the concrete can be prevented. This experiment proves that the stabilization of fly ash ensures the stability of the concrete. The obtained results indicated that when zeolite is present in the mixture of cement and fly ash containing free aged lime, improvement of the cement properties can be achieved. If the fly ash used for the concrete production contains 10 kg/m^3 of free aged CaO, quantities of the order of 20 kg of zeolite pro 1 m^3 of concrete seems to be sufficient to ensure its strength and the quality. The use of zeolite for the stabilization of concrete produced using fly ash can undoubtedly increase the consumption of fly ash for this purpose and considerably contribute to environmental protection.

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Use of natural clinoptilolite for sorption of strontium from polluted water media

N. Lihareva[1], O. Petrov[1], Y. Tzvetanova[1], M. Kadiyski[1] and V.A. Nikashina[2]

[1]*Institute of Mineralogy and Crystallography, Bulgarian Academy of Sciences, Acad. G. Bonchev Street, Block 107, 1113 Sofia, Bulgaria; E-mail: nlihareva@abv.bg*
[2]*Vernadsky Institute of Geochemistry and Analytical Chemistry RAS, Moscow, Russia*

Introduction

The most frequent hazardous pollutants in liquid nuclear waste are ^{90}Sr, ^{60}Co, and ^{137}Cs. Their main pollution sources are the repositories for radionuclide wastes. During their conservation, the elements can penetrate the surrounding environment and especially the ground waters thus causing serious pollution. Especially for ^{90}Sr, the Environmental Protection Agency (EPA) recommends concentrations levels of less than 4mg/L and therefore the control and removal of this pollutant is of great importance.

In the variety of materials and methods tested for this purpose, the sorption on natural zeolites is the most preferable because of their suitable chemical and mechanical stability, high sorption efficiency and low cost (Smičiklas et al., 2007).

In this study, we focus on sorption characteristics of Bulgarian clinoptilolite as exchanger for certain strontium concentrations in water media with regard to be used as a sorption barrier for waste treatment and strontium removal.

Experimental Methods

Clinoptilolite sample used in the study is a clinoptilolite rich tuff from Beli plast deposit (Eastern Rhodopes, Bulgaria). The powder XRD investigation showed that the zeolitized tuff contains about 85 wt.% clinoptilolite and ~ 15 wt.% opal-CT. The sample was crushed, ground, sieved and the fraction < 75 μm was isolated for further use. The total cation exchange capacity (CEC) was determined by sorption of 0.5 M NH_4NO_3 at 60°C and was evaluated to be 2.83 meq/g (123 mg/g).

The sorption experiments for the strontium uptake were carried out by the batch-mode treatment using single metal chloride solution at room temperature. In each case, in a polypropylene bottle with 0.1 g of sorbent 50 mL of strontium solution was added. The mixtures were then shaken on a horizontal shaker, the supernatant was separated by centrifugation and the concentration of strontium in the liquid was determined by AAS. The effect of pH, residence time and initial strontium concentration in equilibrium were analyzed. Different kinetics and equilibrium models were tested to find a proper description of the processes and the parameters of sorption were determined.

Results and Discussion

The pH of the sorbate solution is an important parameter, controlling the adsorption process by determining the charge of the clinoptilolite surface and the chemical form of the sorbed ions. We studied the effect of initial acidity over a range of pH from 2 to 6. In this interval the effectiveness of strontium sorption almost does not change. The initial pH of the mixtures rose from the initial values to near neutral pH = 6.5. The initial pH chosen for the sorption experiments was 5.4.

The kinetics of the sorption process for two different intial concentrations of Sr in the time interval 10-1480 min is shown on Fig. 1. The data demonstrate that the extent of Sr removal after 8 h is practically constant and this contact time could be considered as the equilibrium time.

The rates of sorption were interpreted with the pseudo-first and pseudo-second order kinetic models (Tien and Huang, 1991), fitting the experimental data to the models by least-square regression analysis. The results are shown in Table 1 (the apparent pseudo-rate constants, equilibrium experimental and calculated values of uptake and R^2). A simple pseudo-second order model can be used to describe the exchange process because of the very strong correlation (R^2 ~ 1) and good agreement of q_e and q_t. for both concentrations. This result supposes that the rate of uptake is determined by the availability of the sorption sites and is less dependent on the concentration of ions.

In order to define the actual mechanism of uptake in which surface homogeneity, transport effects as diffusion and chemical reaction like hydrolysis can affect the kinetics rate we applied the equations of intra-particle diffusion and liquid film diffusion (Gupta and Bhattacharyya, 2006). However, the obtained plots were not linear but consist of three parts. Even when separating them in parts for different time periods the intercept is not zero (as the model requires). This indicated that more complex process of uptake and contribution of different factors may be controlling the kinetics and the sorption-exchange mechanisms.

Table 1. Parameters of the kinetic models for Sr^{2+} uptake by natural clinoptilolite

Inital conc. of Sr	Pseudo-first order model			Pseudo-second order model			
$mgSr^{2+}/L$	R^2	k_1 (min^{-1})	$q_{e,calc.}$, (meq/g)	R^2	k_2 ($meq^{-1}.min^{-1}$)	$q_{e, calc}$ (meq/g)	$q_{e, exper.}$ (meq/g)
17.95	0.7509	0.0029	0.0014	0.9999	4.7986	0.0810	0.0807 ± 0.003
200.0	0.9544	0.0077	0.1134	0.9995	0.2253	0.313	0.302 ± 0.009

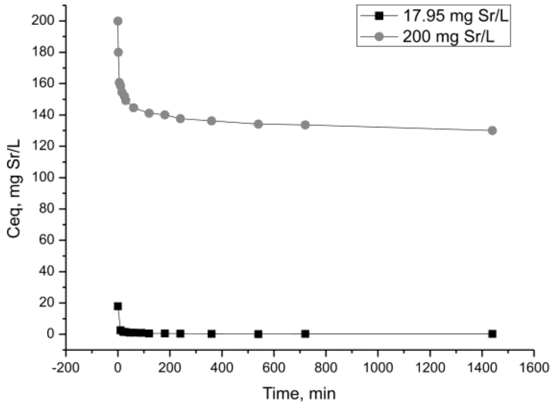

Figure 1. Sr-sorption kinetics for natural clinoptilolite (0.1 g of sorbent, 20 ml Sr solution, $pH_{init} = 5.4$)

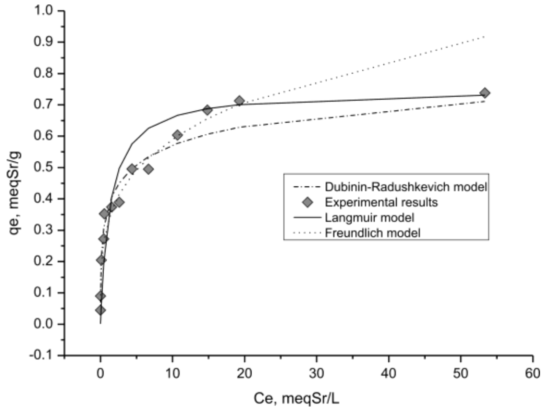

Figure 2. Sorption isotherm of Sr by natural clinoptilolite (0.1 g of sorbent, 20 ml Sr solution, $pH_{init} = 5.4$, t = 480 min)

The equilibrium of the sorption process was studied for the range of initial Sr^{2+} concentrations 10–2500 mg/L. The experimental equilibrium data (Fig. 2) were fitted to the Langmuir, Freundlich and Dubinin–Radushkevich isotherms. The parameters of the adsorption isotherms and calculated equilibrium uptake values are listed in Table 2. The best correlation was found with the Langmuir isotherm model ($R^2 = 0.994$), while the Dubinin–Raduchkevich model was shown to be a little less appropriate. The fit of the theoretical isotherm models to the experimental data is plotted in Fig. 2. The maximum sorption capacity, q_{max}, was calculated to be 32.8 mgSr/g and is less than the CEC. The data from the Dubinin–Raduchkevich model were applied to calculate the mean free energy of sorption, E, that represents the energy change for the transfer of one mol of sorbate to the surface of sorbent and is related to the mechanism of uptake reaction. The obtained value of E (14,14 kJ/mol) is in the range 8–16 kJ/mol and indicates the ion exchange mechanism.

Table 2. Langmuir, Freundlich and Dubinin–Radushkevich isotherm parameters for Sr sorption by natural clinoptilolite

Langmuir model	R^2 0.9940	$q_{max, calc.}$ (meq/g) 0.7490	b, (L meq^{-1}) 0.756	
Freundlich model	R^2 0.9734	$1/n$ 0.263	K_F, meq/g $(meq/L)^{-1/n}$ 0.322	
Dubinin–Raduchkevich model	R^2 0.9847	$q_{max,calc.}$, (mmol/g) 0.4333	β, (mol^2/kJ^2) –0.0027	E, (kJ/mol) 14.14

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Study of the process of carbonation of cement with mineral additives during early hydration period (minutes) up to 24 hours

V. Lilkov[1], O. Petrov[2], D. Kovacheva[4], I. Rostovsky[3], Y. Tzvetanova[2] and P. Savov[1]

[1]*University of Mining and Geology ''St. Ivan Rilski'', Sofia, Bulgaria*
[2]*Institute of Mineralogy and Crystallography, Bulgarian Academy of Sciences, Sofia, Bulgaria;*
E-mail: opetrov@dir.bg
[3]*University of Architecture, Civil Engineering and Geodesy, Sofia, Bulgaria*
[4]*Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, Sofia, Bulgaria*

Introduction

Portlandite and Ca-hydrosilicates in the hardened cement paste are capable of forming carbonate in a longer time period. When the cement composites are subjected to the action of CO_2 the latter is dissolved in the pore-liquid of the cement pastes ensuring CO_3^{2-} ions, which react with Ca^{2+} ions of portlandite and the Ca-hydrosilicate gel to form calcite. In case of prolonged contact of the cement pastes with air and water it is possible to reach complete carbonation with small residue of ettringite, carbo-aluminates and hydrosilicates. The depth of the formed carbonate layer depends on the time of contact with CO_2 and its concentration in the surrounding environment and on the coefficient of diffusion of the hardened cement paste (Wang and Lee, 2009). The volume changes, which accompany the processes of carbonation lead to filling of the empty pore volumes with Ca-carbonates and densify the structure of the hardened cement paste.

The carbonation in the presence of silica fume and zeolites is a more complicated process due to the pozzolanic reactions (Lilkov et al., 1997; Persson, 1998; Abdullah et al., 2004). The products, subjected to carbonation (CH and C-S-H) participate in the pozzolanic reactions (Dunster, 1989; Groves et al., 1990). With the development of the process and the accompanying lowering of the CH-quantity the mean length of the polymer chains of C–S–H progressively increases, the excess of water is released, and with those processes one can explain the carbonation shrinkage.

The present study is on processes of carbonation of cement with natural zeolite (clinoptilolite) during the first minutes, tens of minutes up to the 24th hour of hydration of cement. The carbonation is studied on the surface of the cement past, where the reactions with CO_2 from air are most intensive.

Experimental Methods

The used materials are cement 45 (PC), natural zeolite – clinoptilolite (Bp) – Beli plast deposit, Bulgaria (Table 1).

Table 1. Chemical composition of the starting materials

Sample	Al_2O_3	CaO	Fe_2O_3	K_2O	MgO	MnO	Na_2O	P_2O_5	SO_3	SiO_2	TiO_2	H_2O
PC	5.37	54.9	2.86	1.12	1.08	0.20	0.24	0.14	3.46	23.22	0.22	8.4
Bp	9.68	6.70	0.74	2.79	2.90	0.03	0.29	< 0.03	< 0.03	62.74	0.12	18.5

The following compositions with water-to-solid ratio (by mass) of w/s = 0.5 were prepared for study: plain cement (PC) and 90% cement and 10% clinoptilolite (PCBp). The dry mixture was obtained by mechanical stirring of cement and the mineral additive. The samples are wetted with water and intensively homogenized for 2 min to obtain a paste which is placed in the sample holder for powder XRD measurement. The sample was placed in an desiccator and periodically scanned starting after 3 min of relaxation and at time intervals of 10 min up to the 50th min and the at 30 min up to the 24th hour (Fig. 1).

The XRD measurements were performed at room temperature on a Bruker D8 Advance diffractometer (Cu Kα radiation and LynxEye detector). The detector scans the pattern (8÷50° 2 theta) for less than 1 min, which ensures registration at exact time intervals revealing the status of the hydrating cement samples.

Results and Discussion

Figs. 1 and 2 demonstrate the phase changes during hydration of the sample PCBp (cement plus clinoptilolite) and PC. It is seen that during the entire range of time intervals there are no portlandite (Po) and/or ettringite (Et) formed. A constant and steady increase of calcite (Cc) is observed and at 24 h calcite is dominating as a newly formed product.

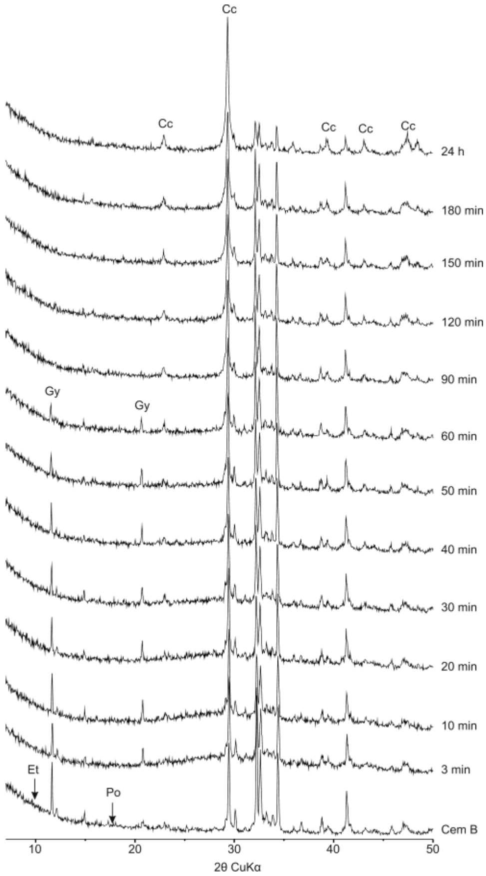

Figure 1. Powder XRD patterns of sample PCBp during hydration in a minutes-to-24 hours interval

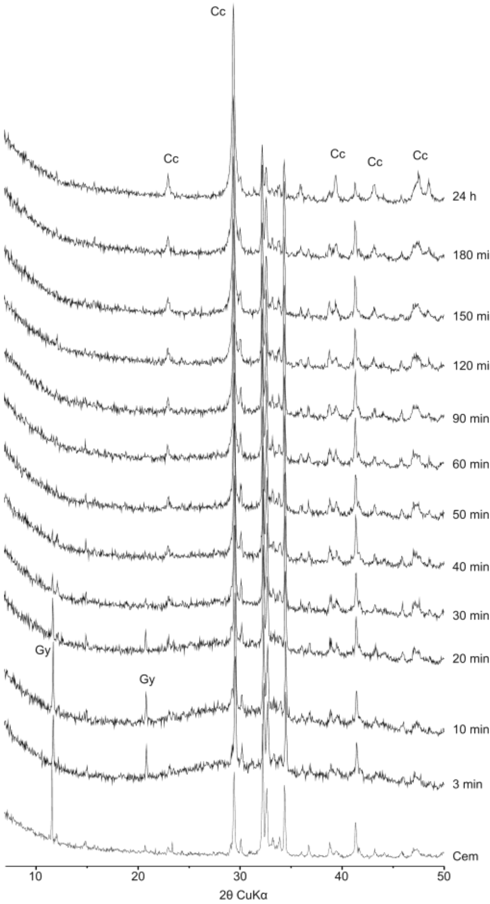

Figure 2. Powder XRD patterns of sample PC during hydration in a minutes-to-24 hours interval

In the cement paste with clinoptilolite the rate of total dissolving of gypsum (Gy) is lowered by about 20–30 minutes compared to the plain cement paste for which the diffraction lines of calcite (Cc) are more expressed. The missing of the diffraction lines of portlandite and ettringite in both pastes indicates that the process of carbonation on the surface of the cement paste takes place directly between the calcium ions from the solution and the carbon dioxide from air without formation of portlandite and ettringite. The presence of clinoptilolite slows this process.

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Effect of cyclic “heating-cooling” and “freezing-cooling” on the hydration products of cement with addition of clinoptilolite and silica fume

V. Lilkov[1], O. Petrov[2], Y. Tzvetanova[2], P. Savov[1], V. Petkova[2] and N. Petrova[2]

[1]*University of Mining and Geology „St. Ivan Rilski“, Sofia, Bulgaria*
[2]*Institute of Mineralogy and Crystallography, Bulgarian Academy of Sciences, Sofia, Bulgaria;*
E-mail: opetrov@dir.bg

Introduction

The study of the effect of clinoptilolite (from Beli plast deposit, Bulgaria) on the physical-mechanical properties of cement shows that this zeolite is an appropriate pozzolanic mineral additive, which combined with silica fume (SF) and fly ashes (FA) from TEPS improves the strength and densifies the structure of the pores of the cement stone (Lilkov et al., 2011). The purpose of this study is to follow the effect of cyclic “heating-cooling” and “freezing-cooling” on the hydration products of cement with addition of clinoptilolite and silica fume. The influence of temperature on the quality of the cement stone is the subject of a series of studies (Lerch and Ford, 1948; Kjellsen and Detwiler, 1992; Escalante-Garcia, 2003; Martínez-Ramírez and Frías, 2009), which, however are performed at constant temperature of cement hardening. However, in reality cements harden at varying temperature regimes, which markedly vary during the different seasons.

Experimental Methods

The used materials are cement (PC), zeolite (clinoptilolite) from Beli plast deposit (Bp), Bulgaria and silica fume (SF) – waste product from the production of fero-silicon steel.

Four compositions of cement pastes were prepared with water-to-solid mass ratio of W/S=0.5: plain cement (PC); 90% cement and 10% clinoptilolite (PCBp); 90% cement and 10% silica fume (PCSF); the dry compositions were mechanically mixed.

After 24 hours the samples harden at normal conditions under water in plastic containers up to 48 hours and after that they are divided in three groups to be checked under the following daily temperature regimes: “n” – constant temperature of 20 °C; “h” – 16 h at temperature 55 °C and 8 h at 20 °C; “c” – 16 h at temperature –5 °C and 8 h at 20 °C. After 150 cycles of cyclic “heating-cooling” and “freezing-cooling” the samples were studied with the method DTA/DTG.

Results and Discussion

The analysis of the results (Fig. 1) shows that the thermal cycles exert weak influence on the total quantity of the hydrate products compared to the normally hydrating cement – it remains either unchanged or slightly lowers. An increase is registered only in the cycle “heating-cooling” of the composition with 10% SF, which is related to its increased activity at higher temperature (Dillshad, 2011). The content of portlandite is highest in the plain cement pastes irrespective of the regime of hardening – about 17% of the total quantity of the hydrate products. Portlandite content is lowest for the compositions with SF and SF plus Bp – 9–10%. The compositions subjected to cyclic “freezing-cooling” display the formation of Ca-carbonate proved by an endothermal peak at about 700 °C, while for the other compositions additional peaks are registered at temperatures above 800 °C. The quantity of Ca-carbonates (calcite, vaterite, and aragonite) is higher in all cements hardening in a regime of “heating-cooling” during which the process of carbonation of portlandite and Ca-hydrosilicates is stimulated.

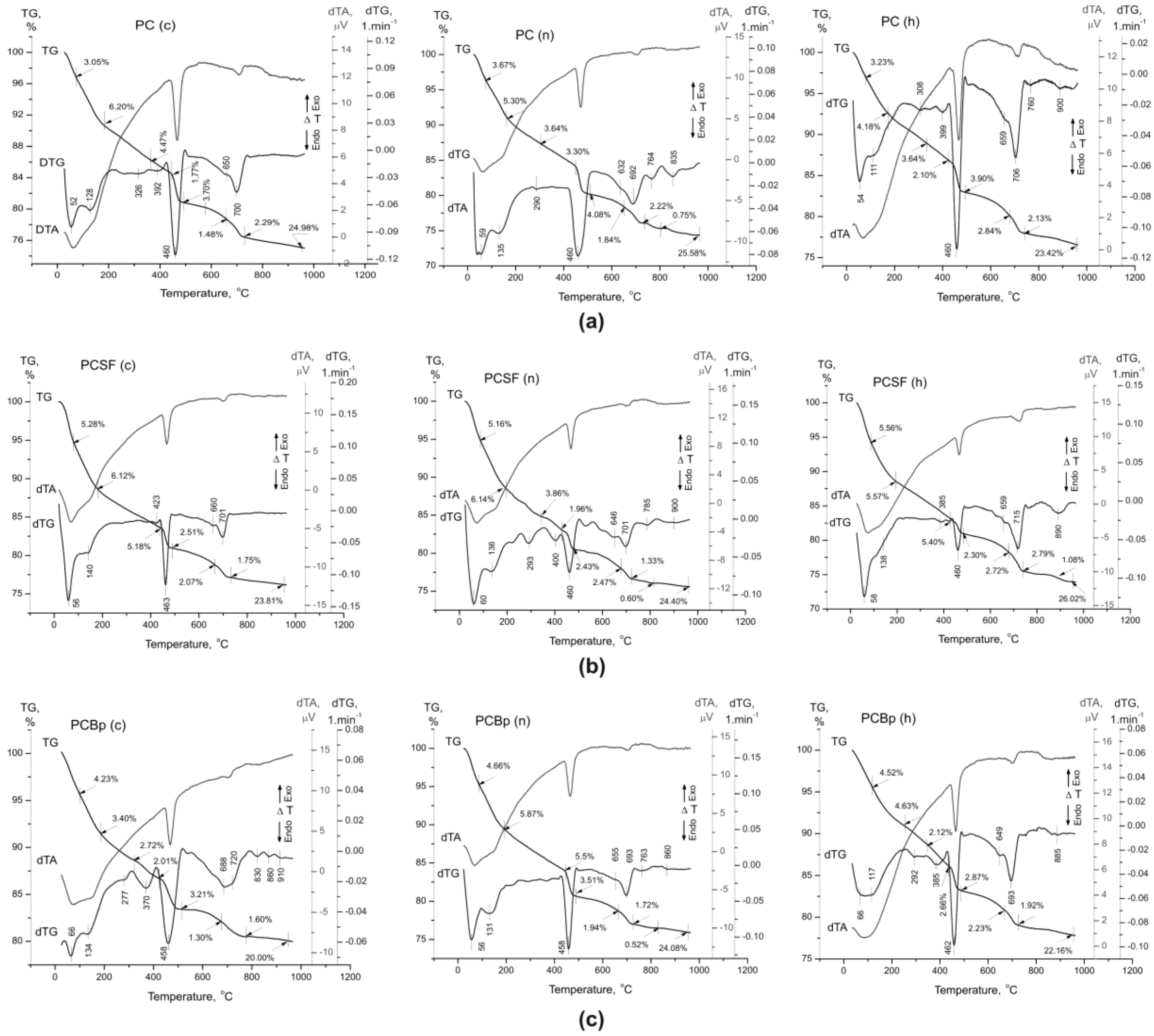

Figure 1. DTA/DTG curves of **(a)** plain cement; **(b)** cement with addition of 10% SF; **(c)** cement with addition of 5% clinoptilolite; hardening at normal conditions (n) and subjected to cycle "freezing-cooling" (c) and "heating-cooling" (h)

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Improvement of saline–alkali soil by natural zeolite—field trials of winter wheat and summer corn

S. Liu[1], C. Han[1], J. Liu[1], X. Sheng[2] and X. Qi[1]

[1]*Key Laboratory of Mineral Resources, Institute of Geology and Geophysics, Chinese Academy of Sciences;*
E-mail: liushanke@mail.iggcas.ac.cn
[2]*Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences*

Introduction

Soil salinization is one of the major issues facing global agriculture. Therefore, many countries are actively exploring causes of soil salinization and methods of soil improvement. According to the data of the second national soil survey, China has about 13.3 million hectares of saline-alkali soils with potential to be cultivated, equivalent to one-tenth of total farmland area of the country. Therefore, it is an effective way to relieve pressure on land in China that the saline–alkali wasteland is turned into the arable land.

Based on its unique structural features, natural zeolite (clinoptilolite) as a soil conditioner was first reported in the sixties of last century in Japan (Brobst and Pratt, 1973), and China also launched the application of zeolite in agriculture in the winter of 1974 (Han, 1994).

Experimental Methods

To investigate effects of zeolite on growth and yield of winter wheat and summer corn in the salinized moisture soil of Binhai, two pieces of land with especially heavier salinization in Yangxin County, Shandong Province was taken as the test fields after both the Institute of Geology and Geophysics, Chinese Academy of Sciences and the Soil and Fertilizer Workstation of Yangxin County Bureau of Agriculture, Shandong Province agreed. One piece of land was planted with winter wheat in Shangdian Town, and another piece of land was planted with summer corn in Shuiluopo Town. Yangxin County, Shandong Province is located along the coast of Bohai Bay, and this area is a continental monsoon climate with four distinct seasons. Physical and chemical properties of the soil of the wheat test field are as follows : salt concentration 2.4 g/Kg, basically NaCl type; pH 8.09; total N 0.05–0.075%; available N 30–45 mg/Kg; available P 3–5 mg/Kg; available K 30–50 mg/Kg. The physical and chemical properties of the soil of the corn test field are almost the same to these ones of the wheat test field, but the salt in the soil of the corn test field is very high, and it reaches 5 g/Kg, which has exceeded the upper limit of salt tolerance for many crops. Both pieces of test field are the fifth level lands; therefore the lands are barren, essentially abandoned by the local farmers.

The area of the wheat test field in Shangdian Town was 466.67 m^2. The wheat field was divided into four plots, and each plot matched one treatment. The area of each plot was 97m^2, and the remaining land was used as protected areas. The area of the corn test field in Shuiluopo Town was 2666.67 m^2. Similarly, the corn field was also divided into four plots, and each plot matched one treatment. The area of each plot was 666.7m^2. Details of each plot on the manure application are shown in Table 1.

Table 1. Details of each plot on manure application

Different treatments	Application of fertilizers
Treatment 1 (control)	Local custom fertilization
Treatment 2	Local custom fertilization + zeolite 22.5 Kg/100m^2
Treatment 3	Local custom fertilization + zeolite 30.0 Kg/100m^2
Treatment 4	Local custom fertilization + zeolite 37.5 Kg/100m^2

Local custom fertilization means the application of mixed N-P-K fertilizers (13.5Kg/100m^2), and the ratio (weight) of N:P:K is equal to 1:0.24:0.53. Natrual zeolite (clinoplolite) was sieved through 40 meshes, its cation exchange capacity is 140mmol/100g. Zeolite was mixed with local custom fertilizers, and the mixture as base fertilizer was applied at 30cm depth in the soil before sowing.

Results and Discussion

At harvest time, samplings of soils and crops were chosen and some properties of them were measured together by the researchers of the Institute of Geology and Geophysics, Chinese Academy of Sciences, the staffs of the County Bureau of Agriculture and the owners of the test lands.

Main biological characteristics of wheat and the soil bulk density of the wheat test field for different treatments are shown in Table 2, and details of corn yield are shown in Table 3.

Table 2. Main biological characteristics of wheat and soil bulk density for different treatments in Shangdian town, Yangxin County

	Wheat spike number/m^2	Wheat grains / per spike (average of 100 spike)	Thousand-grain weight (g)	Yield ($Kg/100m^2$)	Soil bulk density (g/cm^3)
Treatment 1 (control)	334	35.39	33.63	52.76	1.56
Treatment 2	409	39.81	34.50	58.02	1.55
Treatment 3	426	39.85	35.30	59.66	1.50
Treatment 4	422	36.18	33.12	50.24	1.43
Mean of Treatment 2 and 3	418	39.83	34.90	58.84	1.53

Table 3. Details of corn yield for different treatments in Shuiluopo Town, Yangxin Conty

	Treatment 1 (Control)	Treatment 2	Treatment 3	Treatment 4
Yield (Kg/100 m^2)	36.90	38.85	40.29	41.15
Increased yield (Kg/100 m^2)	0.00	1.95	3.39	4.25
Percentage of increased yield (%)	0.00	5.28	9.19	11.50

Note: 1、The test field was severley hit by a continuous rainfall of more than 20 days, and young corns were waterlogged for a long time.
2、If no any natural disasters happen in the test field, the average corn yield is about 37.50 $Kg/100m^2$.

As shown in Table 2, compared with treatment 1 (control), the averages of the test parameters for the treatments 2 and 3 are improved after zeolite application, as follows:

-increased wheat panicles per square meter are 84, and average growth rate is 25%;
-increased wheat grains per panicle are 4.44, and average growth rate is 12.55%;
-increased thousand-grain weight (g) is 1.27 g, and rate of weight growth is 3.78%;
-increased yield ($Kg/100m^2$) is 6.08 Kg, and average growth rate is 11.52%;
-decreased soil bulk density is 0.04 g/cm^3, and decreased rate is 2.24%. In general, the appropriate bulk density of the local land is between 1.10-1.35g/cm^3.

Table 3 data show that, compared with treatment 1 (control), for treatments 2–4 with different amount of zeolite, the yields of summer corn are 1.95–4.25 $Kg/100m^2$, and the percentages of increased yield are 5.28–11.50%. Although the salinity in the test land (5g/Kg) is very high and the corn suffered a severe flood disaster, the application of zeolite improves the environment of crop growth, and greatly increases the yield of summer corn.

The above data show that: after zeolite as the fertilizer is applied into the salinized moisture soil of Binhai, the soil environment becomes better; for example, the soil bulk density is reduced; as a result, the biological properties of wheat and corn are improved. Therefore, the application of an appropriate amount of zeolite in heavy saline-alkali soil will have a positive effect on physical properties of soil, biological characteristics of crops, the increase of crops yield, and so on.

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Testing of zeolites and other sorbents in hot mercury vapours and flue gases

M. Macherzynski[1], M. Wdowin[2], J. Górecki[1], Ł. Uruski[1], R. Panek[3], W. Franus[3] and J. Gołaś[1]

[1]*AGH University of Sciences and Technology, Krakow, Poland; E-mail: macherzy@agh.edu.pl*
[2]*The Mineral and Energy Economy Research Institute of The Polish Academy of Sciences, Krakow, Poland*
[3]*Lublin University of Technology, Lublin, Poland*

Introduction

Despite mercury toxicity, persistence in the environment and long distance transport, there are still many mercury-inducing technologies related mainly to power industry, fuel and waste combustion, non-ferrous metallurgy or cement production which cannot be replaced with others. It is an important reason way to develop mercury reduction technologies and better analytical methods, which would allow for a sensitive and precise determination of this most toxic heavy metal.

In anticipation of more stringent, longer-term mercury emissions reduction targets in power industry, active mercury emissions methods have been investigated recently. Among them, powdered activated carbon (PAC) based sorbents are of most concern, however non-carbon particulate sorbents and solid sorbent beds seem to be more perspective, due to its limited impacts on combustion by-products and recovery capabilities.

In the work, the series of tests was elaborated to determine behaviour of powder and loose materials in different mercury gas medias, flow rates and temperatures, as a test materials are the potential mercury sorbents.

Experimental Methods

Zeolite materials selected to investigations were: natural zeolite (clinoptilolite) from Sokynytsa deposit, Ukraine and synthetic zeolite obtained in hydrothermal synthesis of fly ash with aqua solution of NaOH (Na-X). In order to improve their adsorption properties terms to Hg, the zeolites were silver impregnated by a cation exchange method. Fluidized boiler fly ash, coke dust, and reference commercially available activated carbon impregnated with bromine (AC/Br) were also used. The surface area measurements - BET analysis (ASAP 2020), as well as CEC (cation exchange capacity) for neat samples by NH_4Cl method (Franus and Wdowin, 2010), were performed.

The preliminary elemental mercury sorption tests were performed in a long glass tube fixed bed. Principal mercury capture tests were performed in the AGH laboratory installation, in hot air containing mercury vapours or in flue gases from hard coal combustion in a furnace (coal load ca. 4,8 g/h or more). After filtration the flue gas was enriched in mercury. Mercury load (Hg vapours supplied with a peristaltic pomp) ranged from 2 to 12 μgHg/h, inlet gas flow rate was regulated from 24 to 160 l/h, and the outlet mercury concentration after the reference cell (a cell with empty traps) was set between 50 and 200 $\mu g/m^3$. Materials were placed in the glass vessels inside especially designed glass cells (traps) or in the stationary bed, alone or after mixing with inert materials. Vessels were placed inside a thermostatic furnace. Usual test temperature was 150 ^oC. Mercury was analyzed in an AAS EMP-2 (Nippon Ins. Corp.) analyzer equipped with detector protective and drying scrubbers. Gas transfers were made of Teflon tubes heated to 140-150 ^oC.

Results and Discussion

Table 1 shows a comparison of sorption properties of investigated materials. Neat zeolites BET analyses reveal 260 m^2/g for Na-X and 19 m^2/g for clinoptilolite, respectively. Silver activation caused a little decrease of these values. Subjected neat zeolites have also high cation exchange capacity 242 mval/100g for Na-X and 140 mval/100g for clinoptilolite.

Both zeolite materials (neat and activated) were subjected to elemental mercury adsorption tests in glass tube fixed beds, and referred to AC/Br. The neat zeolites and Ag-activated clinoptilolite have negligible mercury uptake (the breakthrough of a bed had place after few seconds). However Na-X silver activated removed mercury 5 times better than AC/Br. Thus, the Ag- Na-X material was chosen to the subsequent examination in the hot mercury vapours and flue gases. Depending on a flow rate, our traps enabled measurements in stationary, semi-fluidized or fluidized conditions. Initially Ag-Na-X fluidized in our traps very well at flow rates 40-45 l/h. But during prolonged (ca. 2 h) tests at 150°C it gets still, and followed measurements (Figure 2) were performed in a stationary bed conditions.

Table 1. Determined parameters of investigated materials

Material	S_{BET} [m^2/g]	CEC [mval/100g]	Total Hg conc. in sorbent [ppb]	Time to breakthrough (5 %)*, [min]
Na-X	260	242	n/a	2
Ag-Na-X	203	no	159	13017
Clinoptilolite	19	140	n/a	2
Ag-Clinoptilolite	14	no	n/a	5
Fly ash	6.2	n/a	27	n/a
Coke dust	17.5	n/a	12.9	n/a
AC/Br	1015	n/a	8.2	2538

*Breakthrough when 5 % of Hg passes through the sorbent fixed bed (flow rate 80 ml/min)

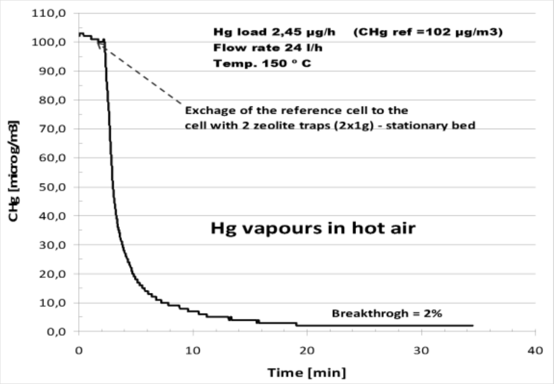

Figure 2. Reduction of mercury on Ag-Na-X from hot

Figure 1 shows on-line measurement of mercury reduction from hot vapours on Ag-Na-X sorbent. Concentration of mercury in the outlet gas decreased from reference 102 to 2 μg/m^3 in ca.15 min (breakthrough = 2%), and was stable. Similar and stable breakthrough = 1.3-2.5 % in 60 min run was observed at flow rate = 45 l/h too.

Figure 2 shows mercury breakthrough at different experimental conditions. Stabilized flue gas was applied in 15 min (the first arrow). The rapid penetration of mercury through the bed was observed up to 68 %. Additional coal loads (next three arrows) caused transient and unstable gas composition, what resulted in next picks, up to almost 100 %. When the flue gas turned off, the breakthrough stabilized at ca. 30 %. The final Hg cut-off showed slow mercury release from the system.

Contrary to the natural zeolite samples, very stable and efficient mercury removal from hot vapours by the Ag-Na-X zeolite was confirmed.

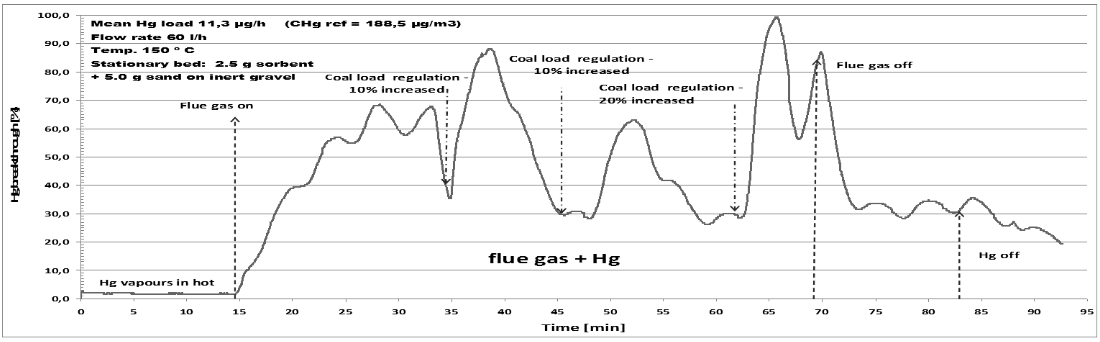

Figure 3. Mercury breakthrough in flue gas on Na-X-Ag sorbent

Results obtained in flue gas conditions indicate considerable influence of changes of exhaust composition and its dynamics on the Ag-Na-X capabilities. However a refinement of a sorbent bed preparation and improvement of a sorbent-gas contact, as well as proper selection of flue gas reference conditions, are required. In order to compare the effects of the flue gas on the zeolite properties, the other materials with similar grain size and potential options for the removal of mercury are simultaneously tested. The work is in progress.

Acknowledgment

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Detection of ethanol vapors by ZnO/ Stilbite Composites

M. P. Mahabole, A. Madhuri, M. A. Lakhane and R. S. Khairnar

Swami Ramanand Teerth Marathwada University, Nanded (MS), India; E-mail: mpmsrtmunsps@gmail.com

Introduction

Stilbite, {(Na_2Ca_8) $[Al_{18}Si_{54}O_{144}]60H_2O$, abbreviated as Ca-stilbite}, is a common zeolite with the distinctive framework topology STI. It is a zeolite usually containing a small amount of sodium in place of calcium. Literature survey shows that stilbite single crystal has been utilized as the alcohol sensor. They used impendence spectroscopy for confirmation of its applicability as an alcohol sensor (Schaf et al., 2006). A detailed study on natural Ca-stilbite and Mg-stilbite based ethanol sensors has been carried out by our group (Mahabole et al., 2013). Ag ion doped stilbite single crystals are also used for detection of gaseous aliphatic components mixed with nitrogen or synthetic air by Sazama and group (Sazama et al., 2008). The thermal stability of natural and ion exchanged stilbite along with adsorption properties have been studied by M. Kasture and group (Kasture et al., 1998). It is found that the sensing characteristics of zeolites can be enhanced by adding ZnO into the sensor matrix (Pugh et al., 2014). In the present communication, we report study on the effect of ZnO on ethanol sensing behavior of stilbite with respect to various ethanol sensing parameters like optimum operating temperature, response/recovery rates and ethanol upload capacities. Moreover, the research work deals with the detection of ethanol by ZnO/stilbite thick film sensors using conductivity measurement approach.

Experimental Methods

Stilbite zeolites are collected from queries near to Pashan Area, Pune (MS), India. The obtained crystals are converted into powder form and are used without further purification. The stilbite zeolite matrix is used as a host matrix while ZnO is used as a guest material to have metal oxide modified zeolite. The simple physical mixture type stilbite/ZnO composites are prepared by mixing (wt %) appropriate quantities of Ca-stilbite and ZnO (25wt %, 50wt % and 75wt%). These materials are thoroughly dry mixed in an agate mortar with pestle for about 1h. The composites are characterized by X-ray diffractometer using CuKα radiation (λ= 0.154056nm) in 2θ scan range of 5 to 60^0. Screen printed thick films are prepared by using stilbite/ZnO composites as the functional materials along with binders. The films are then dried under IR lamp for about 20 min and finally sintered at 650^0C for about 2h. These screen printed composite thick films are used as sensors in further study.

The sensor performance characteristics of these composites to ethanol are studied using indigenous gas sensor unit. The change in electrical resistance of a composite thick film, air and air+ethanol environments, is determined. The gas response (often called as gas sensitivity), defined as (Rg-Ra)/Ra, is also determined and is plotted as a function of temperature to determine an optimum operating temperature. The other parameters like response/recovery and gas uptake capacity are also determined.

Results and Discussion

The XRD spectra of ZnO/stilbite composites are shown in Figure 1 wherein XRD profile of Ca-stilbite is considered as a reference.

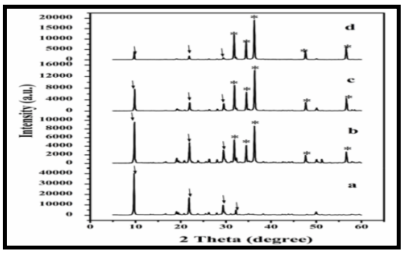

Figure 1. XRD plot for **a** 100% stilbite; **b** 75% stilbite **c** 50% stilbite; **d** 25% stilbite

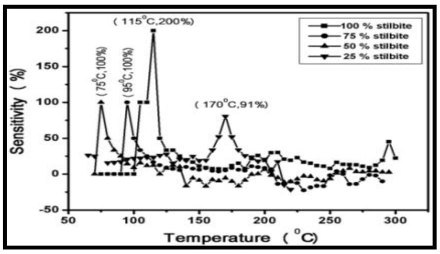

Figure 2. Comparision of ethanol response

The spectra show that as the concentration of ZnO in the stilbite matrix increases, the intensities of the XRD peaks corresponding to ZnO become dominated over the stilbite. The XRD analysis reveals that most of characteristic peaks for ZnO and stilbite perfectly match with the standard for ZnO (ICSD Card #: 067849) and stilbite (Garcia-Martinez et al (1993)).Figure 2 shows the comparative response of Ca-stilbite and ZnO composite stilbite sensor thick films to a fixed known concentration of ethanol for various compositions of ZnO/stilbite as a function of temperature. From the figure it is observed that 100% Ca-stilbite film gives maximum response to ethanol at 110^0C.

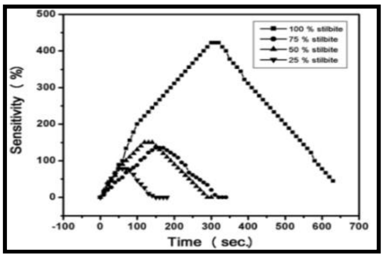

Figure 3. Comparision of ethanol response/recovery

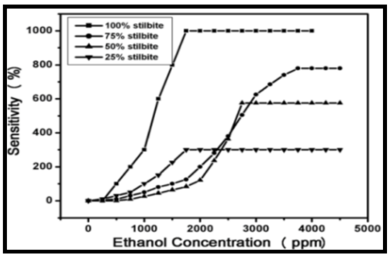

Figure 4. Comparison of ethanol uptake capacity

Figure 3 shows the comparative response/recovery behaviors of Ca-stilbite and ZnO/stilbite thick films as a function of time. Though the response of Ca-stilbite to ethanol vapor is high, it takes longer time (~300 sec) to sense ethanol in comparison with 50%ZnO/stilbite which can sense ethanol within ~120 sec. Figure 4 depicts the change in ethanol sensitivity as a function of ethanol concentration for pure ZSM zeolite and ZSM-5/ZnO composite sensors. The concentration of alcohol is varied from 250ppm to their maximum saturation value. Ca-stilbite film can sense 2750ppm ethanol and after that it saturates and ZnO/stilbite (75% stilbite) composite film can give response to 3750ppm ethanol followed by saturation. Whereas the ZnO/stilbite for 50% stilbite & 25% stilbite composite films saturates at very lower ethanol concentration at 1750ppm and 560ppm respectively. This shows the higher saturation limit of Ca-stilbite film than that of ZnO/stilbite for ethanol.

The characteristic XRD peaks confirm the successful incorporation of ZnO into the stilbite matrix. ZnO/stilbite composite (50% stilbite) can sense ethanol at much lower temperature (75^0c) compared to 100% Ca-stilbite and other ZnO/stilbite composite sensors. It also gives fast response (~120sec) to ethanol compared to other sensors. However, its ethanol uptake capacity is observed to be small as it can sense 1750 ppm ethanol followed by saturation.

Acknowledgment

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Zeolite alteration patterns in the Lefkimi area, N.E. Greece. Contribution to the genetic model of zeolites in the area of Thrace

I. Marantos[1], G. E. Christidis[2], K. Michail[3] and D. Tarenidis[1]

[1]Institute of Geology and Mineral Exploration, 1 Spyrou Loui Str, Olympic Village ,13677 Athens;Greece
E-mail: yanmarantos@igme.gr
[2]Technical University of Crete, Department of Mineral Resources Engineering, 73100 Chania, Greece;
E-mail: christid@mred.tuc.gr
[3]Institute of Geology and Mineral Exploration, IGME, Regional Division of East Macedonia-Thrace,
Mprokoumi 30, 67100 Xanthi, Greece; E-mail: conmichael@hotmail.com

Introduction

Lefkimi-Dadia basin, Evros prefecture, Greece, was formed during Priambonian, on the metamorphic basement of the Rhodope zone and Circum Rhodope zone. The formation of the basin and subsequent sedimentation was accompanied by an intense magmatic activity of Upper Eocene to Miocene age, which produced lavas and volcaniclastic rocks of calk-alkaline to shoshonitic affinities. Subvolcanic rocks of intermediate to acidic composition intrude the various Tertiary formations. In this contribution the alteration pattern of volcaniclastic rocks of the Lefkimi area is studied in detail and is compared with the adjacent Tertiary Feres basin, having similar alteration patterns and evolution history (Marantos 2004; Marantos et al., 2007, 2008), in order to construct a general genetic model for the zeolite deposits in the broader area of Thrace.

Experimental Methods

The area of Lefkimi was mapped in detail in the frames of the Institute of Geology and Mineral Exploration survey projects. About 50 samples of various formations were studied by a combination of analytical methods. Bulk and clay mineralogy were examined by X-ray Diffraction (XRD). Clay mineralogy was determined on oriented <2μm clay fractions in air-dried, ethylene glycol and glycerol solvated and heated samples. Petrographic study and the mode of occurrence of alteration minerals were carried out with a polarizing microscope and a Jeol JSM 5600, Scanning Electron Microscope. Selected samples were analysed for major and trace elements by wavelength dispersive X-ray fluorescence spectrometry (WD-XRF).

Results and discussion

The Tertiary (Priambonian – Oligocene) volcano sedimentary formations of the Lefkimi Dadia basin consist of a lower clastic sequence, (sandstone, mudstone), a middle clastic sequence intercalated by fine ash volcaniclastics and an upper part with extended outcrops of andesitic lavas, pyroclastic breccias and fine ash tuffs, locally intercalated with clastic sediments (Michael et al., 1984). The lower and middle clastic sequences are interbedded with Priambonian limestone lenses. The Priambonian sequence is overlain unconformably by Oligocene acidic fine to coarse ash tuffs, breccias and lavas. In this sequence the sedimentary rocks are almost absent, suggesting a terrestrial deposition environment. These formations have been intruded by small domes and dykes of acid to intermediate composition.

The volcaniclastic rocks, consist of various type glass fragments (shards, pumice, perlitic), plagioclase, K-feldspar, quartz, biotite. Amphiboles and pyroxenes are also present in the andesitic tuffs. The andesitic volcaniclastics and andesites have been altered to calcic zeolites (mainly stilbite), corrensite, smectite, chlorite, SiO_2-polymorphs and locally calcite. K-feldspar may be present also as secondary phase. The calcic zeolites occur mainly in pores, cavities and fissures of the rocks, in the form of elongated crystals, usually outlined by clay minerals. Clay minerals may also occur in the form of spherulitic aggregates. Fine ash vitric tuffs in the sequence may be altered to heulandite and mordenite. The primary texture of the altered rock is well preserved.

In the upper parts of the Priambonian sequence, the high potassium, fine to coarse ash tuffs of dacitic composition have been altered to clinoptilolite, opal-C and K-feldspar, (Skarpelis and Marantos, 1987; Skarpelis et al., 1993). Two distinct clinoptilolitic tuff horizons exist in the area, a lower blue-green tuff, owing its colour to the presence of celadonite and an upper white one. Finally the acid Oligocene tuffs have not been affected significantly by alteration. Perlitic rhyolites locally may be altered to clinoptilolite.

The variation in the alteration mineral assemblages and especially the presence of corrensite, celadonite, smectite, along with secondary feldspar and calcium to potassium zeolites, suggest a complex formation environment for the clay minerals and the zeolites in the area. Based on the mode of occurrence and the alteration mineral pattern an interpretation of the mode of formation is attempted. This interpretation is based on the parent material composition, the deposition mechanism, the pore water chemistry and the temperature prevailing during zeolite formation, which are critical factors during the zeolitization and clay mineral formation.

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First stages of porous materials synthesis starting from clinoptilolite: Molecular Dynamics simulations

Y. Machado-Batista[1], A. Rivera[2], L. J. Alvarez[3] and A. Lam[2]

[1]*Departamento de Ciencias Básicas. Facultad 2. Universidad de las Ciencias Informáticas (UCI). Carretera a San Antonio de los Baños, Km 2 ½. Boyeros. La Habana. Cuba.*
[2]*Zeolite Engineering Laboratory, Institute of Material Science and Technology (IMRE), University of Havana, Havana 10400, Cuba; E-mail: anabel@fisica.uh.cu*
[3] *Laboratorio de Simulación. Instituto de Matemáticas, Unidad Cuernavaca. Universidad Nacional Autónoma de México. AP-273-3 Admon, Cuernavaca, Morelos 62251, México.*

Introduction

The synthesis of porous materials starting from natural sources has attracted considerable interest over the last years due to their large potential in different application areas. It involves a great number of molecular species, such as templates, aluminum and silicon oxides, sodium hydroxide and water. The self-assembly of these species to obtain a material with a hierarchical porosity often requires complementary techniques to clarify the chemical mechanisms involved. Therefore, the use of computational simulation can contribute to the knowledge of the physico-chemical phenomena that take place during the synthesis of these materials. In this work, we report on the simulations of the first stages of the synthesis processes of hierarchical materials using as source of silicon and aluminum different fragments of clinoptilolite framework. These fragments were dimmers of Al and Si, and trimers and tetramers of Si. Molecular dynamics simulations were performed in order to model the first stages of the synthesis. In the simulation, dodecyltrimethylammonium bromide (DETAB) was used as template and Si/Al ratio was equal to 10.

Computational Methods

The silicon and aluminum sources were obtained cutting the elementary cell of clinoptilolite in dimmers, trimmers and tetramers. The valence of the oxygen atoms were completed with hydrogen atoms. In this way, we used in our simulation 54 dimmers, 27 trimmers and 27 tetramers. The 27 dimmers had one aluminum atom and one silicon atom, whereas the rest of the dimmers were pure silicon. The silicon/aluminum ratio in the simulation box was 10 as previously used by Mokaya et al. (Xia and Mokaya, 2006) for the synthesis of mesoporous aluminosilicates. 27 DeTAB molecules and 3326 water molecules were included in the simulation box. The SPC/E potential was employed to model the water molecules interaction (Berendsen et al., 1987). The DeTAB molecule and the oligomers employed were modeled using the potential employed before by Jorge et al. (2009). The charges used for aluminum and the acid proton were 0.8292e and 0.5e, respectively. The Al-O distance was kept fixed at 1.78 Å.

The simulations were carried out using the DL_POLY molecular dynamics simulation package version 2.0. The equations of motion were integrated with the Verlet leapfrog algorithm and a time step of 2 fs was used. The NpT ensemble was employed in all simulations, with the temperature and pressure fixed at 300 K and 1 bar, respectively, applying the Nóse-Hoover thermostat and barostat. The simulation box was cubic, with periodic boundary conditions in all cartesian directions. The Ewald method was applied to deal with long-range electrostatic interactions. The cutoff of the short-range and electrostatic interactions was 10 Å. The simulation time was 22 ns.

Results and Discussion

During the simulation, the surfactant molecules approach the three small forming aggregates with average aggregation number equal 6. The form of these aggregates is approximately spherical and their diameters can reach 25-30 Å.

On the other hand, silicon and aluminum oligomers arrange in a way to form layers where no water or surfactants are included. In previous experimental studies the formation of layered silica in few days synthesis process was observed (Xia et al., 2004). Further studies have shown that the presence of Al does not have any influence on the structural ordering of the mesophases obtaining layered aluminosilicates via hydrotermal synthesis (Xia and Mokaya, 2006).

Figure 1 shows the simulation box replicated in all directions at the end of the simulation. It is possible to observe the formation of sinusoidal layered mesophases that extend at the XY plane (Fig. 1a). The minimal lamellar distance is approximately 14 Å, while the largest is 29 Å. On the YZ plane, it is possible to observe the formation of an irregular pore system with dimensions of 15x35 Å (see Fig.1b). The simulation results suggest that the new material could have a structure different than the clinoptilolite, with a possible hierarchical porosity.

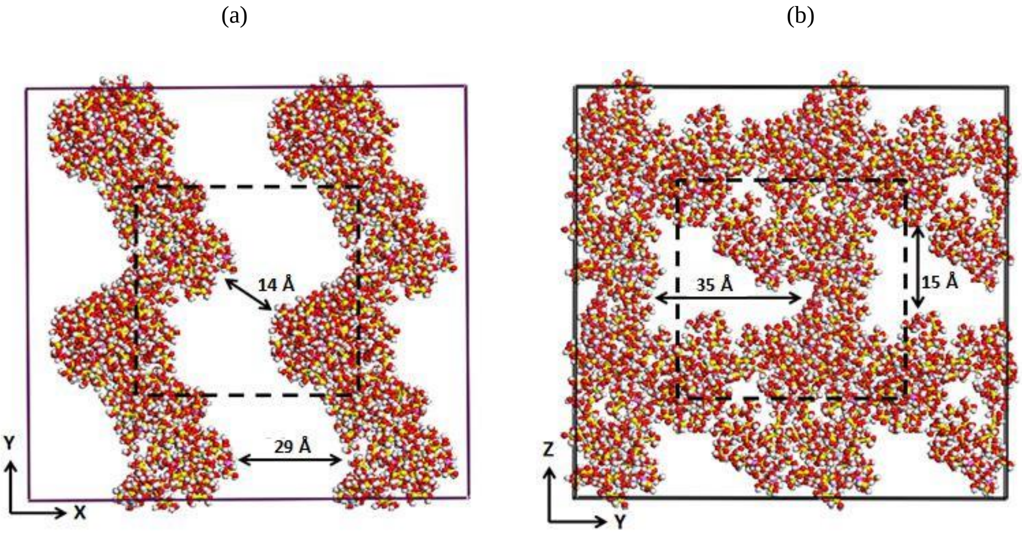
(a) (b)

Figure 1. Different views of oligomers arrangement at the end of the simulation. The simulation box replicated in all directions is marked with dashed line. Water molecules and surfactant are not included. The oxygen atoms are colored red, hydrogen white, silicon yellow and aluminum purple

At the end of the simulation the Si-Si distances were lower than the Al-Al ones. This was expected because of the higher number of silicon atoms than those of aluminum. Also, the aluminum and silicon distribution obtained followed the criterion of Al distribution in zeolites, i.e. the Lowenstein and Dempsey rules. In those dimmers that contain one Al atom, the silicon can get closer to other silicon atoms, favoring the possibility to form a bond. Dimmers were the fragments that could be found closer to micelles due to their small size. They can move more easily in the system and approach fast the micelle surface. However, Al is located more distant to the micelle. This implies that the dimmers of aluminum approach to the surfactant molecules, oriented in such way that the Si is closer to micelle than Al.

Acknowledgment

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Aflatoxin B_1 adsorption by phillipsite- and chabazite-rich tuffs

M. Marković[1], A. Daković[1], G. E. Rottinghaus[2], M. Mercurio[3], P. Cappelletti[4], L. Catalanotti[5], A. Langella[3], M. Kragović[1] and B. de' Gennaro[5]

[1] *Institute for Technology of Nuclear and Other Mineral Raw Materials, Franche d'Epere 86, 110000 Belgrade, Serbia; E-mail: m.markovic@itnms.ac.rs*
[2]*Veterinary Medical Diagnostic Laboratory, College of Veterinary Medicine, University of Missouri, Columbia, MO 65211, USA*
[3]*Department of Science and Technologies, University of Sannio, Via dei Mulini 59/A, 82100 Benevento, Italy*
[4] *DiSTAR, University of Naples Federico II, Naples, Italy*
[5] *DICMAPI, University of Naples, Federico II, Naples, Italy*

Introduction

Mycotoxins produced by fungi can be highly toxic and carcinogenic. Animals and humans who eat food contaminated with mycotoxins may develop a variety of acute and chronic diseases. In recent years, mycotoxin contamination has affected human health and has become a serious problem for the development of society. Of the more than 300 mycotoxins that have been identified, the aflatoxins, zearalenone, ochratoxins, fumonisins, trichothecenes and ergot alkaloids are the most frequently occurring contaminants of various cereal crops throughout the world. *Aspergillus* fungi frequently produce the aflatoxins B_1, B_2, G_1 and G_2. They have been detected as contaminants of crops before harvest, in storage, and after processing and manufacturing. Aflatoxin B_1 (AFB1) is the most toxic and carcinogenic of the aflatoxins. Its metabolite, aflatoxin $M_{1,}$ appears in milk and milk products as a direct result of the animal ingesting feed contaminated with AFB_1 (Zeng et al., 2013; Carraro et al., 2014). At present, the most promising approach for controlling mycotoxin contamination is the addition of non-nutritive adsorbent materials to the contaminated animal feed. Aluminosilicates are the prefered adsorbents. Many clay minerals, such as montmorillonite, sepiolite and kaolinite, have been shown to have a strong affinity for AFB_1. The use of natural zeolites, namely clinoptilolite and mordenite-rich tuffs, in animal nutrition began in Japan in the mid 1960s. Efficacy testing was initially done with swine and poultry, but has been extended to other animals. The results were, in general, good to excellent with improved growth and consequent increase in productivity (Zeng et al., 2013; Collela, 2011 and references therein). In the natural form, clinoptilolite has also been shown to be an adsorbent of AFB_1 (Daković et al., 2005). The aim of this reaseach was to investigate, if other type of zeolites – phillipsite and chabazite, are also effective in adsorbing AFB_1, under *in vitro* conditions.

Experimental Methods

The materials used in this study were a chabazite-rich rock from a deposit in San Mango sul Calore, (Avellino, Italy), belonging to the Campanian Ignimbrite formation (39,000 ybp), the most important volcanic episode of the Campi Flegrei (Southern Italy), named CHA_SM; and phillipsite-rich rock from Campania (Italy) which occurs in the Neapolitan Yellow Tuff deposit (15,000 ybp), the product of one of the largest and most powerful eruptions of Campi Flegrei, named PHI_SAV. These materials were characterized from mineralogical, chemical and technological points of view [XRPD, XRF, SEM/EDS, FTIR, Surface Area (BET method), Cation Exchange Capacity (CEC) and External Cation Exchange Capacity (ECEC)]. The batch exchange method (BEM) (Cerri et al., 2002) was applied to assess the CEC by extracting Na^+, K^+, Mg^{2+}, and Ca^{2+} cations with a solution of ammonium chloride.

Aflatoxin B_1 was obtained from Sigma-Aldrich Co. A primary AFB_1 stock solution (1,000 ppm) was prepared in acetonitrile. AFB_1 test solutions for adsorption studies were prepared by addition of acetonitrile stock solution to 0.1M phosphate buffer adjusted to pH 3. In the study, duplicate aliquots of 0.1M phosphate buffer containing 4 mg AFB_1/L in solution (10 mL) were added to 15 mL screw cap Falcon polypropylene tubes to which had been added 20, 10, 5 or 2 mg of CHA_SM or PHI_SAV. In order to eliminate exogenous peaks, controls were prepared by adding 10 mL of 0.1M phosphate buffer (pH 3) plus 20 mg of each adsorbent to Falcon tubes. Following adsorption experiments (pH 3), desorption was measured by decanting the supernatants and the residues containing 20 mg of CHA_SM or PHI_SAV-AFB_1 complexes were mixed with 4 mL of pH 6.5 buffer. In all adsorption and desorption experiments, the control and duplicates were placed on a rotator shaker for 30 min at room temperature. Each AFB_1 test solution and control was then centrifuged at 13,000 rpm for 5 min and 2 mL of the aqueous supernatant removed for HPLC analysis.

Results and Discussion

Table 1 reports the quantitative mineralogical analyses of the selected samples. The CHA_SM sample shows a chabazite content of 71% along with a small percent of phillipsite, K-feldspar (approximately 16%) which should be considered as a pyrogenic phase. Pyroxene, mica, and amorphous matter were present in minor amounts. The PHI_SAV sample was enriched by gently crushing the specimen and magnetic separation. This treatment increased the phillipsite content to approximately 70 wt.%.

Table 1. Quantitative mineralogical evaluation for the selected samples (XRD)

	Chabasite	Phillipsite	Analcime	Pyroxene	K-Feldspar	Mica	Amorphous*
CHA_SM	71.2	5.2		3.1	16.2	1	3.3
PHI_SAV	4.5	69.6	3.3	3.3	13.3	Tr	6.0*

*Amorphous matter, estimated by difference, also includes partially or disordered phases

The results of AFB_1 adsorption by CHA_SM and PHI_SAV at pH 3, as well as the results of the stability of CHA_SM-AFB_1 or PHI_SAV-AFB_1 complexes at pH 6.5 are presented in Table 2.

Table 2. AFB_1 adsorption by CHA_SM and PHI_SAV

	CHA_SM		PHI_SAV	
	AFB_1 adsorption	AFB_1 desorption	AFB_1 adsorption	AFB_1 desorption
Amount of sample, g/L				
2	40.38	none	91.53	none
1	16.50		70.00	
0.5	9.50		37.50	
0.2	9.00		17.75	

From the results presented in Table 2, it can be seen that adsorption of AFB_1 by CHA_SM and PHI_SAV increased with increasing amounts of each adsorbent in suspension. At all investigated levels of solid phase in suspension, the PHI_SAV sample had much higher AFB_1 adsorption at pH 3 than the CHA_SM sample. No desorption of AFB_1 was visible at pH 6.5 with either PHI_SVA-AFB_1 or CHA_SM-AFB_1 complexes, suggesting a strong binding of AFB_1 by both adsorbents. However, much higher AFB_1 adsorption by phllipsite than chabasite suggests that phillipsite may prove useful as adsorbent for AFB_1. Further investigations will be focused on phillipsite and the determination of the AFB_1 adsorption isotherms in order to determine toxin adsorption capacity.

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Nitrogen removal from wastewater UASB reactor with natural zeolite powder

H. N. Martins[1] and F. Borsatto[2]

[1] *University of Sao Paulo; Brazil; E-mail: henrique.neto@usp.br*
[2] *Industry Celta Brasil Ltda; Brazil; E-mail: fernandoborsatto@celtabrasil.com*

Introduction

Eutrophication of water bodies is a problem mainly found in tropical countries and is the accelerated growth of algae due to the release of municipal and industrial wastewater and runoff from agricultural areas in rivers and lakes, which are enriched with nutrients, mainly nitrogen. (Braga et al., 2005). In tropical countries like Brazil, one of the most used systems for wastewater treatment is the UASB reactor type, this system has high efficiency in removing organic matter, however poor or no removal of ammonia-N (von Sperling et al. 2001). Thus this study aims to assess how the use of natural zeolite powder type clinoptilolite from Cuba, benefited in Brazil from the Industry Celta Brazil, can contribute to the removal of nitrogen from treated sanitary effluent in UASB aimed at reducing eutrophication of bodies water.

Experimental Methods

For the study was used 5.0 liters of wastewater treated by a UASB reactor with ammonia-N concentration of 65 mgN / L and pH 7.65, divided into five reactors with one liter capacity each. The reactors numbered 1 to 5, operating under batch and continuous mixing for 1 hour, received doses of 500, 1000, 1500, 2000 and 3500 mg / L of natural zeolite clinoptilolite with a grain size # 325 mesh. Samples were collected every 10 minutes, filtered and analyzed by spectrophotometer single beam and direct reading, Smart Spectro model, manufactured by Policontrol.

Results and Discussion

Table 1 shows the results obtained during the test time and the respective levels of zeolite in each reactor. Table 2 presented the efficiencies obtained in each system. Figures 1 and 2 illustrate the results of the respective tables.

Table 1. Results obtained in tests with natural zeolite powder (# 325 mesh)

Identification	Reactor Nº 1	Reactor Nº 2	Reactor Nº 3	Reactor Nº 4	Reactor Nº 5
Dosage	500 mg/L	1000 mg/L	1500 mg/L	2000 mg/L	3500 mg/L
Time (min)	Concentration of ammonia nitrogen in the effluent (mg N/L)				
0	65.0	65.0	65.0	65.0	65.0
10	56.4	49.0	42.4	44.6	27.4
20	56.4	56.6	44.2	42.4	34.8
40	57.0	49.8	46.0	44.6	32.0
60	56.6	54.0	45.0	44.0	33.2

The removal of ammonia-N occurs during the first 10 minutes of reaction, therefore suggests that the minimum time for the process. However, the curves of the reactors 2, 3 and 5 there is low ammonia-N release after this period, probably due to the removal of other compounds or due to the adsorption equilibrium.

The results also indicate that there was a significant removal of N-ammonia only in the reactor 5, whose efficiency was 57.8% but this reactor was the one using the largest dosing series.

Table 2. Efficiency results obtained in tests with natural zeolite powder (# 325 mesh)

Time (min)	Reactor Nº 1	Reactor Nº 2	Reactor Nº 3	Reactor Nº 4	Reactor Nº 5
0	0.0%	0.0%	0.0%	0.0%	0.0%
10	13.2%	24.6%	34.8%	31.4%	57.8%
20	13.2%	12.9%	32.0%	34.8%	46.5%
40	12.3%	23.4%	29.2%	31.4%	50.8%
60	12.9%	16.9%	30.8%	32.3%	48.9%

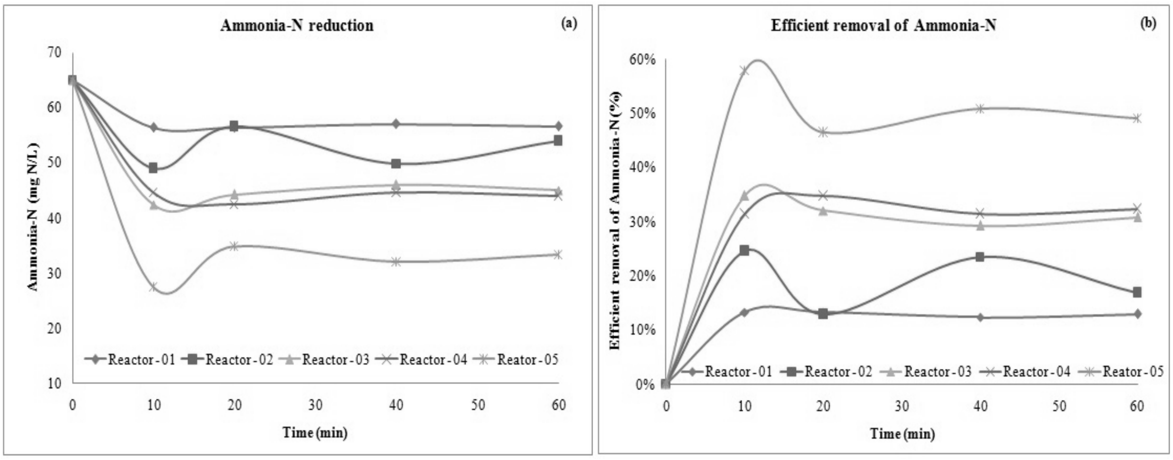

Figure 1. (a) Ammonia-N reduction and (b) Efficient removal of Ammonia-N

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The use of natural zeolite-rich rocks as additive to swine feeding stuffs: new insight onto methodology of the quality control analysis

M. Mercurio[1], B. de' Gennaro[2], L. Esposito[3], P. Cappelletti[4], A. Langella[1], F. Iannaccone[3], V. Monetti[4] and F. Bovera[3]

[1]*Department of Sciences and Technologies, University of Sannio, Via dei Mulini 59/A, 82100 Benevento, Italy; E-mail: mariano.mercurio@unisannio.it*
[2]*DICMAPI, University of Naples, Federico II, P.le Tecchio 80 Naples, Italy*
[3]*Department of Veterinary medicine and Animals sciences, University of Naples Federico II, Via F. Delpino 1, 80137 Naples, Italy*
[4]*DiSTAR, University of Naples Federico II, Via Mezzocannone 8, 80134 Naples, Italy*

Introduction

Zeolitized materials have been far back proposed as additives in animal diets as, further than their function as antiagglomerant and binding agents, they also act as cation exchangers thus immobilizing the ammonium ion during the digestive process. The positive effects of such a behaviour are: a lower environmental dispersion of ammonia from the animal faeces and a weight gain of finishing pigs. Such advantages are particularly evident in those areal contexts where a high concentration of livestock holdings occurs such as, for example, the swine livestocks of the Modena district (Italy). As any kind of product destined to the formulation of animal feeding, thus indirectly entering the human food chain, it is necessary to follow well defined CE regulations which assess the maximum allowable limits of noxious elements, in particular for those commonly defined as heavy metals: Pb, Cd, As, and Hg. Minerals admitted in the formulation of animal feeding are clinoptilolite and, more recently, phillipsite which was equalized to the E536 additive natrolite-phonolite. For both phases the Commission Guidelines (UE) n. 744/2012 of 16th August 2012, which modify attachments I and II of the 2002/32/CE Guideline of European Parliament, establish the allowable limits for As, F, Pb, Hg, endosulfan, dioxins, Ambrosia spp., diclazuril and sodic lasalocid A as well as the critical threshold for dioxins. As far as the above reported heavy metals are considered they were evaluated following the method described by Mercurio et al. (2012). Such leaching method was particularly aggressive, definitely not comparable with the real environment occurring in the digestive apparatus of the animals. Considering the large use of zeolites in the swine feeding a detailed investigation was set up in cooperation with the veterinary researchers.

Experimental Methods

The present research took advantage of geological resources widely occurring on the Campania region (Southern Italy) and commonly used in the zootechnical sector. Samples belong to the yellow facies of the Campanian Ignimbrite formation and were collected in Dugenta, Caserta (DUG samples, ETEP Quarry) and Comiziano, Naples (APO samples, Apostolico quarry). Mineralogy of all samples was evaluated by X-ray powder diffraction (XRPD) using a PANalytical X'Pert Pro modular diffractometer (CuK$_\alpha$ radiation, 40 kV, 40 mA, 4–50° 2θ scanning interval, 0.017° equivalent step size, 60 s per step equivalent counting time, RTMS X'Celerator detector). Powders with grain size <10 μm were obtained using a McCrone micronising mill (agate cylinders and wet grinding time 15 min). An α-Al_2O_3 internal standard (1 μm, Buehler Micropolish) was added to each sample in an amount of 20 wt.%. Quantitative evaluations were performed both by RIR/Rietveld methods. An in vitro digestibility trial was made to simulate the passage of the samples throughout the whole digestive tract of the pigs. Approximately 1 g for each sample was weighed in 27 replicates and placed in 100 ml glass bottles. The bottles were filled with 75 ml of a pH 2 solution with 10 mg of pepsin and incubated at 39° C for 6 hours to simulate the gastric digestion according to Huang et al. (2003). Both the samples and the liquids of incubation and rising were collected. Nine filtered samples were then dried at 65 °C until constant weight and stored until spectrometric analysis. The other 18 samples were used to simulate the passage in the other tracts of the pig digestive system. The gastric-digested samples were placed again in 100 ml glass bottles. The whole digestive tract of three Italian Large White × Italian Landrace pigs (live weight 143.2 ± 4.3 kg) was collected in a specialized slaughter house, linked at the ends and transported as soon as possible (around 30 minutes) in the laboratories of the Department of Veterinary medicine and Animal Science. The content of the small intestine was diluted 2:1 with a buffered solution (pH 6.8) and 75 ml of this solution was added to the 18 glass bottles with the stomach-digested samples. The bottles were incubated at 39 °C for 18 hours. At the end of incubation, the same procedure as the gastric digestion was followed. Nine samples were dried and stored. The other 9 samples were placed in glass bottles filled (75 ml) with the content of the large intestine diluted 1:4 with a buffered solution (pH 6.8) and incubated at 39°C for 24 hours. At the end of incubation, a similar procedure as reported for stomach and small intestine digestion was followed. All the solutions obtained following the above reported procedures were analysed by ICP-OES, using the methodology described by Mercurio et al. (2012), to determine the following elements: Ca, Na, K, Mg, Al, Si, Fe, Mn, Sb, Pb, Cd, As and Hg.

Results and Discussion

A careful characterization of raw materials used for the experiments definitely represent the fundamental stage to be carried out before the *in vitro* treatments in order to evaluate the chemical and mineralogical modifications generated after the interactions. Zeolite contents (PHI + CHA) ranges between 55% (APO) and 36 % (DUG). Smectite traces along with some amorphous matter range on average between 20% (APO) and 28% (DUG).

Treatments with organic solutions determine a content variation of some phases, most of them occurring after the contact with solutions simulating the stomach environment. In particular, chabazite content decreases of about 21% (15 →10,7%) in APO and about 23% (23,2 → 17,8%) in DUG. As far as phillipsite is considered such variations are of about 20% (35 →28%) in APO and about 38% (12,7 → 7,9%) in DUG. The decrease of zeolite content is accompanied by an overall similar increase of the non crystalline fraction (amorphous) likely linked to the residual undissolved portion of zeolites after their breakdown.

The following treatments with organic liquids of the small and large intestine of the pig, characterized by a physiologic 6,8 pH value, do not define significant variations of the amount of both zeolites in the two investigated materials, well within the analytical error, thus witnessing the good performances of these two minerals under these chemical and physical conditions.

The above reported behavior of the zeolites in acid environment is in good agreement with the results reported by de Gennaro et al. (1983; 1984) for phillipsite and chabazite of the main pyroclastic deposits of Campania region treated with solution at pH ~ 3 by H_2SO_4. Such pH value is very similar to the one measured in gastric solutions (stomach) of pigs (pH= 3÷2 by HCl).

As far as noxious elements are considered (Pb, Cd, As, Hg) their concentrations in the liquids of the three tracts of the pig digestive system (stomach, small and large intestine) are constantly below the detection limits. The only lead shows a very limited release after interaction with the simulated stomach liquids, even lower (one order of magnitude) after interaction with liquids of the small and the large intestine. The recorded concentrations (0,138 mgl^{-1} APO 1 and 0,147 mgl^{-1} DUG 1) are definitely lower than those admitted in animal feeding. Among the other noxious elements only Cd showed values slight above the detection limits.

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May the joint use of natural zeolites and steamed smectites be envisaged in oenological refining process?

M. Mercurio[1], D. L. Bish[2], P. Cappelletti[3], B. de' Gennaro[4], C. Grifa[1], V. Mercurio[5], V. Morra[3] and A. Langella[1]

[1]*Dept. of Sciences and Technologies, University of Sannio, Via dei Mulini 59/A, 82100 Benevento, Italy; E-mail: mariano.mercurio@unisannio.it*
[2]*Dept. of Geological Sciences, Indiana University, 47405 Bloomington, USA*
[3]*DiSTAR, University of Naples Federico II, Via Mezzocannone 8, 80134 Naples, Italy*
[4]*DICMAPI, University of Naples, Federico II, P.le Tecchio 80 Naples, Italy*
[5]*Winemaker, Salita Santa Croce 27, 80053 Castellammare di Stabia, Naples, Italy*

Introduction

Storage and transportation of white wines have always represented a great problem for the oenological companies, as these "operative procedures" require a suitable wine colloidal stability (Ribéreau-Gayon et al., 2004). Since about one century, this result is achieved by using natural minerals, namely bentonites characterized by high content (about 80 wt. %) of dioctahedral smectite (montomorillonite), currently representing the most advantageous procedure for the oenological process, slightly affecting the quality of the product. Such consolidated use (Saywell, 1934; Blade and Boulton, 1988; Achaerandio et al., 2001; Ribéreau-Gayon et al., 2004) resulted in the resolution OENO 11 (2003) of the "Organization Internationale de la Vigne et du Vin" (OIV), which defines the chemical, mineralogical and technological requirements of the bentonite to be suitable for its application to the wine industry. It is well known that, in natural systems such as those characterizing bentonite clay deposits, chemical-physical and mineralogical homogeneities are quite hard to find so that the choice of these materials must be careful in order to avoid the use of batches with features different from those required. The main purpose of the present research is strictly related to this aspect and, in particular, it aims at a suitable and careful characterization of the phases occurring in the bentonite samples used in oenological treatments as well as at the evaluation of the possible variation of surface properties of smectite after a steam treatment which reduces the osmotic swelling of this mineral. So far, the unique scientific research which considered the use of vapor treated bentonite in the oenological sector was carried out by Sarmento et al. (2000) although the material was not characterized and information available were only those provided by the supplier. The same authors conclude that the steamed bentonite was not particularly effective in the protein adsorption process. The open question is: the use of steamed bentonites should be conclusively disregarded in the oenological sector or are there further perspectives of possible utilization?

Experimental Methods

Ten commercial products bearing bentonites (ten samples) used in enologic sector and distributed in Italy have been selected for this research. A quantitative mineralogical (X-Ray Powder Diffraction analysis by Rietveld using Topas) and chemical (ICP-MS) characterization was also carried out on untreated and steam treated specimens according to the method described by Bish et al. (1999). Z-potential was also evaluated before and after the steam treatments to better understand the aspects concerning the surface charges. Some technological features were also identified following some standardized methods (CEC, AEC, BET). To evaluate the protein absorption capacity of unsteamed and steamed samples some adsorption isotherms of Bovin Serum Albumin (BSA), fraction V, were carried out at room temperature using a model wine solution, made of an ethanol solution with K-bitartrate by simulating the relevant conditions for the protein adsorption process: pH, dielectric constant and ionic strength. BSA was dosed in a UV/VIS spectrophotometer (HITACHI U-2000) at 280 nm.

Results and Discussion

XRPD (Table 1) patterns, CEC, and AEC analyses did not evidence significant variations from a mineralogical and technological point of view, thus confirming literature data reporting the marked decrease of the osmotic swelling after the vapor treatment due to a transition of smectite from a hydrophilic to a hydrophobic state. CEC values range between 0.94 and 1.56 mEq/g, typical of clay minerals with good technological properties. AEC values are always equal to zero (before and after the steam treatment). Z-potential ranges between -47 and -27 mV although in some cases the distribution curve of this parameter gave slight positive values, up to 20/30 mV.

As far as the protein adsorption capacities are concerned, significant differences were found out between unsteamed and steamed samples. Starting from a BSA concentration of 500 mg/L in a model wine solution (12 % v/v ethanol; 2 g/L of potassium hydrogen tartrate in distilled water), a total adsorption was achieved using 750 mg/L of unsteamed sample and 2000 mg/L of steamed sample. Such a good result shed new light on the opportunity of the use of steamed smectites in oenological applications, possibly in combination with natural zeolites (Mercurio et al., 2010). Actually, a smectite/zeolite mix design may provide double advantageous effects such as an improvement of the protein stability (by effect of the steamed smectite adsorption) and an optimization of the tartaric stability, due to the high selectivity of phillipsite and chabazite towards potassium.

Table 1. XRPD quantitative analysis by Rietveld using TOPAS of some commercial bentonites used into oenological sector. Mtl=Montmorillonite, Cb=Cristobalite, Gy=Gypsum, Qz=Quartz, Cc=Calcite, Ab=Albite, K-f=K-feldspar, Kl=Kaolinite, Cp=Clinoptilolite

	Mineral phases (wt.%)											
Unsteamed bentonite samples	Mtl	Opal CT	Cb	Gy	Qz	Cc	Ab	K-f	Mica	Kl	Cp	Sum
BT1	89.7			tr.	5.3	tr.	2.4	1.5	1			99.91
BT2	97.9		tr.		tr.		1.2		tr.			99.1
BT3	90.3		1				3.3	5.2	tr.			99.8
BT4	81	9.5	3	tr.	1		2	1	tr.	tr.	1	98.5
BT5	84		4.2				5.9	4.6	1			99.7
BT6	78.6		3.5		3.8		2.7	7.1	2.8	1.4		99.9
BT7	84.5				1.3		8.1	2.1			3.9	99.9
BT8	67.1	7.6	9.2	1.2	7		1.6	1.8	1		3.5	100
BT9	89		3.2		1	tr.	2.2	1.9	tr.		1.5	98.8
BT10	84		9	tr.	1.2		2	2	tr.	1	tr.	99.2

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Effect of zeolites on phosphate rock dissolution: Response Surface Methodology study

M. Mihajlović[1], L. Pezo[2], M. Stojanović[1], M. Petrović[1], J. Petrović[1], Z. Lopičić[1] and T. Šoštarić[1]

[1]Institute for Technology of Nuclear and Other Mineral Raw Materials, 86 Franchet d'Esperey St. Belgrade, Serbia; E-mail: m.mihajlovic@itnms.ac.rs
[2]Institute of General and Physical Chemistry, University of Belgrade, Studentski Trg 12 - 16, Belgrade, Serbia

Introduction

Fertilizer mixtures that combine an ion-exchange agent with phosphate rock (PR) have the ability to retain nutrients in the soil and increase the solubility of PR, thus allowing a slow and sustainable release of major nutrients available to the plants (Barbarick et al., 1990). Beside the phosphate rock, basic components of these mixtures are zeolites loaded with selected cations, such as ammonium ions (Allen et al, 1993). It is suggested that ion-exchange-induced dissolution occurs when plant uptake of NH_4^+ liberates the exchange sites of zeolites, which then are occupied with Ca^{2+} from PR, thereby releasing both phosphate and ammonium ions and inducing further dissolution of PR (Pickering et al., 2002). The aim of this study was to investigate and compare the effectiveness of natural and NH_4-saturated zeolite to increase the solubility of PR using Response Surface Methodology (RSM). Simple regression models have been proposed for calculation of phosphorus concentration as function of proposed process parameters (different experiment duration and different zeolite content in the fertilizer mixture). Analysis of variance (ANOVA) has been applied to show relations between applied assays.

Experimental Methods

Zeolite originating from deposit Baia Mare, Romania (K-clinoptilolite) and phosphate rock (PR), apatite, from ore deposit "Lisina" Bosilegrad, Serbia (containing 10% P_2O_5) were used in the study. Complete mineral characterization of these materials is presented elsewhere (Mihajlović et al., 2013, Radulović 2011). Modification of zeolite with ammonium sulfate was performed according to the procedure described by Mihajlović et al (2013). Zeolite fractions from 50 μm to 100μm and PR fraction of < 37 μm were used. In accordance with literature data, both fertilizer mixtures, PR/NH_4-zeolite and PR/natural zeolite, were assembled in three different ratios: 1:5, 1:10 and 1:15, where each system initially contained 4g of PR (Lai et al 1985, Barbarick et al., 1990). Each mixture was placed in a 300 ml volumetric flask to which was added 200 ml of distilled water. Samples were shaken on a rotary shaker for 24, 48 and 72 h at 220 rpm. After draining, the P content of the resulting solutions was determined using a colorimetric technique. The experimental data used for RSM were obtained using a 3^2 full factorial experimental design (3 level-2 parameter), with 9 runs (1 block). RSM was used to design tests for concentration of released phosphorus in both zeolite systems (P_{SZ} and P_{NZ}), considering two factors: duration of the experiment and zeolite content in the mixture. The following second-order polynomial (SOP) model was fitted to the data. Two models of the following form were developed to relate two responses (Y) and two process variables (X):

$$Y_k = \beta_{k0} + \sum_{i=1}^{2} \beta_{ki} \cdot X_i + \sum_{i=1}^{2} \beta_{kii} \cdot X_i^2 + \beta_{k12} \cdot X_1 \cdot X_2, \ k\text{=1-2} \qquad (1)$$

where: β_{k0}, β_{ki}, β_{kii}, β_{k12}, are constant regression coefficients; Y_k, P_{SZ} or P_{NZ}; X_1 – duration of the experiment; X_2 – zeolite content in the mixture. The evaluation of one-way ANOVA of the obtained results was performed using StatSoft Statistica 10.0® software.

Results and Discussion

Analysis of variance and the following post-hoc Tukey's HSD test were evaluated for comparison of phosphorus release from two types of fertilizer mixtures for different process parameters. The concentration of phosphorus under different processing conditions was found to be statistically significant in almost all samples. The investigated samples are characterized by a relatively high quantity of released phosphorus, especially in the case of increased zeolite weight and reaction time. According to ANOVA (Table 1), all response variables (P_{SZ}, P_{NZ}) are significantly affected by zeolite content in the mixture. The reaction time variable was very influential and was statistically significant at $p<0.05$ level. Linear terms were most influential in the mathematical model (Eqn. 2) and, according to ANOVA, these terms were statistically significant at $p<0.05$ level, 95% confidence limit. To verify the significance of the developed models, coefficients of determinations (r^2) were calculated in ANOVA, and the results indicated that all models were significant with minor lack of fit, suggesting that they adequately represented the relationship between responses and factors. The average error between the predicted values and experimental values (calculated by Eqn. (2)) were below 10%, indicating an adequate fit for practical purposes.

Table 1. ANOVA calculation

	dF	P_{SZ}	P_{NZ}
t	1	0.059*	0.006*
t^2	1	0.003*	0.000
Zeolite	1	0.064*	0.109*
Zeolite^2	1	0.003*	0.000*
t × Zeolite	1	0.004*	0.000
Error	3	0.000	0.000
r^2		0.992	0.999

*Significant at $p<0.05$ level, level 95% confidence limit, error terms were found statistically insignificant

Figure 1 illustrates the three-dimensional graphic of the experimental data, for the purpose of showing the fits of the regression models ($P_{SZ}$and P_{NZ}) to experimental data. All plots showed a "rising ridge" configuration.

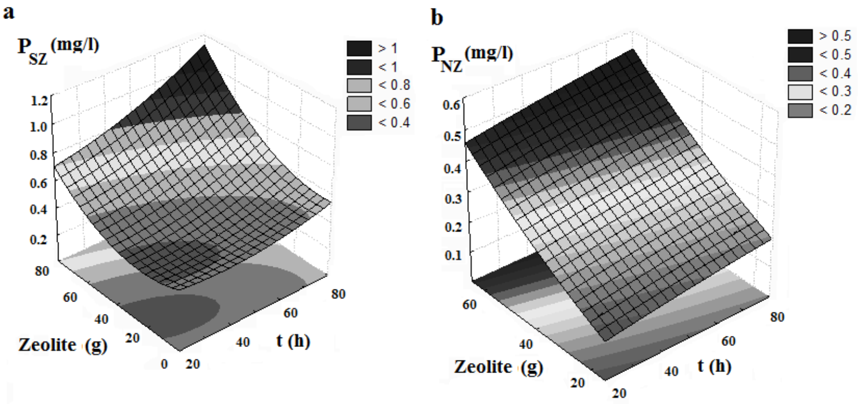

Figure 1. Observed responses affected by processing time and zeolite content in fertilizer mixtures; NH_4^-zeolite/PR (a) and natural zeolite/PR (b)

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Cetylpyridinium chloride functionalized clinoptilolite as efficient adsorbent for pesticide removal

M. Milojević-Rakić[1], B. Nedić Vasiljević[1], A. Jović[1], M. Kragović[2], K. Cvetanović[1], Lj. Damjanović[1] and V. Dondur[1]

[1]*Faculty of Physical Chemistry, University of Belgrade, Studentski trg 12-16, 11158 Belgrade, Serbia;*
E-mail: maja@ffh.bg.ac.rs
[2]*Institute for Technology of Nuclear and Other Mineral Raw Materials, Franše d'Eperea 86, Belgrade, Serbia*

Introduction

Clinoptilolite modification with different surfactants leads to enhanced adsorption properties, when compared to unmodified zeolite, toward different classes of organic molecules. Modified zeolites were effective in diclofenac sodium (Krajišnik et al., 2011) and various mycotoxines adsorption studies (Daković et al., 2005). In this work, we investigated the pesticide removal from aqueous solution by adsorption on clinoptilolite and samples modified with cetylpyridinium chloride (CPC). Glyphosate (N-(phosphonomethyl) glycine) is a broad-spectrum, non-selective systemic herbicide. It is useful on essentially all annual and perennial plants including grasses, sedges, broad-leaved weeds and woody plants. Glyphosate is highly adsorbed on most soils especially those with high organic content (Borggaard and Gimsing, 2008), therefore, improved adsorption behavior should be expected in the presence of CPC-modified zeolite samples.

Experimental Methods

A natural zeolite used in this study was the raw clinoptilolite rich zeolitic tuff (ZVB) from Zlatokop deposit (Vranje, southern Serbia). Cationic surfactant CPC was used for the preparation of functionalized zeolites. The aqueous suspension of initial zeolitic tuff was treated with surfactant amounts equivalent to 50 and 100 % of its external cation-exchange capacity (ECEC-10 meq/100g). The organic phase monolayer and hydrophobic surface are obtained in the sample modified with 100 % ECEC which is denoted as ZCP-10. On the other hand, partially hydrophobic surface was achieved with CPC loading of 50 % ECEC – sample ZCP-5. For determination of the glyphosate adsorption isotherms, dispersions comprising 30 ml of glyphosate standards (concentration in the range 0.1–4.0 g/L) and 50 mg of zeolite and CPC-modified zeolite samples were allowed to equilibrate for 3 h. The dispersions were then centrifuged, filtered through a nylon filter and the amount of glyphosate present in the supernatant was measured by high-performance liquid chromatography (HPLC - Bischoff). The amount of adsorbed glyphosate was calculated from the difference between initial and final glyphosate concentrations. Infrared spectra of the starting zeolitic tuff as well as the obtained composites were recorded in the range of 4000–400 cm^{-1} using a ThermoNicolet 6700 FTIR Spectrometer with 2 cm^{-1} resolution. The samples were dispersed in KBr and compressed into pellets. X-ray powder diffraction (XRPD) patterns were recorded at room temperature on a Philips PW-1710 diffractometer using Cu Kα radiation (λ = 1.54178 Å), operated at 40 kV and 30 mA.

Results and Discussion

The FTIR spectra of clinoptilolite and CPC – modified zeolite samples are presented in. Fig.1a. The FTIR band connected with the internal Si–O(Si) and Si–O(Al) vibrations in tetrahedral or alumino- and silico-oxygen bridges lies in the range of 1200–400 cm^{-1}. The bands due to the presence of zeolite water lie in the range of 1600–3700 cm^{-1}.The characteristic bands are positioned at 3623, 3418 and 1631 cm^{-1} and are assigned to acidic hydroxyls Si–O(H)–Al, hydrogen-bonding hydroxyl groups and deformation vibration of absorbed water, respectively (Korkuna et al., 2006). The bands which correspond to the CPC, associated with C–H stretching vibrations of the hydrocarbon chain are positioned at 2922 and 2852 cm^{-1} (Krajišnik et al., 2011). The relative intensity of surfactant bands increases with increasing CPC content.

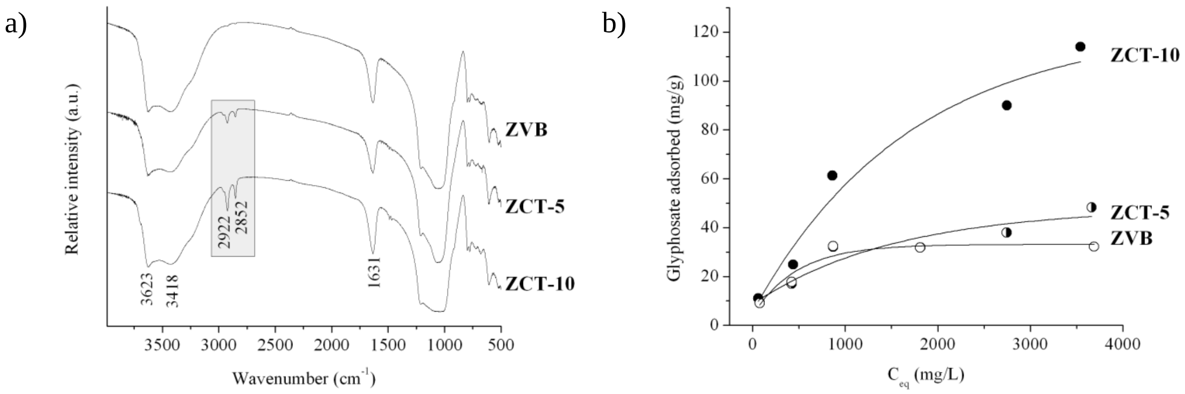

Figure 1. a) FTIR spectra of ZVB and CPC-modified samples and b) Glyphosate adsorption isotherms on ZVB and CPC-modified samples

XRPD patterns showed that zeolite structure was preserved with the introduction of CPC. The presence of clinoptilolite, quartz and plagioclase minerals was identified. Measurements of pH values of the glyphosate/zeolite suspensions and the acid-base equilibria constants of glyphosate confirmed that zwitter-ion and monoanion forms of glyphosate are dominant species. Zeolite modification with CPC improved adsorption characteristics as compared to the pure zeolite, see Fig.1b. Monolayer of organic phase the zeolite surface in ZCT-10 sample enabled adsorption of large pesticide amount - 114 mg of glyphosate per gram of CPC modified zeolite sample. Adsorption behavior of different organic pollutants such as acetochlor and polycyclic aromatic hydrocarbons was also investigated.

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Pesticide adsorption on zeolites, polyaniline and their composites

M. Milojević-Rakić[1], A. Janošević-Ležaić[2], V. Dondur[1] and G. Ćirić-Marjanović[1]

[1]*Faculty of Physical Chemistry, University of Belgrade, Studentski trg 12-16, 11158 Belgrade, Serbia; E-mail: maja@ffh.bg.ac.rs*
[2]*Faculty of Pharmacy, Department of Physical Chemistry and Instrumental Methods, University of Belgrade, Vojvode Stepe 450, 11221 Belgrade, Serbia*

Introduction

N-(Phosphonomethyl)glycine (glyphosate) is a broad-spectrum, systemic, post-emergence, non-selective, herbicide which is widely used for weed control and classified as toxic to aquatic life with long lasting effects (Franz et al., 1997). In order to investigate the possibility of glyphosate removal from aqueous solution, glyphosate adsorption on soils and soil components was thoroughly studied. Polyaniline (PANI) is one of the most important conducting polymers and the removal of various toxic and ecotoxic substances from aqueous media by PANI and its composites has received growing attention in recent years. Herein, we report prospective use of granular and nanostructured PANIs as well as PANI/zeolite ZSM-5 nanocomposites for efficient removal of glyphosate from water. The influence of molecular structure, composition, and morphology of the protonated and deprotonated PANIs and PANI/ZSM-5 composites on their adsorption behavior toward glyphosate is discussed.

Experimental Methods

PANI/ZSM-5 composites designated as PZ1/1, PZ1/5 and PZ1/10 were prepared by the oxidative polymerization of aniline with ammonium peroxydisulfate (APS) in water (without added acid), by using weight ratios HZSM-5/aniline of 1, 5 and 10, respectively (Ćirić-Marjanović et al., 2009; Milojević-Rakić et al., 2013.). Nanostructured PANI was prepared by the same method without added zeolite (Ćirić-Marjanović et al., 2009; Milojević-Rakić et al., 2013). Granular PANI (named PANI/S) and PANI/ZSM-5 composite PZ1/1S were prepared by the oxidative polymerization of aniline with APS in the presence of H_2SO_4, without HZSM-5 and by using weight ratio HZSM-5/aniline=1, respectively (Milojević-Rakić et al., 2013). A portion of all prepared samples was treated with an excess of 5% ammonium hydroxide to transform it to base form. The deprotonated samples have suffix *d* in their name. Morphology of samples was determined by scanning electron microscope (SEM) JOEL JSM-6390LV. FTIR spectra of the powdered samples, dispersed in KBr and compressed into pellets, were recorded using a Nicolet 6700 FTIR Spectrometer (Thermo Scientific). For determination of the adsorbed glyphosate amount, dispersions comprising 5 ml of glyphosate standards (concentration in the range 0.1–4.0 g/L) and 50 mg of PANI or PANI/ZSM-5 composite were allowed to equilibrate. The dispersions were then centrifuged, filtered through a nylon filter and the amount of glyphosate present in the supernatant was measured by high-performance liquid chromatography (HPLC - Bischoff). The amount of adsorbed glyphosate was calculated from the difference between initial and final glyphosate concentrations.

Results and Discussion

While pure PANI prepared in water without added acid contains predominately nanotubes and nanorods, the morphology of protonated PANI/ZSM-5 composites prepared in water was found to be significantly influenced by the initial ZSM-5/aniline weight ratio (Ćirić-Marjanović et al., 2009; Milojević-Rakić et al., 2013). Nanotubes (outer diameter 70–170 nm) and nanorods (diameter 60–100 nm) are still present in the nanocomposite PZ1/1, as seen in Fig. 1a, but their content significantly decreased in PZ1/5. The composite PZ1/10 contains only aggregates of irregular shape and size, similarly to pure HZSM-5. The materials prepared in H_2SO_4 have granular morphology. The deprotonation procedure had no effect on the morphology of studied materials. FTIR spectra showed the shifting of several bands with the increase of zeolite content in the samples (Fig. 1b). The band due to the ring stretching in polaron/bipolaron PANI structures shows a blue-shifting with the increase of zeolite content: 1579, 1580, 1591 and 1593 cm^{-1} for PANI, PZ1/1, PZ1/5 and PZ1/10, respectively. On the other hand, the bands due to the zeolite external tetrahedron-asymmetric stretching and T–O bending in internal tetrahedron show a red-shifting with the increase of zeolite content and appear at 1226, 1225 and 1223 cm^{-1} and 456, 453 and 451 cm^{-1} for PZ1/1, PZ1/5 and PZ1/10, respectively (Milojević-Rakić et al., 2013). These shifts indicate interactions between PANI and zeolite that become more pronounced with the increase of ZSM-5 content.

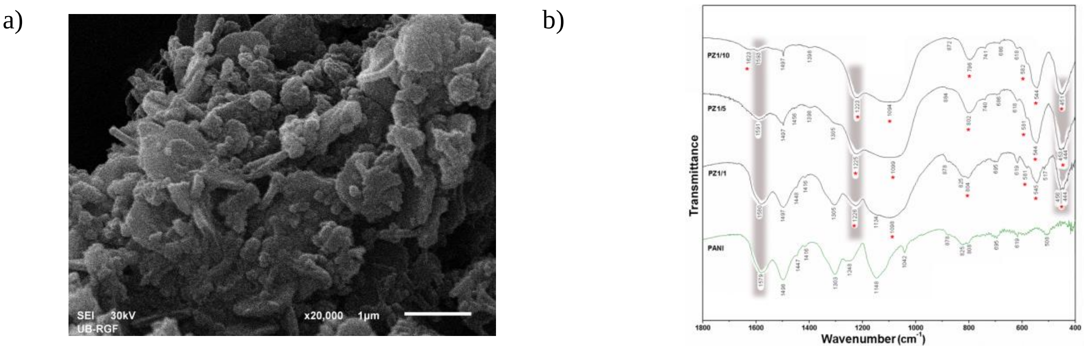

Figure 1. a) SEM image of composite PZ1/1d; b) FTIR spectra of pure PANI and PANI/ZSM-5 composites in their protonated form. The samples are synthesized in water, without added acid. The bands marked with (*) are assigned to the zeolite component of the composites.

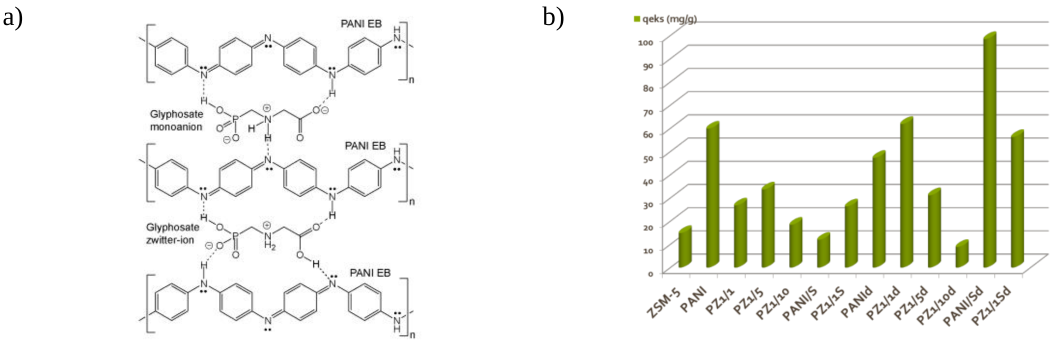

Figure 2. a) Hydrogen bonding interactions between glyphosate zwitter-ion/monoanion and PANI emeraldine base (EB) segments; b) Adsorbed glyphosate amount on PANIs, HZSM-5 zeolite and their composites

Based on pH values of the glyphosate solutions before the addition of adsorbents and acid-base equilibria of glyphosate it was concluded that glyphosate zwitter-ion and monoanion forms are prevalent species which undergo adsorption processes in studied systems. The possible hydrogen bonding interactions of these two glyphosate forms with PANI emeraldine base (EB) are shown in Fig. 2a. Synthesized materials showed high adsorption capacity in the range of 8.9 to 98.5 mg of glyphosate per gram of tested adsorbent (Fig. 2b) (Milojević-Rakić et al., 2013). The most efficient adsorption (q_{exp} = 98.5 mg/g) was achieved by the deprotonated granular PANI, synthesized in solution of H_2SO_4 (PANI/Sd). Very high adsorption capacity was also measured for the deprotonated composite with the lowest content of zeolite, PZ1/1d (q_{exp} = 61.9 mg/g) and the protonated nanostructured PANI (q_{exp} = 59.9 mg/g), both prepared in water. Excellent adsorption characteristics of PANI/Sd were attributed primarily to its regular, linear EB chain structure and homogeneous surface, which enabled good interactions with glyphosate. The applied method enables preparation of synthetic materials with improved adsorption characteristics as compared to the pure zeolite. Obtained results indicate promising application of PANIs and their composites with various zeolites for wastewater treatment.

Acknowledgment

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Cu(II) removal from aqueous solution by a mixture of zeolite and *Myriophyllum spicatum*

J. Milojković, M. Stojanović, M. Mihajlović, Z. Lopičić, M. Petrović, T. Šoštarić and J. Petrović

Institute for Technology of Nuclear and Other Mineral Raw Materials, 86 Franchet d'Esperey St Belgrade, Serbia; E-mail: j.milojkovic@itnms.ac.rs

Introduction

Apart from physical and chemical methods of treatment, biological methods are used as a standard method for wastewater treatment (Gadd, 2009). Conventional methods for removing metal ions from aqueous solution have been proposed, such as chemical precipitation, filtration, ion exchange, electrochemical treatment, membrane technologies, adsorption on activated carbon, evaporation etc. (Wang and Chen, 2009). Mainly, these technologies are expensive and energy-demanding, leading to the search for economically favorable, alternative solutions, both in developed and in less developed countries (Kivaisi, 2001). Biosorption may be simply defined as the removal of substances from solution by biological material (Gadd, 2009). Biosorbents are easy available, low cost with high efficiency, and that is the reason why biomaterials have been intensively investigated as potential materials for removal of heavy metals from wastewater (Wang and Chen, 2009). In many countries, as well as in Serbia, *Myriophyllum spicatum* presents an undesirable aquatic weed which needs to be continuously removed. Since it has been shown that aquatic plants can be used for the removal of heavy metals (Milojković et al., 2013) herein Cu(II) biosorption onto *M. spicatum* was investigated. Physical, chemical and mineralogical characteristics of aluminosilicate mineral raw material - zeolite show a definite sorption properties toward heavy metals and other pollutants, also it is low-cost, widespread and environmental acceptable, so that is the reason why it is extensively used in wastewater treatment and remediation of contaminated land (Bhattacharyya and Sen Gupta, 2006).

In the present study the (bio)sorption efficiency of two different materials: zeolite and *Myriophyllum spicatum* for the removal of copper ions from aqueous solution has been investigated.

Experimental Methods

Zeolite originated from deposit Baia Mare, Romania (K-clinoptiloite) and dry samples of *M. spicatum* from the artificial Sava Lake, Belgrade, Serbia were used in the study. The complete mineral characterization of used zeolite was presented in details (Mihajlović et al., 2013) and characterization of *M. spicatum* was presented in details (Milojković et al., 2013). Particle size of used materials was 100µm. The experiments were carried out in 100 ml Erlenmeyer flasks with 50 ml of copper solution. The flasks were stirred at 250 rpm in a Heidolph unimax 1010 orbital shaker at room temperature. Using a precise pH meter (Sension MM340), the pH value was adjusted to 5 using 0.1 M HNO_3 or 0.1 M NaOH (analytical grade). Concentration of cooper ions in solutions was 100 mg/L, *M/V* ration 4 g/L. In order to examine the influence of the materials on (bio)sorpion of Cu(II) in the mixture the various ratio of zeolite and *M. spicatum* were applied. After the specified contact time, the solid phase was separated from the solution Cu(II) concentration in filtrate was determined with atomic absorption spectrophotometer.

The amount of Cu(II) adsorbed by materials was calculated using equation 1:

$$q = \frac{V(C_i - C_e)}{M} \tag{1}$$

where sorption value q is the amount of Cu(II) adsorbed by materials at any time (mg/g), C_i and C_e are the initial and equilibrium metal concentrations (mg/L), V is the volume of Cu(II) solution (l), and M is the mass of the sorbent (g). Metal removal efficiency (R) is calculated from equation 2:

$$R = \frac{C_i - C_e}{C_i} \cdot 100 \tag{2}$$

Results and Discussion

Comparing the results shown in Table 1 it is evident that the highest level of removal *R* and *q* (bio)sorption capacity had a mixtures: 75%*M.spicatum*+25% zeolite. It can be concluded that the mixture of zeolite and *M.spicatum* has a synergistic effect on the removal of copper ions from aqueous solution. The application of such a material (mixture) is highly preferred because it is efficient, available, low-cost and environmentally friendly.

Table 1. (Bio)sorption of Cu(II) with different amounts of zeolite and *M. spicatum*

(Bio)sorbent	Contact time (h)	C_i initial (mg/L)	C_e equilibrium (mg/L)	Cu removed (mg/L)	*q* (bio)sorption capacity (mg/g)	*R* removal efficiency
M.spicatum	2	94.5	25.53	68.97	17.24	72.98
zeolite	2	94.5	62.83	31.67	7.917	33.51
M.spicatum	1	94.5	37.75	56.75	14.19	60.05
zeolite	1	94.5	71.67	22.83	5.707	24.16
75%*M.spicatum* +25% zeolite	2	94.5	23.66	70.84	17.71	74.96
25%*M.spicatum* +75% zeolite	2	94.5	44.5	50	12.5	52.91
75%*M.spicatum* +25% zeolite	1	94.5	22.33	72.17	18.04	76.37
25%*M.spicatum* +75% zeolite	1	94.5	42.33	52.17	13.04	55.21
50%*M.spicatum* +50% zeolite	2	94.5	29	65.5	16.37	69.31
50%*M.spicatum* +50% zeolite	1	94.5	26	68.5	17.12	72.49

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Interaction of natural zeolites with actinides and lanthanides.

P. Misaelides[1] and A. Godelitsas[2]

[1]*Department of Chemistry, Aristotle University, 54124 Thessaloniki, Greece;E-mail: misailid@chem.auth.gr*
[2]*Faculty of Geology and Geoenvironment, University of Athens, GR-15784 Athens, Greece*

Introduction

The actinides (5f electron elements) have a rather complex chemistry, exhibit multiple oxidation states and form a variety of molecular species (Choppin, 2003). Their presence in the environment is closely related with the production of nuclear energy or the development and testing of nuclear weapons.

Uranium is the most important actinide for the nuclear industry whereas thorium can gain importance in the future. Transmutation and decay of the U-fuels in nuclear reactors generate large amounts of neptunium-, plutonium-, americium- and curium-containing wastes. Smaller amounts of berkelium and californium are also produced. In the case of direct disposal of the consumed fuels to a repository, the uranium, the rest actinides and the fission products remain together until an eventual failure of both cladding and containment allows their gradual leaching by the groundwater. In the case of fuel reprocessing, the most of uranium and plutonium are separated whereas the long lived fission products and the minor actinides are left in the waste. The mixture is then solidified and disposed in the same way as the intact fuel.

The investigation of the environmental chemistry and behavior of the actinides are subjects of extreme scientific and technical interest, because their strong radiotoxicity and their involvement in various geochemical and biogeochemical cycles. The transport of actinides in the biosphere mainly takes place through aquatic pathways and their mobility strongly depends on the geologic environment (site-specific minerals), the temperature and pressure profiles, the pH of the local waters, the redox potential (Eh) and concentration of inorganic (e.g. carbonates) or organic (e.g. humic acids) ligands. The interaction of their dissolved species with the highly sorptive natural microporous materials also influences their migration behavior (Runde, 2000, Maher et al., 2013). Unfortunately, only few studies concerning the geochemical behavior of actinides can be performed in-situ and therefore laboratory experiments are necessary to elucidate their environmental behavior. Laboratory experiments are also necessary in order to evaluate the effectiveness of these materials to act as actinides decontamination agents, as backfill and sealing materials in nuclear repositories and as permeable reactive barriers for cleaning of waters (Misaelides, 2010 and 2011). The chemical processes taking place include sorption through different mechanisms (e.g. adsorption/ surface sorption, absorption/ion exchange, surface precipitation), complexation (mainly with carbonate anions) as well as formation of colloidal- and pseudocolloidal systems. However, the hydrolysis of the actinides plays the determining role in the interaction processes. In general, the solid/liquid distribution coefficients (R_d) measured in a given solution /sorbent system, mostly not taking into account the underlying molecular reaction mechanism, the use of adsorption isotherms and their modelling using semiempirical equations as well as surface-complexation modelling are used for the quantification of the retention in performance assessment calculations.

The natural zeolites gained, among the other natural materials, early attention and were utilized for decontamination and nuclear waste treatment purposes (Misaelides and Godelitsas, 1999). They exhibit high cation sorption capacity and selectivity, enhanced thermal and hydraulic properties and relatively high availability in the nature. The modification of the zeolites by quaternary amines (e.g., HDTMA, ODTMA, N-cetylpyridinium) provide them with ability to sorb anionic species from aqueous solutions (Bowman, 2003). It is well-known that the actinides and lanthanides (4f electron element group) form, in presence of carbonates, a number of anionic carbonato- and hydroxyl-carbonato-species also existing in natural waters.

Almost all lanthanide elements possess stable isotopes (except promethium) and are abundant in the nature. The lanthanides are frequently used, because of their similar chemical behaviour with the actinides, as their analogues in laboratory studies. Especially interesting are the trivalent lanthanides showing the similar behaviour with the highly radioactive and radiotoxic trivalent actinides (e.g. Am(III), Cm(III)).

The literature concerning the interaction of actinides with natural zeolites mainly focuses on the interaction with HEU-type zeolites. This type of zeolites is the most abundant on the Earth. Crystals of HEU-type zeolites constitute, along with clays, the geological formations of locations proposed for geological nuclear waste repositories (e.g., Yucca Mountain, Nevada, USA (Bish et al., 2003).

A previous publication of the same authors (Misaelides and Godelitsas, 1999) reviewed the work performed on the interaction of actinides with natural microporous materials performed up to 1998. This review contains works performed using tuffs but also pure zeolite crystals. The recent works (performed during the last 15 years) on this subject also mainly concerns the interactions of HEU-type zeolitic materials. Only few publications on the interaction of actinides with other zeolitic materials (e.g. chabazitic- and phillipsitic tuffs) recently appeared in the literature (e.g., Al-Shaybe and Khalili, 2009; Misaelides, 2010; Warchoł, 2012). Very limited are also the works concerning the interaction of modified zeolites with anionic actinide species (actinyl carbonato- or hydroxy-carbonato complexes) (e.g. Nikashina et al., 2006, Misaelides et al., 2014).

Rather limited is also the number of recent publications concerning the interaction of lanthanides with natural zeolites. The aim of these works was not only the simulation of the trivalent actinides sorption behavior but also the preparation of fertilizers based on natural zeolites modified by lanthanides. It is well-known that lanthanum, cerium, neodymium, and samarium, exhibit an enhanced biological activity and are used as fertilizers. Lanthanum sulfate catalyzes the fixation of atmospheric nitrogen by Azobacter in legume crops whereas sulfates and nitrates of neodymium and samarium are involved in humus accumulation and activate the nitrogen and carbohydrate metabolism in plants. Recently works on the interaction of La(III), Pr(III), Nd(III), Sm(III) Eu(III), Gd(III) and Tb(III) solutions with clinoptilolitic tuffs as well as of Ce(III) and Sm(III) with mordenite-bearing tuffs appeared in the literature.

The objective of this contribution is to review and comment the research works on the interaction of natural zeolites with actinides and lanthanides that recently appeared in the international scientific literature.

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Neptunium removal from carbonate solutions by a Greek HDTMA-modified HEU-type zeolite containing tuff

P. Misaelides[1], D. Fellhauer[2], X. Gaona[2], M. Altmaier[2] and H. Geckeis[2]

[1]*Department of Chemistry, Aristotle University, 54124 Thessaloniki, Greece; E-mail: misailid@chem.auth.gr*
[2]*Institut für Nukleare Entsorgung (INE), Karlsruher Institut für Technologie(KIT), P.O.Box 3640, D-76021 Karlsruhe, Germany*

Introduction

Neptunium behavior in aquifer systems and its interaction with natural materials are still subjects of great interest because of their environmental relevance and possible connection with the far-field in underground repositories for nuclear waste disposal. Under sub-oxic and oxidizing redox conditions, neptunium is mainly found in its +V redox state. Due to the low effective charge of the neptunyl cation (NpO_2^+, Z_{eff} ~2.3), Np(V) shows weak hydrolysis, high solubility and weak sorption. These properties facilitate its mobility in the environment, which can be further enhanced in the presence of carbonate. Among the natural materials, the zeolites are important and are frequently used as decontamination agents for soils and water basins, backfill and sealing materials in conventional and nuclear repositories and as permeable reactive barriers for cleaning of water (Misaelides, 2011). The zeolites exhibit, compared to the other natural material, high cation sorption capacity, enhanced thermal and hydraulic properties and relatively high availability in many, even economically weak, parts of the world. The modification of the zeolites by quaternary amines (e.g., HDTMA, ODTMA, N-cetylpyridinium) provides them with the additional ability to sorb anions, non-polar organic species and pathogens from aqueous media. Their original cation sorption capacity is also partly retained (Bowman, 2003). The aim of the present work was to investigate the ability of a greek hexadecyl-trimethylammonium (HDTMA)-modified HEU-type zeolite tuff to bind Np(V) anionic species from carbonate solutions. Although a few examples of the sorption of neptunium by natural zeolites have already appeared in the literature (e.g., Triay et al., 1996), the removal of anionic carbonate and hydroxo-carbonate neptunium complexes by surfactant-modified zeolitic materials has not been investigated sufficiently.

Experimental Methods

The tuff used for the experimental work was from Petrota, Thrace, Greece. Its mineralogical composition was 89% (Ca, K) HEU-type zeolite, 3% micas + clays, 6% feldspars and 2% quartz and its total cation exchange capacity (CEC) was 229 meq/100 g (Filippidis and Kantiranis, 2007). The particle size of the material used was <1 mm. The modified form of the tuff was prepared by treating 5 g of the material with 25 mL of 60 mM HDTMABr solution at 60 ^oC for 24 hours (s. also Schick et al., 2010). The neptunium sorption experiments were performed under inert atmosphere (Ar) glove-boxes using ^{237}Np(V) solutions of $2.6 \cdot 10^{-5}$ M concentration. Both HDTMA-modified and raw tuff were utilized for this purpose. Finally, for comparison purposes, Np-sorption experiments using raw pulverized heulandite single crystals from Poona, India were also performed under the same conditions. In order to cover the region of pH6-11, two series of experiments were performed, one using solutions of 0.25 M total carbonate concentration prepared with Na_2CO_3/$NaHCO_3$ buffers and the other of $3 \cdot 10^{-4}$ M carbonate concentration. In the second case MES, PIPES, HEPES and TRIS buffer solutions were used for the adjustment of the pH. The determination of ^{237}Np ($t_{1/2} = 2.144 \cdot 10^6$ years) in the solutions was performed by liquid scintillation (Wallac/ Perkin-Elmer QUANTULUS).

Results and Discussion

The Np-sorption coefficients (($R_d = [Np]_s / [Np]_{aq}$)) for the investigated materials are given in Figure 1. A significantly higher uptake (20–50 times) is observed for the HDTMA-modified tuff (mod. HEU-tuff). For all materials assayed, the uptake was lower at near-neutral pH while showing a maximum at pH ~9 and again decreases at more hyperalkaline conditions. These observations can be interpreted in relation to the aqueous speciation of Np(V) (Figure 2) and the carbonate concentration within this pH-range. Hence, NpO_2^+ and $NpO_2CO_3^-$ species coexist at pH 6- 9 and lower carbonate concentrations (organic buffers), whereas highly charged anions prevail at $9 \leq pH \leq 11$ and $[CO_3]_{tot} = 0.25$ M. The latter species are expected to promote a stronger uptake by the modified tuff. Above pH = 9, the fraction of CO_3^{2-} increases (in detriment of HCO_3^-), thus competing with Np(V) species for the sorption sites of the material and consequently decreasing R_d. The total Np(V)-uptake from solution of high carbonate concentration (Na_2CO_3/$NaHCO_3$-buffered solutions) by the HDTMA-modified tuff varies between 0.24 and 0.35 mg·g^{-1}, whereas the corresponding values for the raw tuff varies between 0.07 and 0.14 mg·g^{-1}. These values, although not especially high, represent a significant decrease of neptunium concentration in solution with respect to the upper solubility limit expected for Np(V) under these conditions (oxidizing, high carbonate concentration) and thus confirm the potential of this material for specific environmental applications.

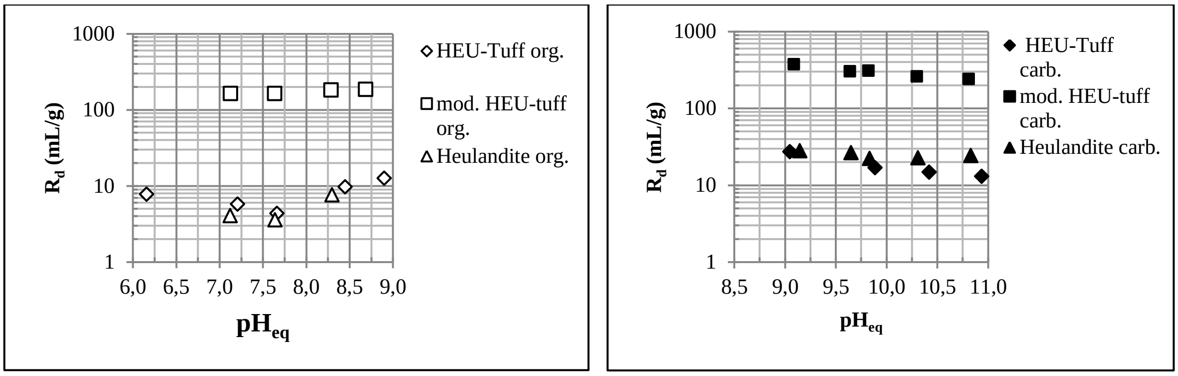

Figure 1. Sorption coefficients for the Np(V)-removal from carbonate solutions (left: 3·10^{-4} M and right: 0.25 M total carbonate concentration) by raw- and HDTMA-modified Petrota tuff and heulandite

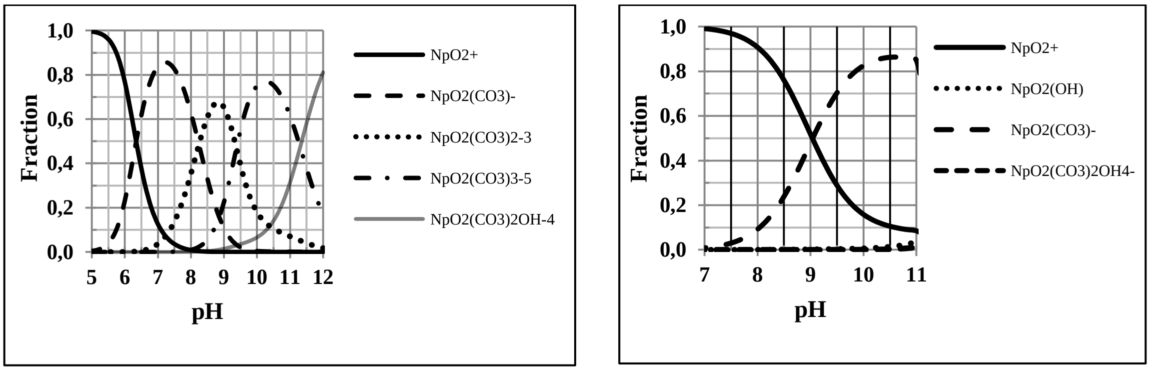

Figure 2. Fraction diagrams of Np(V)-species in solutions of varying pH in the presence of 0.30 mM (left) and 250 mM (right) carbonate. Total Np(V) concentration: 10 μM. Calculations performed with the computer code MEDUSA using data from the OECD-NEA Thermochemical Database for T = 25 °C (Puigdomènech, 1983; Guillaumont, 2003). Ionic strength corrections performed using the extended Debye-Hückel approach

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Thorium removal from carbonate solutions by HDTMA-modified HEU-type zeolite-, chabazite- and phillipsite-bearing tuffs

P. Misaelides[1], X. Gaona[2], M. Altmaier[2] and H. Geckeis[2]

[1]*Department of Chemistry, Aristotle University, 54124 Thessaloniki, Greece; misailid@chem.auth.gr*
[2]*Institut für Nukleare Entsorgung (INE), Karlsruher Institut für Technologie (KIT), P.O. Box 3640, D-76021 Karlsruhe, Germany*

Introduction

Thorium is a primordial radioactive element. Its most stable isotope, ^{232}Th, has a half-life of $1.41 \cdot 10^{10}$ years. The presence of thorium in the environment is not only due to natural reasons but also to a number of human activities including the power production (both nuclear and conventional) and the production and use of phosphate fertilizers. Released thorium can be transferred in the geosphere through aquatic pathways and endangers human health (ATSDR, 1990). Therefore, the interaction of thorium with rocks and minerals and its removal from water and wastewater is still subject of enhanced scientific interest. The most stable redox state of Th is +IV, which shows a strong tendency to hydrolyze above pH = 2 forming both mononuclear (e.g., $ThOH^{3+}$, $Th(OH)_2^{2+}$ and $Th(OH)_3^{+}$) and oligomeric species of the general type $Th_x(OH)_y^{(4x-y)}$. The number of hydroxyl ligands depends on the Th concentration and strongly rises with increasing pH. In carbonate containing solutions, Th forms a series of carbonato- and hydroxy-carbonato- complexes of the general type $Th(OH)_y(CO_3)_z^{4-y-2z}$ (e.g. $Th(CO_3)_5^{6-}$, $ThOH(CO_3)_4^{5-}$, $Th(OH)_2(CO_3)_2^{2-}$ and $Th(OH)_4(CO_3)_2^{-}$). The formation of these species is strongly dependent on the pH and carbonate concentration. Several methods have been proposed for Th-removal from water and wastewater including solvent extraction, ion-exchange and adsorption by natural and synthetic zeolites, raw- and modified clays, biosorbents, carbons etc. Among the natural inorganic sorbents, the zeolites are important and are frequently used as decontamination agents for soils and water basins, backfill and sealing materials in conventional and nuclear repositories and as permeable reactive barriers for cleaning of ground-waters. The zeolites, because of their negatively charged surface, exhibit high efficiency in sorbing cationic species. The modification of their surface using quaternary amines (e.g., HDTMA, ODTMA, N-cetylpyridinium) provides them with the additional ability to sorb anions, non-polar organic species and pathogens from aqueous media. Their original cation sorption capacity is also partly retained. The objective of the present work was to investigate the ability of three HDTMA-modified zeolitic materials (HEU-type zeolite-, chabazite- and phillipsite-bearing tuffs) to remove thorium from alkaline carbonate-rich aqueous solutions. Although a few examples of thorium sorption by natural zeolites have already appeared in the literature, the removal of anionic carbonate and hydroxy-carbonate thorium complexes by surfactant-modified zeolitic materials has not been investigated.

Experimental Methods

The following zeolitic materials were used for the experimental work:

1. Tuff from Petrota, Greece, containing 89% HEU-type zeolite (Filippidis and Kantiranis, 2007).
2. Chabazite-rich tuff from the Vesuvio area, Italy, supplied by G. Apostolico & C. Tanagro (http://www.atzzeoliti.it/zeolites.htm). Max. zeolite content: 79% (incl. small amounts of phillipsite).
3. Phillipsitic tuff from the Naples area, Italy, marketed by I.Z. as PHIL-75.

Mineralogical composition: phillipsite 46%, chabazite 5%, analcime 9%, smectite 10% plus 30% of non-exchanging phases (Jucolano, 2005). The modified form of the tuffs was prepared by treating 5 g of the material with 25 mL of 60 mM HDTMABr solution at 60 °C for 24 hours. The sorption experiments were performed using 9.7×10^{-5} M ^{232}Th(IV) in carbonate solutions between pH 9.0 and 10.8 ($Na_2CO_3/NaHCO_3$ buffering; total carbonate concentration 0.25 M). The solid to liquid ratio was 10 $g \cdot L^{-1}$ and the contact time 48 hours. The Th-determination was performed by ICP-MS (Perkin-Elmer, Elan 6100).

Results and Discussion

Th sorption coefficients ($R_d = [Th]_s / [Th]_{aq}$) for the zeolitic materials are given in Figure 1. A very high sorption was observed for the modified tuffs at pH 9 where the predominance of highly charged anions

($Th(CO_3)_5^{6-}$ and $ThOH(CO_3)_4^{5-}$, see Figure 2) promotes the strong uptake by the HDTMA-modified materials. The decrease of R_d with increasing pH values can be explained by the increase of [CO_3^{2-}] in solution and the consequent competition for the sorption sites of the modified tuffs. The increase in sorption observed at pH > 10.5 is attributed to the precipitation of the $Th(OH)_4$(am) solid phase. This hypothesis is further confirmed by the similar R_d values obtained with the unmodified materials (Figure 1). These results highlight the potential of the materials evaluated for specific environmental applications.

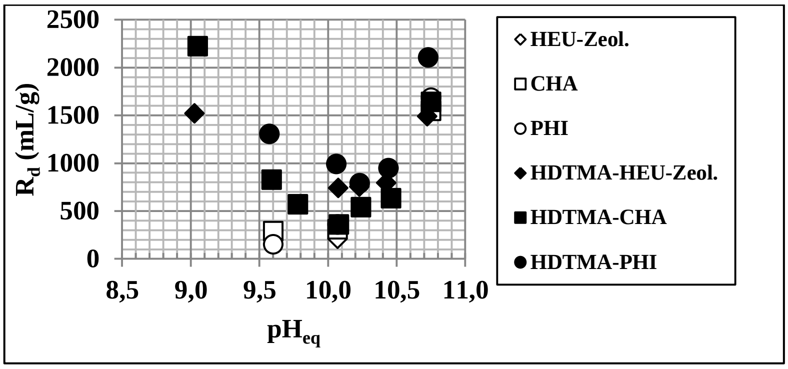

Figure 1. Sorption coefficients for the Th(IV)-removal from carbonate solutions by the raw- and HDTMA-modified HEU-type zeolite-, chabazite- (CHA) and phillipsite- (PHI) tuffs (Th conc.: 9.7 10^{-5} M; carbonate conc.: 250 mM)

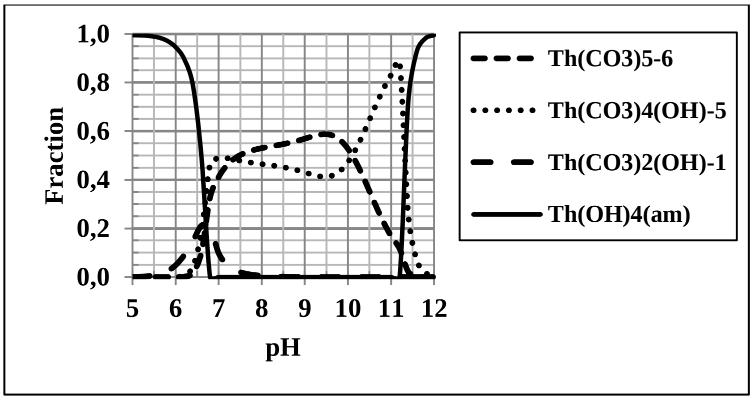

Figure 2. Fraction diagrams of Th calculated for 5<pH<12 and $[CO_3^{2-}]_{tot} = 0.25$ M and $[Th]_{tot} = 10^{-4}$ M. Calculations performed using the code MEDUSA and the OECD-NEA Thermochemical Databank for T = 25 °C (Puigdomènech, 1983; Rand et al., 2009)

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The use of organozeolite in broilers for uranium protection

B. M. Mitrović[1], G. Vitorović[1], M. Stojanović[2], A. Daković[2], N. Krstić[1], M. Lazarević-Macanović[1], V. Andrić[1] and D. Vitorović[3]

[1]Faculty of Veterinary Medicine, University in Belgrade, Bulevar Oslobođenja 18, Belgrade, Serbia; E-mail: slavatab@vet.bg.ac.rs
[2]Institute for Technology of Nuclear and Other Mineral Raw Materials, 86 Franche d'Epere 86, 11000 Belgrade, Serbia
[3]Faculty of Agriculture, University of Belgrade, Nemanjina 6, 11080 Belgrade, Serbia

Introduction

Mineral supplements, such as monocalcium and dicalcium phosphate, are a major source of uranium in animal feed. Dicalcium phosphate may contain uranium from 30 to 200 ppm (corresponding to an activity range from 388 to 2,444 Bq/kg) (Arruda-Neto et al, 1997), as we are established to our measurements (Mitrović et al, 2013). The contamination of animals with uranium may occur by ingestion, inhalation and transcutaneous. Ingestion is a major pathway for animals contamination with uranium, because phosphate mineral supplements are added in animal feed. Contamination of animals through ingestion of uranium began in the earliest period of life (cows, pigs, sheep immediately after weaning), usually through dicalcium phosphate, and it is up to the slaughter. Uranium is a radioactive and chemical toxic heavy metal. After the contamination, the primary target organ for uranium in broilers is kidney (Mitrović et al., 2013), where were observed histophatological changes.

Natural and modified zeolite can be use as an adsorbent of micotoxins (Rizzi et al., 2003), radionuclides (Mitrović et al, 2012, 2013) and heavy metals (Papaioannou et al. 2005).

The aim of present study was to investigation the distribution of uranium (uranyl nitrate hexahidrate, UN) in meat and organs of broilers after a 7-day contamination with 50 mg/UN per day, and to determine the possibility of protection using organozeolite.

Experimental Methods

The zeolitic sample used in these experiments was from the Beočin deposit (Fruška Gora, Serbia). It mainly consists of heulandite with smaller amounts of quartz, feldspar, and calcite. The organozeolite was prepared by treatment with hexadecyltrimethylammonium chloride (HDTMA) supplied by Hoechst AG (Germany). The procedure for preparation of organozeolite was described by Matijašević et al. (2006).

Experiments were performed on thirty-five-day-old broilers of linear hybrid Hybro, showing a mass of about 1,000 g. By the method of the random sampling, 12 broilers were selected and divided into 2 experimental groups. Food and water intake were ad libitum. The broilers in control group (1) were contaminated via gastric tube, with uranyl nitrate water solution ($UO_2(NO_3)2\cdot 6H_2O$) (Sigma-Aldrich Co.), in quantity of 50 mg UN/per day. After UN contamination, the broilers in group 1 received 0,2g organozeolite per day (OZ), immediately after contamination. On the eighth day, the birds were stunned and then killed by cervical dislocation, and uranium concentration was determined in muscle, kidney, liver, and brain of broilers.

Uranium content in the initial solution, filtrate, muscle and organs of broilers (kidney, liver, brain) was determined by fluorometry based on the fluorescence of uranium in a fused mixture of NaF, Na_2CO_3, and K_2CO_3, on a ''Jarrell Ash 26-000 Division''. Uranium extraction process and method were described previously (Mitrović et al, 2013).

Results and Discussion

After the contamination of broilers with UN (50 mg/per day), was observed significant distribution of uranium in kidney (Table 1). Our previous studies, with lower uranium doses, have also shown that kidneys are target organs for uranium in broilers (Mitrović et al, 2013). Physiological characteristics of the kidney to reabsorb and accumulate divalent metals, makes kidney target organ in the state of intoxication with heavy metals (Kurttio et al., 2002). Soluble forms of uranium, within 24-48h excreted from the body and leads to the temporary accumulation in the kidney of rats (Zhu et al., 2008).

Uranium concentration in liver was 1,8 times lower than in kidney. In brain, uranium concentration was 4,7 times lower than in kidney and 2,6 times lower than in liver. Ozmen and Yurekli (1998) investigated the subacute toxicity of uranium in mice, and they reported that are uranium deposits in the brain. After the UN contamination and protection with organozeolite, uranium concentration in organs was significantly lower. By administering of organozeolite we achieved a reduction of uranium distribution in organs. In liver, the application of organozeolite reduced uranium concentration by 92%, in kidney 86% and in brain 37%.

Compared to the organs, the distribution of uranium in muscle was low, and the application of organozeolite reduced uranium concentration by 31%.

Table 1. Uranium residues in muscle and selected organs of broilers (μg/g)

Group	Muscle	Kidney	Liver	Brain
UN control (group 1)	0.16±0.05	4.32 ±1.15	2.35±0.15	0,92±0.07
UN + OZ (group 2)	0.11±0.02	0.61±0.06	0.18±0.05	0,58±0.14

Chickens in intensive production grown under strictly controlled environmental conditions, so that each feed component and feed supplement used in the diet, should be subjected to detailed control. In all situations where there may be a risk of alimentary contamination with uranium, the use of organozeolite is therefore recommended.

Acknowledgment
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Thermal analysis of Philippine natural zeolites

F. M. Mulimbayan, E. M. Olegario-Sanchez and R. B. Cervera

Department of Mining, Metallurgical and Materials Engineering University of the Philippines, Diliman, Quezon City, Philippines; E-mail: eleanor.olegario@gmail.com

Introduction

Zeolites are microporous, inorganic materials which have found extensive use as catalysts, adsorbents and ion exchangers (Cruciani, 2006). In its structure, three main components are found – aluminosilicates framework, extra framework (EF) cations and zeolitic water (Wang et. al., 2010). Among these three, aluminosilicates framework is the most stable component that defines the type of zeolite structure and are built from infinitely extending three-dimensional network of tetrahedral of silica $[SiO_4]^{4-}$ and alumina $[AlO_4]^{5-}$ that are linked to each other by sharing of oxygen atoms (Georgiev et. al., 2009). The framework structure contains linked channels or interconnected voids with pore sizes roughly between 3 and 10 Å occupied by EF cations and zeolitic water. Each tetrahedron bears a net negative charge that is balanced by these EF cations either monovalent or divalent located together with zeolitic water (Wang et. al., 2010). EF cations are delocalized and typically subjected to ion exchange if exposed to aqueous environment while zeolitic water may be reversibly removed through application of heat (Van et. al., 2011).

The structural formula of a zeolite is based on the crystallographic unit cell, represented by:

$$M_{x/n}\,[(AlO_2)_x(SiO_2)_y\cdot wH_2O] \tag{1}$$

Here, n is the charge of alkali or alkaline earth EF cations, w is the number of water molecules per unit cell, x and y are the total number of tetrahedral atoms per unit cell. The y/x ratio indicates the Si/Al ratio and its value usually ranges from 1 to 5 or 10-100 for high silica zeolites (Georgiev et. al., 2009). The type and density of the EF cations influence the stability of the cavities and the thermal behavior of a zeolite. When subjected to heat, zeolites with higher Si/Al ratios will tend to have higher crystal structure stability (Ates et. al., 2012). Vezzalini (1984) grouped zeolites according to the structural changes caused by dehydration process: (I) those with reversible dehydration accompanied by rearrangement of EF cations and residual water molecules without remarkable changes in the framework and in the cell volume, (II) those which exhibit complete or nearly complete reversible dehydration accompanied by a strong distortion of the framework and a large decrease of the cell volume and (III) those with dehydration accompanied by topological changes in the framework, as a consequence of the breaking T-O-T bridges. Evoking that each O atom is shared between two T atoms where T is either Si^{4+} or Al^{3+}. This study primarily aims to initially investigate the thermal behavior of Philippine natural zeolites to know and understand its thermal properties as basis for further applications such as building stone, lightweight aggregate, ceramic foam, concrete bricks and pozzolanic additive.

Experimental Methods

Zeolite samples were taken from Mangatarem, Pangasinan, Philippines. Using a Micromill machine, zeolites were ground until particles were of 200 to 325 mesh size. The resulting powdered sample was sun dried and then subjected to chemical analysis using Atomic Absorption Spectroscopy (AAS), UV-Visible Spectroscopy (UV-Vis), wet analysis technique and oven-dry method. It was characterized by recording the XRD patterns on a diffractometer. To assess the thermal behavior of the zeolitic sample, thermal characterization methods such as thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed. For TGA, the sample was mounted in a thermogravimetric analyzer (Shimadzu TGA-50) from room temperature to 1000°C under air atmosphere. For DSC, another sample was mounted to a differential scanning calorimeter (TA instrument DSC Q10) in which temperature was increased from room temperature to 550°C under N_2 atmosphere. Both TG and DSC were performed at a heating rate of 10°C/min with flow rate of 50 mL/min.

Results and Discussion

The XRD pattern analysis in Fig. 1 (a) shows that the sample zeolite is mainly composed of mordenite with d-values at 9.02 (1), 3.97 (0.70), 3.47 (0.45) and trace amounts of quartz with d-values at 3.20 (1), 4.51 (0.22), 1.88 (0.14) and hematite with peaks at 2.97 (1), 1.69 (0.60), 2.28 (0.50).Based from the result of the chemical analysis done, the silica and alumina content of the zeolite sample are 61.93 and 11.62%, respectively, resulting to silica-to-alumina (Si/Al) ratio of 5.33. Cruciani (2006) observed that: (i) zeolites with Si/Al ratio ≥ 3.80 are very stable, (ii) zeolites with Si/Al ratio ≤ 1.28 are quite unstable and; (iii) zeolites stability in the intermediate Si/Al range cannot be directly predicted from Si/Al ratio. Thus, based from the Si/Al ratio, the zeolite sample is considered thermally stable. Increased in Si/Al ratio implies more energy requirement to break the Si-O bond compared to al-O bond. Thermal stability is therefore dictated by relative amount of silica and alumina in which higher silica content results to higher stability.

Fig. 1b shows the TGA result showing the weight loss as the sample is subjected to higher temperature. As observed in Fig. 1b, TG curve depicts a gradual weight loss which can be attributed to evaporation or dehydration of water in the zeolite structure. It can be said that mordenite, which is the main component of the natural zeolite, exhibits reversible dehydration showing no modification in its framework; thus falling under category I.

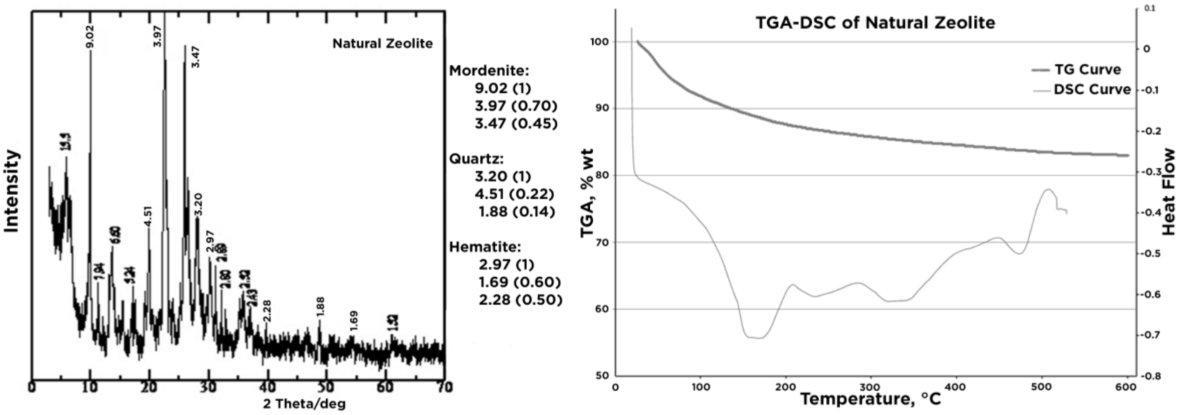

Figure 1. (a) XRD (left) and (b) Overlay of TG and DSC plot (right) of heat treated Philippine natural zeolite

Based from DSC (Fig. 1b), it was found out that there are three types of water that evaporate during heating, as depicted by the endothermic peaks – surface, loosely-bound and tightly-bound zeolitic water. The major loss of water occurred at the first stage at 154.82°C with enthalpy of 68.38 J/g due to evaporation of water on the surface. The second stage resulted in the evaporation of loosely bound water in the zeolitic structure while the last stage can be associated with the evaporation of tightly-bound water 600°C - 1000°C. Hence, according to the weight loss observed from TG and DSC analysis, evaporation of water is the major reaction taking place in the zeolite sample as the temperature is increased.

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Removal of ammonium ion from aqueous solution by natural zeolite

D. Munkhjargal[1], R. Ulambayar[2], J. Oyuntsetseg[2], L. Tsogtzandan[3], R. Lkhagvajav[4]

[1] Mongolian National University, Mongolia; E-mail: munkhjargal26@yahoo.com
[2] Minerlogy and Hydro-Chemical Laboratory. Institute Chemistry and Chemical Technology, Mongolian Academy of Science, Ulaanbaatar, Mongolia; E-mail: oyuntsetsegj@yahoo.com
[3] Mongolian International University
[4] Khunnu Sunnu Co.Ltd

Introduction

The aim of the present study is to investigate that ammonium ion removal from aqueous solution by using natural Mongolian clinoptilolite.

The country of Mongolia has large deposits of volcanic materials containing zeolites. These natural zeolites have similar ion-exchange capacities as artificial zeolites. A Mongolian – Soviet geologic expedition has found more than 30 deposits of natural zeolites in Mongolia. Among these deposits the biggest one, namely the Urgun deposit zeolite.

This study assessed Urgun natural zeolites which had been converted to Hydrogen and Sodium form. The effect of relevant parameters, such as pH, adsorbent dosage, contact time and initial ammonium concentration were examined, in batch experiment. The result shows that the pH affects the ammonium removal efficiency because it can influence both the characterofthe exchanging ions and the clinoptilolite itself.

Ammonia nitrogen contributes to accelerated eutrophication of lakes and rivers, dissolved oxygen depletion and fish toxicity in receiving water. The most widely used traditional processes ammonia removal are air stripping, ion exchange and biological nitrification-denitrification. The efficiency of the process of air stripping, and biological nitrification- denitrification is significantly impaired by the low temperature in winter. Ion exchange, therefore, is more competitive because of little influence of the low temperature in winter in the of Mongolia and particularly its relative simplicity of application and operation. In our country, wastewater treatment plant effluent in ammonium permissible level most during the year in excess of the Environment and metrology lab report shows [1]. Therefore, it is necessary to reduce the ammonium contents.

Clinoptilolite, one of natural zeolites, has been found very effective in removing ammonia from water by means of its excellent ion exchange capacity since the seventies of last century. Natural zeolite is porous material with high cation exchange capacity (CEC), cation selectivity, higher void volume and great affinity for NH_4^4 [2]. The general formula of a zeolite is follows:

$$(M_x^+, M_y^{2+})\ (Al_{(x+2y)}\,Si_{\,n-(x+2y)}\,O_{2n}) \cdot mH_2O \qquad (1)$$

Where M^+ and M^{2+} are monovalent and divalent cations such as Na^+, K^+ and Ca^{2+}, Mg^{2+}, Ba^{2+} respectively. Thee are called the exchangeable cations. Al^{3+} and Si^{4+} are known as the structural cations, and they make up the framework of the structure with oxygen[2]. In several studies, authors have also reported the use of natural zeolite as a sorbent for trace metals, N compounds and cations [3-9]. The main objectives of this study were to investigate the effect of pH, dosage of adsorbent and shaking time on ion exchange of NH_4^+ by the natural Mongolian (Urgun deposit) zeolite from aqueous solution and determine the equilibrium isotherms. In batch study, the effect of relevant parameters, such as pH, adsorbent dosage, contact time and initial ammonium concentration were examined, respectively. The results snow that the pH has an effect on ammonium removal efficiency as it can influence both the character of the exchanging ions and the clinoptilolite itself, ammonium removal by clinoptilolite occurs rapidly within first 15 min of contact time, the ammonium removal capacity of clinoptilolite increases with increase of initial ammonium concentration. The Langmuir and Freundlich model were applied to describe the equilibrium isotherms for ammonium uptake and the Freundlich model (R^2=0.99) agree very well with experimental data. Based on the results, it can be concluded that the natural zeolite is suitable for the removal of NH_4^+ ions in wastewater treatments.

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Comparison of linear and non-linear Ho pseudo-second-order models for the sorption of copper ions on synthesized geopolymer

M. N. Mužek, S. Svilović and J. Zelić

Faculty of Chemistry and Technology, University of Split, Teslina 10/V., 21 000 Split, Croatia;
E-mail: muky@ktf-split.hr

Introduction

Sorption processes have been proved to be an effective method for the removal of various pollutants such as heavy metals and dyes from wastewaters. Therefore, the prediction of batch sorption kinetics is important for sorption processes design.

In previous work (Mužek et al., 2013), the Ho pseudo-second-order model showed the best fitting with experimental data gained for the sorption of copper ions on synthesized geopolymer. For that reason, a comparison of five different linear forms and one non-linear form of the Ho pseudo-second-order model was made in the present study in order to obtain the optimum sorption kinetic parameters using the experimental kinetic data obtained for the sorption of copper ions on synthesized geopolymer.

Experimental Methods

The chi-square test χ^2 was used to test the agreement of linear and non-linear forms of the Ho pseudo-second-order model (Ho and McKay, 1998, Kumar, 2006). The least square method was used to obtain parameters of the linear forms of the Ho pseudo-second-order model and non-linear regression for the parameters of the non-linear form.

Results and Discussion

Comparison of linear and non-linear forms of the Ho pseudo-second-order model for various concentrations

Table 1. The calculated parameters of the Ho pseudo-second-order model for copper ions sorbed on geopolymer by linear and non-linear regression analysis for various initial concentrations

Models / Parameters			3.881 mmol dm^{-3}	5.915 mmol dm^{-3}	7.780 mmol dm^{-3}	9.898 mmol dm^{-3}	11.763 mmol dm^{-3}
		$q_{eexp.}$	0.775	1.058	1.099	1.114	1.136
L 1	$\frac{t}{q_t}=\frac{1}{k_2q_e^2}+\frac{1}{q_e}t$	q_e	0.770	1.063	1.108	1.126	1.153
		k_2	25.7345	0.999	0.719	0.691	0.567
		χ^2	0.013	0.174	0.294	0.233	0.376
L 2	$\frac{1}{q_t}=\left(\frac{1}{k_2q_e^2}\right)\frac{1}{t}+\frac{1}{q_e}$	q_e	0.778	1.017	1.033	1.045	1.047
		k_2	9.136	2.115	1.807	1.568	1.455
		χ^2	1.760×10^{-3}	0.014	0.032	0.044	0.070
L 3	$\frac{1}{t}=\frac{k_2q_e^2}{q_t}-\frac{k_2q_e^2}{q_e}$	q_e	0.780	1.026	1.051	1.069	1.082
		k_2	8.408	1.920	1.521	1.292	1.114
		χ^2	0.450	0.564	0.160	0.165	0.413
L 4	$\frac{q_t}{t}=k_2q_e^2+k_2q_eq_t$	q_e	0.780	1.033	1.064	1.085	1.105
		k_2	8.542	1.782	1.357	1.138	0.952
		χ^2	0.341	9.066×10^{-3}	0.185	0.132	0.072
L 5	$q_t=q_e-\left(\frac{1}{q_e}\right)\frac{q_t}{t}$	q_e	0.778	1.023	1.044	1.060	1.067
		k_2	9.430	1.992	1.651	1.412	1.279
		χ^2	1.069×10^{-3}	0.014	0.035	0.048	0.077
NL	$q_t=\frac{t}{\frac{1}{k_2q_e^2}+\frac{t}{q_e}}$	q_e	0.783	1.031	1.061	1.084	1.100
		k_2	9.544	1.776	1.358	1.111	0.933
		χ^2	9.624×10^{-4}	0.010	0.025	0.033	0.054

Comparison of linear and non-linear forms of the Ho pseudo-second-order model for various temperatures

Table 2. The calculated parameters of the Ho pseudo-second-order model for copper ions sorbed on geopolymer by linear and non-linear regression analysis for various temperatures

Models / Parameters		298 K	308 K	318 K
	$q_{eexp.}$	1.136	1.183	1.217
L 1	q_e	1.153	1.191	1.225
	k_2	0.567	0.568	1.067
	χ^2	0.376	0.466	0.071
L 2	q_e	1.047	1.101	1.185
	k_2	1.455	1.550	1.856
	χ^2	0.070	0.035	9.072×10^{-3}
L 3	q_e	1.082	1.123	1.194
	k_2	1.114	1.297	1.714
	χ^2	0.413	0.158	0.107
L 4	q_e	1.105	1.138	1.200
	k_2	0.952	1.157	1.613
	χ^2	0.072	8.179×10^{-3}	0.107
L 5	q_e	1.067	1.114	1.191
	k_2	1.279	1.413	1.763
	χ^2	0.077	0.044	0.013
NL	q_e	1.100	1.135	1.200
	k_2	0.933	1.146	1.600
	χ^2	0.054	0.029	8.921×10^{-3}

Linear forms are more or less successful in describing the sorption process of copper ions on geopolymers. Linear form L 2 of Ho pseudo-second-order is the most suitable; values of χ^2 – test are the lowest ones and maximum amount of copper retained on geopolymer, q_e is in a good accordance to the experimental values of maximum amount of copper retained on geopolymer.

Values of χ^2 – test for non-linear form are much lower than ones gained for linear forms of Ho pseudo-second-order-model and q_e values are in better agreement with those gained experimentally.

Taking all the results into consideration, the non-linear form of the Ho pseudo-second-order model proved to be more efficient in describing sorption of copper ions on geopolymer for various initial concentrations of sorbent, as well as for various temperatures.

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Removal of acid red 37 from waste water using modified zeolite with apolaccase enzyme

H. Nadaroglu[1], E. Kalkan[2] and N. Celebi[1]

[1]*Ataturk University, Erzurum Vocational Training School, Chemistry Department, 25400 Erzurum, Turkey; E-mail: hnisa25@atauni.edu.tr*
[2]*Ataturk University, Oltu Erath Sciences Faculty, Geological Engineering Department, 25240 Oltu-Erzurum, Turkey*

Introduction

Industries like plastic, tannery, packet, food, paint, paper, pulp and textile ones are abundantly using more than 10.000 synthetic dyes (Noroozi *et al*., 2007). Only textile dyes are produced in more than 7×10^5 tons per year (Nagda and Ghole 2008). The using dyes were released to be waste 10-15% at the result of the production process (Guivarch 2003). Waste dyes are very dangerous for ecology, health, and environmental being toxic and causing cancer. Todays, the decolorization of dyes from waste water is very important and attractive for study because they can be with hazardous effects. In this study, removing of Acid red 37 from aqueous solutions has been studied using zeolite waste material after its modification with laccase from Russulaceae *Lactarius volemus*. Laccase was purified by using saturated precipitate $(NH_4)_2SO_4$, DEAE-cellulose and immobilized on zeolite. Adsorption isotherm and kinetic studies have been performed to describe the adsorption process.

Experimental Methods

Acid Red 37 dye was purchased from Sigma-Aldrich Co. Ltd. The natural zeolite was collected from open pit mine in Gördes (Manisa) (West Anatolia). The zeolite material was first sieved through sieve and then washed with distilled water. The washed material was heated at 100±5 °C for 24 h. The solid fraction was washed five times with distilled water following the sequence of mixing, settling, and decanting. The last suspension was filtered and the residual solid was then dried at 105ºC, ground in a mortar, and sieved through a 200-mesh sieve. The product was used in the study. Synthetic wastewater was prepared by dissolving Acid Red37 (AR37) dye. The absorbance of the solutions was measured at 504 nm with spectrophotometre (PG Instrument T80 Spectrophotometer). A calibration curve was prepared in the range 0-40 $mgmL^{-1}$ of AR37 dye according to the general procedure.

Results and Discussion

AR37 dye is dissociated anionic sulfonate in aqueous solution with a molecular structure. It is used mainly in dyes for wool manufacturing, wood coatings, silk and leather (Greluk and Hubicki, 2010; Won *et al.,* 2006). The chemical structure and the general characteristics of AR37 are summarized in Table 1, respectively.

Table 1. General characteristics of AR37 dye

Chemical formula	Molar mass	Color index number	λ_{max}
$C_{18}H_{14}N_4Na_2O_8S_2$	524.44 g/mol	17045	504 nm

In the study, laccase was purified from *Lactarius volemus* in two steps. Firstly, it was partially purified by precipitation 40-60% in $(NH_4)_2SO_4$ was dialyzed against 0.2 M phosphate buffer (pH: 7,0) which contains 0,075 M dipicolinic acid. By this approach almost 100% pure apoenzyme was obtained (Demir *et al.,* 2005).
The effect of apolaccase immobilized on zeolite was studied by varying surface material concentration (0.0125-0.2 mg). The activity of this catalyst to decolorize AR37 was tested by different parameters such as contact time from 0 to 360 min (Fig 1). The amount of the removal increased with the increase of the contact time and reached a constant value. This may be due to the attainment of equilibrium condition at 60 min of contact time, which is fixed as the optimum contact time.
The effect of pH in the range 3-9, optimum temperature in the range of 20-80 °C (Fig. 1) was obtained in initial concentration of AR37 (Fig. 1).

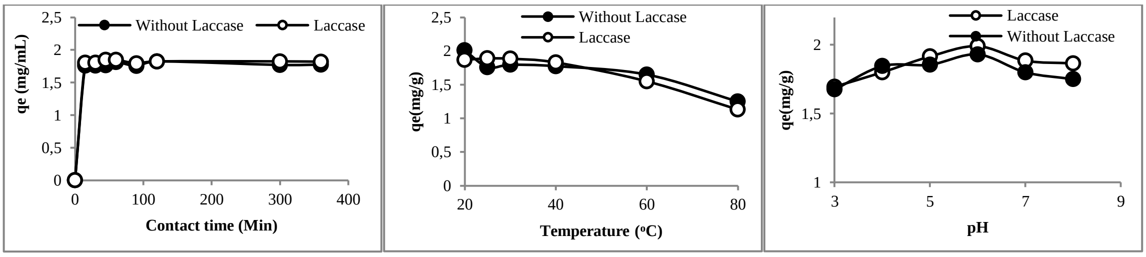

Figure. 1. Effect of contact time, temperature and pH on the removal of AR37 by laccase modified-zeolite

In all the study runs, as described above, other parameters (which ones) were kept stable and samples were taken at regular time for analysis (Nadaroglu et al., 2013). The decolorization efficiency (DE) % of AR37 was defined as follows:

$$DE(\%) = \frac{(C_o - C_t)}{C_o} \qquad (1)$$

Chemical and mineralogical compositions of laccase immobilized zeolite samples were determined by scanning electron microscopy. It was shown that AR37 was adsorbed on the modified zeolite surface (Fig 2).

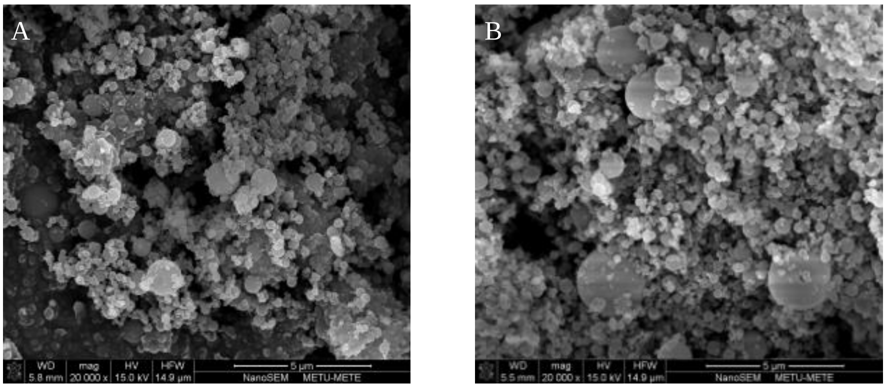

Figure 2. SEM images of native zeolite (A) and AR37 loaded laccase modified-zeolite (B)

Based on the results, laccase modified-zeolite can be used as a relatively efficient and low cost absorbent for the removal of AR37 dye from textile wastewater.

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Dehydration kinetics of local clinoptilolite-rich natural zeolite

G. Narin

Usak UniversityFaculty of Engineering, Department of Chemical Engineering, Usak Turkey;
E-mail:guler.narin@usak.edu.tr

Introduction

Thermal dehydration kinetics of a local clinoptilolite-rich natural zeolite was investigated using dynamic thermogravimetry at three different heating rates under nitrogen flow. The non-isothermal dehydration data were analyzed using Flynn–Wall–Ozawa, Kissinger–Akahira–Sunose and Freidman model-free isoconversional methods and the apparent activation energy of dehydration was determined as 34.54, 30.99 and 27.94 kJ/mol, respectively. The activation energy was found to depend slightly on conversion in the temperature range of 30–200 °C, suggesting a single-step dehydration in this temperature range.

Experimental Methods

Natural zeolitic material from Gördes (Western Anatolia) was wet sieved to 75–150 μm, washed with hot water and characterized by SEM, XRD, N_2 and CO_2 adsorption at -196 °C and 30 °C, respectively, and by ICP-AES. Dehydration kinetics of the zeolite was investigated based on thermogravimetric analyses performed using a thermal gravimetric analyzer (TGA-51, Shimadzu) by heating the samples from room temperature to 1000 °C at heating rates of 5, 10 and 20 °C/min, under 40 mL/min N_2 flow.

Results and Discussion

Fig. 1a and b illustrate the dynamic thermal gravimetric (TG) and derivative TG (DTG) curves, respectively. The TG curves were analyzed using the method reported in the literature in order to distinguish the water adsorbed with a range of energies (Knowlton et al., 1981): externally adsorbed water desorbed up to 150 °C, loosely bound water desorbed between 150 °C and 400 °C, and tightly bound water desorbed above 400 °C.

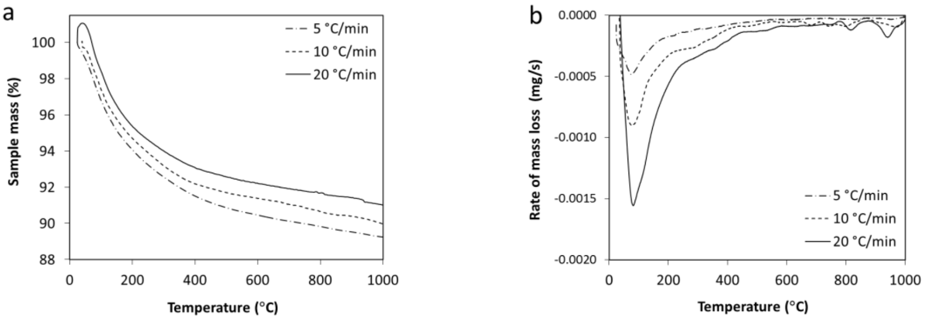

Figure 1. TG and DTG curves for the natural zeolite collected at different heating rates under 40 mL/min N_2 flow

The isoconversional model-free kinetic methods assume that the reaction rate at a given conversion (α) is only a function of the temperature and allow the apparent activation energy (E_a) to be determined as a function of α without pre-assumption of the reaction model. The methods employed in the present study to determine the E_a for dehydration of the natural zeolite are Flynn-Wall-Ozawa (FWO) method:

$$\ln\beta = \ln\left[\frac{AE_a}{\mathrm{R}g(\alpha)}\right] - 5.331 - 1.052\frac{E_a}{\mathrm{R}T} \tag{1}$$

Kissinger–Akahira–Sunose (KAS) method:

$$\ln\left(\frac{\beta}{T^2}\right) = \ln\left[\frac{A\mathrm{R}}{E_a g(\alpha)}\right] - \frac{E_a}{\mathrm{R}T} \tag{2}$$

and differential Friedman method:

$$\ln\left[\beta_i\left(\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right)_{\alpha,i}\right] = \ln\left[Af(\alpha)\right] - \frac{E_{a,\alpha}}{\mathrm{R}T_{\alpha,i}} \tag{3}$$

The slopes of FWO plots drawn according to Eq. (1) within the temperature range of 30–1000 °C (not shown) varied for α >0.30 indicating variation of E_a withα. For α<0.30 (30–200 °C) independence of E_a on α obtained (Fig. 2a) indicates that the dehydration follows a single-step reaction. Hence further kinetic analyses were performed in this limited temperature range. Similarly from the plots of KAS and Friedman methods, according to Eqs. (2) and (3), shown in Fig. 2b and c, respectively, the fitted lines were parallel over the whole α range indicating independence of E_a on α. E_a values calculated using FWO, KAS and Freidman methods exhibited similar dependence on α (Fig. 3). The small discrepancies can be due to the assumptions made for derivation of the model equations.

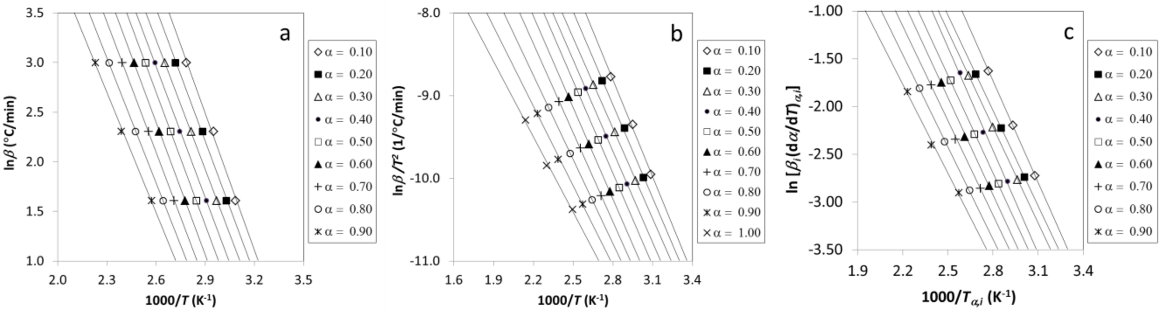

Figure 2. (a) FWO (ln β versus 1/T) plots, (b) KAS (ln β/T^2 versus 1/T) plots, and (c) Friedman (ln[$\beta_i(\mathrm{d}\alpha/\mathrm{d}T)_{\alpha,i}$] versus 1/$T$) plots for dehydration in the temperature range of 30–200 °C.

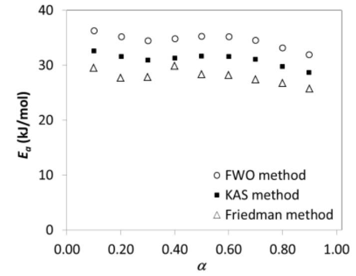

Figure 3. Activation energies as a function of conversion for dehydration in the temperature range of 30–200 °C

In the literature, E_a values for dehydration of various synthetic zeolites have been reported in the range of 8.37–120 kJ/mol (Kulkarni and Kulkarni, 1982; Dondur and Vučelić, 1983; Joshi et al., 2002; Majchrzak-Kuceba and Nowak, 2004). Since the E_a values calculated in the present study are below the enthalpy of vaporization of bulk water (40.7 kJ/mol at 100 °C) (CRC, 2002), it was concluded that the dehydration process of the natural zeolite in the temperature range of 30–200 °C is limited by diffusion of water out of the zeolite particles (Prado and Vyazovkin, 2011).

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Study of Sr^{2+} sorption kinetics from surface drinking water on clinoptilolites from Russian and Bulgarian deposits

V. A. Nikashina[1], I. B. Serova[1], T. G. Kuzmina[1], I. A. Roschina[1], N. L. Lihareva[2] O. E. Petrov[2] and I. N. Gromyak [1]

[1]*Vernadsky Institute of Geochemistry and Analytical Chemistry RAS, Moscow, Russia;*
E-mail: nikashina_v@mail.ru; nikashina@geokhi.ru;
[2]*Institute of Mineralogy and Crystallography, BAS, Sofia, Bulgaria*

Introduction

The natural clinoptilolite (CPT) is characterized by high selectivity for a number of ions, including Sr^{2+}, and can be used at the natural conditions as a permeable reactive barrier (Park et al., 2002). The scale of ion-exchange processes taking place in geochemical barriers and a variety of the environmental conditions (the ground water concentration, the contact time of CPT and solution, etc.) determine the necessity of their mathematical modeling. Ion exchange process on the CPT is described by 2 kinetic stages (relatively fast and much slower) (Thompson et al., 1986). Therefore it is necessary to investigate all ion-exchange kinetic stages in detail. Nikashina et al. (2013) have studied Sr^{2+} sorption kinetics on Na-CPT Khonguruu deposit (Russia) from the surface drinking water (C_{Sr}^{2+} = 0.18-0.20 mg/L) using the "thin layer" method (Boyd et al. 1947). However, the experiment continued more of 7 monthes, and only 30% of Sr^{2+} equilibrium capacity was realized. The aim of the present study is to carry out detailed the investigation of the Sr^{2+} sorption kinetics from surface drinking water contained the increased Sr^{2+} concentration (C_{Sr}^{2+} = 3 mg/L), at using NH^{+}_{4}-forms of CPT's from three deposits – Khonguruu and Kholinskoye (Russia) and Beli Plast (Bulgaria).

Experimental Methods

The content of CPT in the studied zeolite tuffs (determined by powder XRD) is the following (wt. %): Khonguruu- 80; Beli Plast- 82; and Kholinskoye- 60. The CPT graining is , (mm): Khonguruu -0.6+0.3; Beli Plast and Kholinskoye -0.5+0.25; The crystallite size of CPT was determined by XRD profile fitting analysis of 020 diffraction line and is as follows, (nm): Khonguruu ~ 50 ; Beli Plast ~ 33; Kholinskoye ~ 25;
The composition of surface drinking water is (mg/L): (42.0-50.0) Ca^{2+}; (6.9-9.8) Mg^{2+}; (4.0-6.0) K^{+}; (6.5-10.5) Na^{+} ; (2.8-3.0) Sr^{2+}. The water analysis was carried out by AAS or ICAP-9000.
The ion- exchange isotherms of Sr^{2+} on NH_4- forms of CPT from this solution were determined and the corresponding distribution coefficient of Sr^{2+} (K_d) was calculated (Nikashina et al., 1977). The contact time of solution and CPT was 3 months.
The kinetic experiments were carried out in a column with diameter of 5 cm and height of 10 cm, divided on two sections by a mesh. The water was fed to the column from bottom to top. The filtration flow rate of the solution was 1500-1800 ml/min (~1.5 cm/s). The sorbent was "fluidized" that provided a constant concentration of ions at CPT grains surface. The water supply was regularly suspended for a short time (3-5 minutes) in order to take CPT aliquot for analysis. The selected aliquots were washed with distilled water, dried and analyzed. The chemical composition of CPT and the aliquots taken from the kinetic experiments were determined by X-ray fluorescence spectrometer Axios Advanced PANanalytical, the Netherlands.

Results and Discussion

The results of the kinetic experiments are presented in Figure 1 (a, b). As shown from Fig. 1 (a, b) the initial section of Sr^{2+} kinetic dependence (from experiment beginning to time of $t=5\text{-}6 \cdot 10^{4}$s) is described by the particle diffusion law for all three CPT's. Sr^{2+} particle diffusion coefficients of the studied CPT (D_{Sr}^{2+}) were calculated based on fitting experimental and theoretical kinetic dependences (Nikashina et al, 1977). Calculated D_{Sr}^{2+} of Kholinskoye, Bely Plast and Khonguruu CPT in NH_4 form are the following, (cm^2/s): $2.8 \cdot 10^{-10}$; $2.3 \cdot 10^{-10}$; $3.6 \cdot 10^{-11}$, respectively. Further, a delay of ion-exchange process occurs on all studied CPT's. The process comes to a stop in time interval of $2.5 \cdot 10^{5}$- $5 \cdot 10^{5}$s, then an increase of Sr^{2+} sorption is observed again. It should be noted, that K^{+} sorption is decreased simultaneously with the Sr^{2+} sorption increasing on this stage. It could be assumed that Sr^{2+} begins to occupy the K^{+} sites in the channels of CPT structure. But this assumption requires special structural studies. In the case of CPT from Kholinskoye the experimental data confirm that the process has reached equilibrium, because even after 70 days of "rest", the re-start of the sorption process shows practically no change in the Sr-sorption. For CPT from Beli Plast after 14 days of filtration break the Sr^{2+} sorption increased a little again. Possible explanations for the above specificities and differences in the sorption behavior of the studied CPT's may be found in the varying CPT contents, crystallite sizes, chemical content, and structural defects, which we intend to clarify lately.

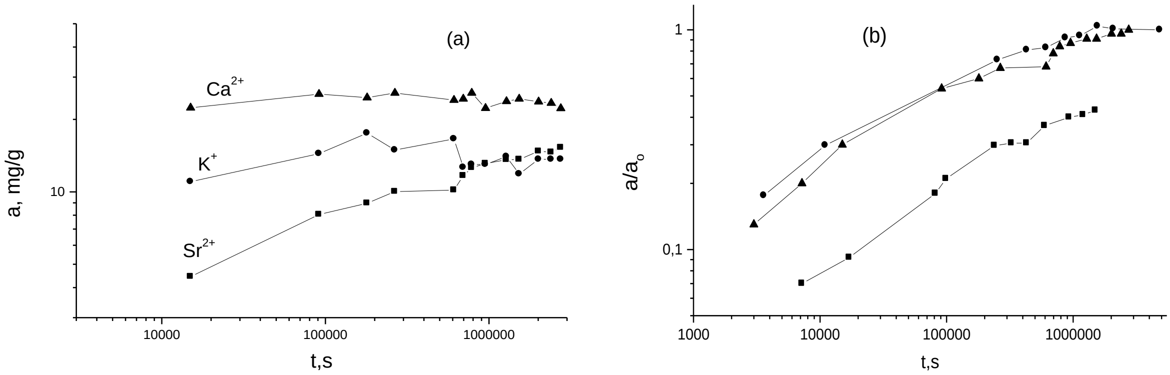

Figure 1 (a) Sorption kinetics of Sr^{2+}, K^{+}, Ca^{2+} on NH_4-CPT Beli Plast from surface water; **(b)** Comparative Sr^{2+} sorption kinetics on NH_4-CPT of different deposits from surface drinking water. ■-■-Khonguruu;▲-▲-Beli Plast; ♦-♦-Kholinskoye

Concluding, the kinetics of Sr^{2+} ion-exchange process on CPT from surface drinking water was investigated in detail for the first time. It was shown, that the kinetic process on CPT includes 3 stages: a) the particle diffusion process described by the particle diffusion coefficient, b) the delay of sorption process, described appropriate kinetic coefficient, and c) third stage-secondary increase of Sr^{2+} sorption, which ends after reaching equilibrium. The particle diffusion coefficients of Sr^{2+} describing the first stage of the sorption process on CPT of different deposits were calculated.

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Geopolymeric Materials Based on Natural Zeolites

A. N. Nikolov[1] and I. A. Rostovsky[2]

[1]*Bulgaria, Sofia, 1-3 Hristo Smirnenski blv., Faculty of Civil Engineering, Department of Building Materials and Insulations, E-mail: y8sashko@yahoo.com*
[2] *Bulgaria, Sofia, 1-3 Hristo Smirnenski blv., Faculty of Civil Engineering, Department of Building Materials and Insulations, E-mail: i_rostovsky@abv.bg*

Introduction

Geopolymers are a new class building materials, obtained through geosynthesis which forms the inorganic mineral material. They consist of chains or networks of inorganic molecules linked with covalent bonds. The resulting product is an amorphous structure, containing a large number of zeolitic phases in the form of nanocrystals. Necessary raw material for obtaining geopolymers is the source of amorphous Al and Si. These may be natural materials such as kaolin, zeolite, volcanic ash and other natural pozzolan or thermally treated materials like metakaolin, fly ash, granulated blast-furnace slag, calcined shale, etc. The second main raw material is the activator. Mostly used activators are sodium and potassium hydroxide, sodium carbonate, sodium water glass and sodium sulfate.

Geopolymerization begins with the mixing of the alkali activator and alumosilicate component. The first stage is the disaggregation process based on severing the Me–O, Si–O–Si, Al–O-Al and Al–O–Si bonds in the starting material. The OH- ions and the high pH initiate the rupture of the above mentioned bonds. The degree of silicon hydroxylation may rise to more than two or three units, forming intermediate complexes that decompose into silicic acid Si(OH)4 as well as oligomeric, anionic species containing Si–O– groups. The presence of alkaline metal cations neutralizes the resulting negative charge. The appearance of Si–O—Na+ bonds hinders the reverse reaction from forming siloxane bonds (Provis and Deventer, 2009). The accumulation of silicon and aluminium monomers increases and enhances the contact between the dissolved products, forming a coagulation structure where polycondensation takes place. The result is forming new Si-O-Si bonds. The monomers are converted into dimmers, dimmers into trimmers, etc. The resulting alumosilicate gel is oversaturated and precipitates, getting amorphous product containing a large number of phases in the form of zeolitic nanocrystals as sodalite, LTA, faujasite, MFI, ZSM-5, etc.

Experimental Methods

The composition and porous structure of produced geopolymers based on natural zeolites were studied in this research. Three types of activators were used - sodium hydroxide, sodium carbonate and sodium silicate. Alumosilicate component was a natural zeolite from deposits in Beli Plast (Bulgaria), i.e. practically pure clinoptilolite. Chemical composition of zeolite is shown in Table 1 (Rostovsky and Lilkov, 2010).

Table 1. Chemical composition of natural zeolite (%)

Al_2O_3	CaO	Fe_2O_3	K_2O	MgO	MnO	Na_2O	P_2O_5	SO_3	SiO_2	TiO_2	LOI	Humidity
9.68	6.73	0.74	2.79	2.90	0.03	0.29	0.03	0.03	62.74	0.12	13.47	5.00

Crushed zeolite is oven-dry to constant mass and grinded to cement fineness in a ball mill. Geopolymeric samples in this study are prepared in a fixed ratio water/solid state = 0.55. This ensures the same initial volume of the pores. The homogenization and compaction of the samples were manually operated. The samples were cubes with edge length 40 mm. The zeolite powder was added into the activator and the homogenized mixture was casted and compacted in shuttering forms and stored in polyethylene bags. A significant shrinking process was observed to all compositions during the hardening. This cause deplanation of the samples planes, which could compromise the results of mechanical test if the specimens are not capped prior to testing. Some expanding of the samples prepared with sodium hydroxide was stated. The thermal effects in geopolymers up to 900^oC at 28-day age have been measured using differential thermal analysis (DTA) and thermal gravimetric analysis (TGA). X-ray analysis was performed by Bruker D8 diffractometer with CuKa radiation generated at 30 mA and 40 kV.

Results and Discussion

The geopolymer binders, like other binders which harden at room temperature, remain amorphous, (Davidovits, 2011). This was confirmed by the X-ray diffraction results (fig.1) in a broad diffuse halo with some crystalline inclusions. The amorphous structure is best expressed when NaOH was used as activator, although in all the geopolymers clinoptilolite-Ca is almost completely dissolved. Moreover, geopolymers activated with water glass show higher mechanical strength (studied in previous works). The structure of samples activated with Na_2CO_3 almost did not change in comparison with the structure of the input raw material, watching the additional formation of calcite ($CaCO_3$).

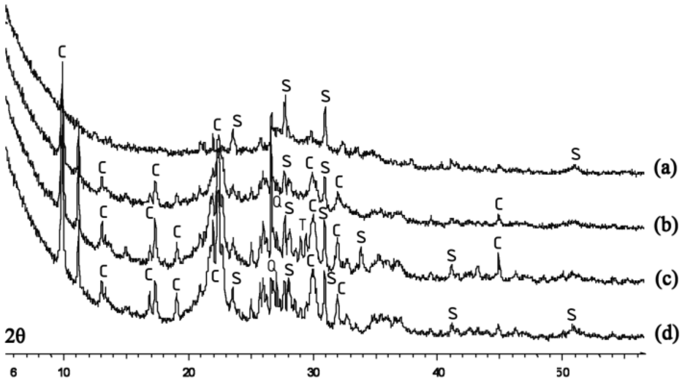

Figure 1. X-ray patterns for geopolymers activated with sodium hydroxide (a), water glass (b), sodium carbonate (c) and pure clinoptilolite (d); C – clinoptilolite-Ca, S – sanidine, Q-quartz, T – calcite

The type of activator influences a process of thermal transformation. They all show endothermic peaks respectively at 106(fig. 2a), 173 (fig. 2b) and 109 (fig. 2c) due to the evaporation of the water adsorbed by geopolymeric structures. In (fig. 2a) the peak is followed and attenuated by an exothermic one at 209, probably caused by crystallization of excess alkali. Two exothermic peaks in (c) at 310 and 439 are related to recrystallization of some of the components. TG curves show a smaller mass loss in geopolymer activated with water glass - 11.08%, followed by NaOH - 13.35% and Na2CO3 - 14.10%.

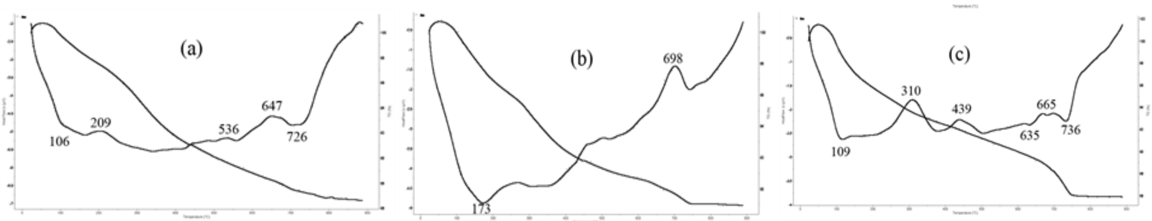

Figure 2. DTA/TG for geopolymers activated with sodium hydroxide (a), water glass (b), sodium carbonate (c)

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Cathodoluminescence characterization of natural zeolites

H. Nishido

Department of Bio-Geosphere Science, Okayama University of Science
1-1 Ridaicho, Kitaku, Okayama, 700-0005 Japan, E-mail: nishido@rins.ous.ac.jp

Introduction

Cathodoluminescence (CL), the light emission induced by electron irradiation, has been widely applied in mineralogical and petrological investigations, especially for carbonates and silicates. The nature of the luminescent centers for a CL emission results from an intrinsic (lattice defects) and/or extrinsic (impurities) properties of the crystal. CL method enables observation of trace element distribution and defects in the lattice, which is quite hard to be detected with other techniques. Although the CL measurements of not a few geological materials have been reported by the investigators, no CL data on zeolite minerals are available. A scanning electron microscopy-cathodoluminescence (SEM-CL) allowed CL spectral measurements of natural zeolites with high resolution at various temperatures. We have observed CL emissions from bikitaite, brewsterite, erionite, ferrierite, gonnardite, harmotome and stilbite, most of which show pale green to bluish green, but blue for bikitaite. In this study, I will characterize the CL emission centers in natural zeolites, and discuss CL emission caused by radiation damage in bikitaite and an intense green CL emission from brewsterite, which shows an unusual temperature effect on its CL.

Experimental Methods

Bikitaite from the lithium pegmatite in Zimbabwe (constituting one of the largest deposits of lithium) occurring with petalite, stilbite, calcite, allophane, simpsonite, alumotantite, ferrotapiolite and zirconian hafnon, was used for this study. Aggregates of pure crystals were selected for CL measurements. Brewsterite was obtained from the hydrothermal cavities in granitic schist in Strontian, Argyllshire, Scotland, U.K. Its single crystal with $Sr_{0.58}Ba_{0.30}Ca_{0.12}$ was used for CL measurements.

CL spectra and CL images were obtained employing a new system of CL-SEM, which comprises a SEM (Jeol JSM-5400) combined with an integral grating monochromator (Oxford Mono CL2) with high sensitive and high spatial resolutions over the wide wavelength range of 300 nm to 800 nm. The sample stage can be controlled at various temperatures from –194 ˚C to 400 ˚C. The system was operated at 15 kV with 1 nA to 2 nA of the incident beam current in a scanning mode (X1000) to prevent the surface damage of the sample by electron bombardment.

Results and Discussion

Radiation-induced defect center:

Bikitaite shows a bright emission with a thin band as CL halo along the surface and the fractures (Fig. 1). Its spectrum has a broad peak centered at 460 - 470 nm in blue region. No activator of impurity elements can be assigned to the emission center, but structural defect might be the cause for this center based on the spectral peak width. By considering its occurrence in pegmatite, the blue CL of bikitaite might be assigned to structural defects as observed in quartz and feldspar with radiation-induced damage closely associated with natural radionuclide minerals.

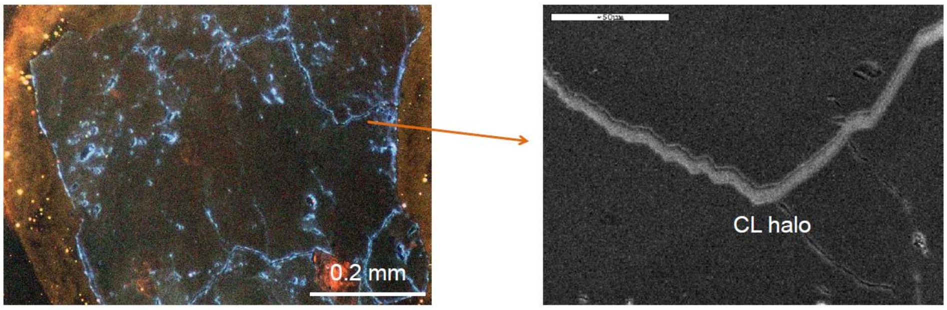

Figure 1. CL images of radiation-induced defect centers in bikitaite

Therefore, the alpha particles from radioactive pegmatite solution containing radioactive elements such as U and Th during the formation processes can cause structural defects (e.g. oxygen deficient center) in the structure of bikitaite. It leads to an energy loss process of specific ionization along the track of a charged particle, suggesting luminescence halo as a thin band along the surface and the fractures of the bikitaite grain. This analytical method provides valuable applications to geodosimetry and geochronology, *e.g.*, estimating leakage of nuclear waste from geologic disposal facility and dating of sedimentary zeolites coexisted with natural radionuclide.

Unusual temperature effect:

Brewsterite shows an intense and broad emission band centered at approximately 500 nm after total instrumental correction. Such green CL might be arisen from impurity centers of divalent Mn ions as an activator, but Mn concentration is almost lower than a detection limit of EPMA method. CL spectra at various temperatures (–194 ˚C ~ 50 ˚C) indicate a notable reduction of CL intensity with a decrease in sample temperature. In general, however, CL intensity can be expected to be increased at lower temperature due to temperature quenching. This phenomenon unique to brewsterite has been virtually unknown in minerals. Above room temperatures, a weak and broad emission at around 350nm in blue-UV region was observed, suggesting defect centers in the lattice.

In general, luminescence efficiency decreases with rising temperature due to an increase in non-radiative transitions. This phenomenon has been recognized in a number of different materials as temperature or thermal quenching. Therefore, this process was quantitatively analyzed by the Mott–Seitz model assuming an increase in the probability of a non-radiative transition with a rise in sample temperature.

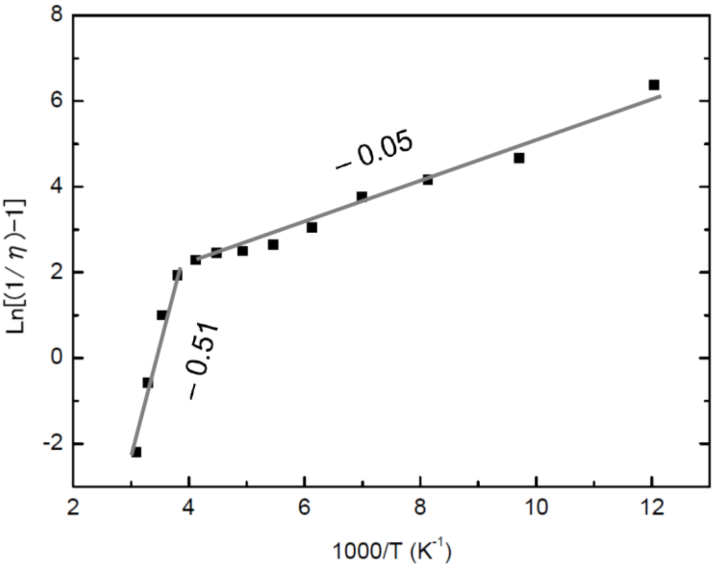

Figure. 2. Arrhenius plots for temperature sensitizing process in brewsterite

The CL spectra in energy units can be fitted by a Gaussian curve, suggesting a luminescent contribution from one type of impurity center. Therefore, the luminescent efficiencies at individual temperature were quantitatively estimated from the integrated intensity calculated by a Gaussian fit. Arrhenius plots reveal that there are two straight-line relationships indicating different kinds of temperature sensitizing mechanisms, which can be clearly explained on the basis of Mott-Seitz theory. The CL of this zeolite has two temperature sensitizing processes with low activation energy of approximately 0.05 eV from –194 ˚C to –50 ˚C and high activation energy of approximately 0.51 eV from –50 ˚C to 50 ˚C. The former might be nearly same order of the energy related to O-Si(Al)-O bending vibration, and the latter to O-H stretching vibration. At lower temperature the sensitizing energy for a radiative transition could be transferred from the lattice vibration in T-O framework, and at higher temperature pronounced sensitizing energy from water molecule vibration in a channel. Such sensitizing mechanism has not been reported in minerals up to now.

Uptake of Pb and Zn from binary solutions onto different fixed bed depths of natural zeolite - BDST model approach

I. Nuić, M. Trgo, J. Perić and N. Vukojević Medvidović

Faculty of Chemistry and Technology, Universitiy of Split, Teslina 10/V, 21000 Split, Croatia;
E-mail: ivona@ktf-split.hr

Introduction

Industrial wastewaters are considered to be the greatest source of pollution by heavy metals. Their removal from wastewaters to concentrations below the permissible limits is possible by tertiary treatment processes: adsorption, ion exchange and membrane techniques. The present study examines the lead and zinc uptake on different zeolite fixed bed depths. Experimental breakthrough curves have been analyzed with the BDST model. Calculated parameters confirmed satisfactory fitting of the model with the experimental data.

Experimental Methods

Sample preparation

The raw zeolite sample originates from the Zlatokop mine in Vranjska Banja (Serbia) and consists of up to 80% clinoptilolite. The zeolite was sieved to the particle size of 0.6-0.8 mm, rinsed with ultrapure water and dried at 60°C.

Column experiments

Laboratory column tests were carried out in three 500 mm long glass columns of 12 mm internal diameter, filled with the zeolite sample up to 40, 80 and 120 mm. The binary feed solutions of lead and zinc, prepared by dissolving $Pb(NO_3)_2$ and $Zn(NO_3)_2 \times 6\ H_2O$ in ultrapure water, were fed through the fixed beds in the down-flow mode at the constant flow rate of Q = 1 ml/min, using the vacuum pump. The experiments were conducted at room temperature, at the constant total feed concentration of $c_o \approx 1$ mmol/l, with $c_o(Pb)/c_o(Zn)$ concentration ratios of ≈ 1. After exhaustion, the zeolite bed was regenerated with the $NaNO_3$ solution, c = 176.5 mmol/l, under identical conditions as the service cycles. In all experiments, the effluent samples were periodically collected and analyzed for Zn concentration on a Methrom 761 Compact IC liquid chromatograph and total (Pb+Zn) concentration by the complexometric method. After each service cycle, zeolite samples were analyzed using SEM/EDS.

Results and Discussion

The experimental data obtained at three different zeolite bed depths are shown in Figure 1, where breakthrough curves were plotted as $c(Pb+Zn)/c_o(Pb+Zn)$ versus service time. The results indicate that all breakthrough curves follow the S shape profile. By increasing the bed depth, breakthrough and exhaustion points appeared later, higher volume of metal solution was treated, and time between breakthrough and exhaustion decreases. The height of the mass transfer zone h_Z was calculated and approximately equal at all examined bed depths. The number of units of mass transfer zone H/h_Z is proportional to the bed depth which insures longer contact time and greater removal efficiency. From regeneration curves, the maximum eluted c(Pb+Zn) ions increased proportionally to the bed depth. In order to mathematically describe the fixed bed column behavior, experimental breakthrough data were tested using the Bed Depth Service Time (BDST) model (Cooney, D.O. 1999, Ko, D.C.K. et al., 2000, Perić, J. et al., 2009). A linear relationship between bed depth and service time is given by Equation 1:

$$t = \frac{q}{c_o \cdot v} \cdot H - \frac{1}{k \cdot c_o} \ln\left(\frac{c_o}{c_t} - 1\right) \tag{1}$$

where t is service time (h), q is removal capacity of the zeolite (mmol/l), H is bed depth (m), c_o is influent solute concentration (mmol/l), v is influent linear velocity (m/h), k is a constant related to the transfer rate of ions from the liquid to the solid phase (l/mmol h) and c_t is the effluent solute concentration at time t (mmol/l). Equation 1 can be expressed in the form of a straight line as $t = a \cdot H + b$, where a is the slope and b is the intercept of the respective line. It allows the service time t to be determined for a specific bed depth H of zeolite, when the concentration c_t in the effluent is reached. To develop the BDST correlation, experimental points at time corresponding to (Pb+Zn) removal percentages of 95, 70, 50, 40 and 5% were plotted for each bed depth. The obtained t-H lines are shown in Figure 2.

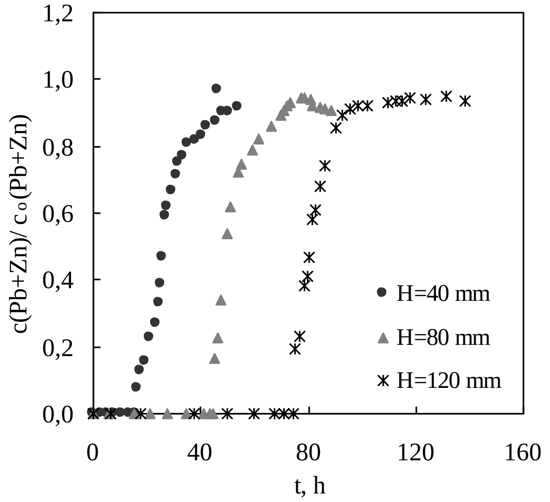

Figure 1. Experimental breakthrough curves for bed depths of 40, 80 and 120 mm

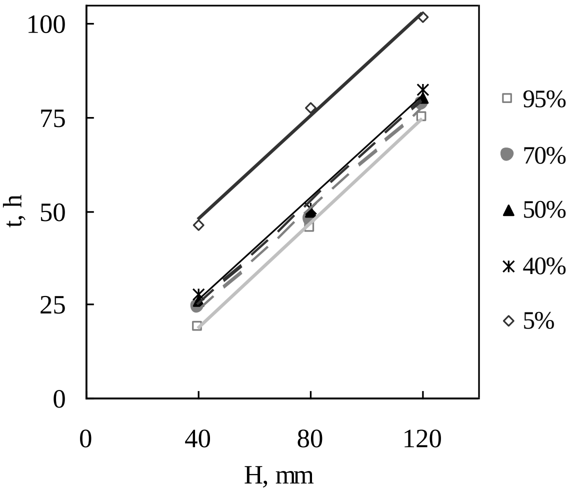

Figure 2. BDST plots at different removal percentages for bed depths of 40, 80 and 120 mm

From the slope and the intercept of these lines, the parameters k and q have been calculated, assuming a constant influent concentration and linear velocity at all service cycles. The lines in Figure 2 show excellent fitting of experimental points with the model ($R^2 > 0.98$) and have almost identical slopes. This confirms successful application of the BDST model on the experimental data at the examined range of bed depths. Calculated capacities q have close values and correspond to experimental exhaustion capacities. The values of rate constants k decrease to the inflection on the breakthrough curve, which is probably related to the change in the mechanism of the process.

It can be concluded that the BDST equation can be used for estimation of breakthrough curves of Pb and Zn uptake from binary aqueous solutions in the zeolite bed by column mode, for various experimental conditions.

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Thermal induced phase transformation of Cs-exchanged clinoptilolite

M. Omerašević[1], M. Čebela[1], A. Savić[2], V. Maksimović[1], N. Vuković[3] and A. Radosavljević-Mihajlović[1]

[1]*Laboratory for Material Science, Institute of Nuclear Sciences ″Vinča″, University of Belgrade, Belgrade, Serbia; E-mail:mia@vinca.rs*
[2]*Laboratory of Chemical Dynamics and Permanent Education, Institute of Nuclear Sciences ″Vinča″, University of Belgrade, Belgrade, Serbia*
[3]*Faculty of Mining and Geology, University of Belgrade, Belgrade, Serbia*

Introduction

^{137}Cesium is considered as one of the most hazardous radiotoxic elements for the environment. The aim of this study is to find out the best method to remove radioactive cesium from nuclear waste streams. Cs^+ exchanged form of natural zeolite - clinoptilolite were prepared by standard procedure. The application of the ion exchange procedure and Zeolite thermally induced transformation (ZTIT) method is particularly appropriate, because, it could be an alternative way to safely store Cs^+ - ions entrapping and blocking them into a zeolite framework. It is based on a thermal treatment that destroys the zeolite structure and form structurally new, stabile, cesium aluminosilicate phases – pollucite phase.

Experimental Methods

The presence of different cations and success of ion exchange was determined by SEM-EDS analysis.
High temperature phase transformations of Cs^+ exchanged zeolite (clinoptilolite) were investigated by X-ray diffraction (XRD).

Results and Discussion

Results of SEM-EDS analyses of the natural and Cs^+-exchanged clioptilolite are presented in Tables 1 and 2.

Table 1. SEM-EDS (semi-quantitative) analysis of natural clinoptilolite – before ion exchange

Cation	Na	Mg	Al	Si	K	Ca	Fe	Cs	O
weight%	0.22	0.62	7.10	35.90	2.72	3.21	0.43	0.00	49.78

Table 2. SEM-EDS (semi-quantitative) analysis of Cs^+ – exchanged clinoptilolite

Cation	Na	Mg	Al	Si	K	Ca	Fe	Cs	O
weight%	0.08	0.25	5.68	27.95	0.65	0.30	0.40	25.68	39.00

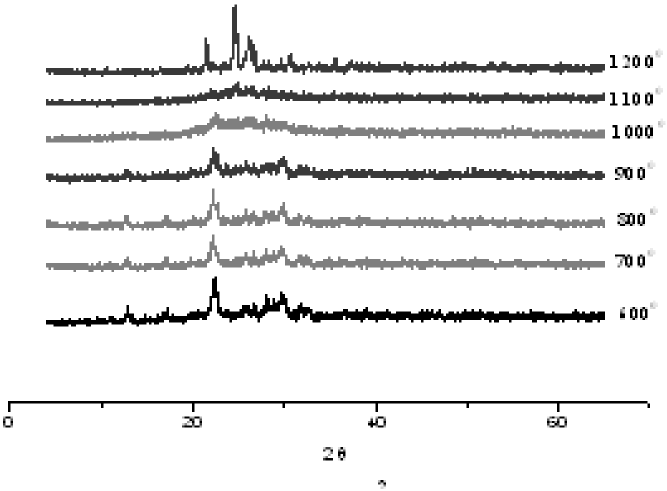

Figure 1. XRD patterns of thermally treated Cs-exchaned form of clinoptilolite

After ion exchanges, cesium-form of the zeolite was obtained, containing more than 25 % wt. of Cs^+ ion which is very satisfactory result. The formation of an amorphous substance of Cs-form of clinoptilolite started approximately between 1000 °C and 1100 °C. Cs-form of clinoptilolite recrystallized at 1200^0C into new stable phase- pollucite phase.

Acknowledgment

This project was financially supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia (Project number: III 45012).

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Real structure of natural mordenite from Mátra Hill (Hungary)

Sz. Ormándi[1] and I. Dódony[2]

[1] Department of Mineralogy, Eötvös Loránd University, Pázmány Péter stny. 1/C Budapest, 1117 Hungary;
E-mail:ormszi12@gmail.com
[2] Department of Mineralogy, Eötvös Loránd University, Pázmány Péter stny. 1/C Budapest, 1117 Hungary;
E-mail:dodony@t-online.hu

Introduction

Zeolites are crystalline microporous alumosilicates whose unique pore and channel systems are the reason for their importance in catalysis, separation and ion exchange. In the case of the mordenite two different varieties are distinguished, large-port and small-port mordenite by the accessible of 12-membered ring channels (Sand, 1968). The reason of this are stacking faults disrupting the structure (Raatz et al., 1985). Zeolites in the mordenite group are built up from five-membered rings of tetrahedra, and the structures composed of puckered sheets made up of six-membered rings of tetrahedra (Figure 1). The members of the mordenite group are: mordenite, dachiardite, epistilbite, ferrierite and bikitaite (Meier, 1978).

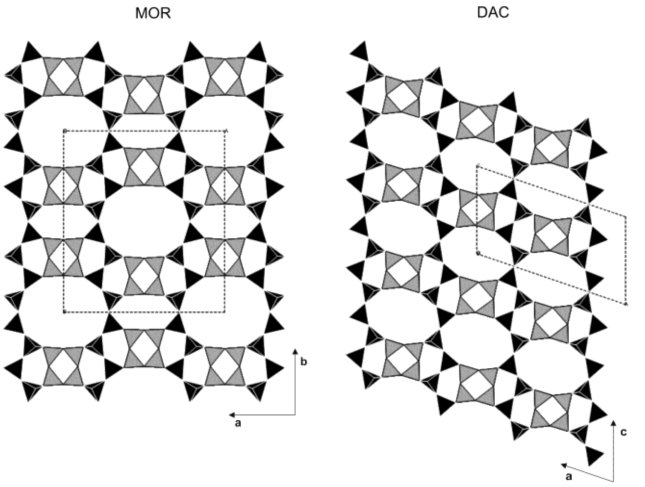

Figure 1. The mordenite framework projected along the **c**-axis *Cmcm* (a=18.1, b=20.5, c=7.5 Å) and dachiardite along the **b**-axis *C2/m (*a=18.6 b=7.5 c=10.4 β=108.9°) (IZA data base). The structure is composed of puckered sheets (dark grey shading)

Experimental Methods

The locality of the measured samples is Lengyendi-galya (Gyökeres-tető) Mátra Hill (NE-Hungary). The mordenite bundles occur in hydrothermally highly altered andesite, the typical associating minerals are harmotome, heulandite, chabazite, stilbite, smectite and silica. We used X-ray powder diffractometry for phase identification, scanning electron microscopy (SEM) for morphological and textural observations and selected area electron diffraction (SAED) for structural characterization of mordenite.

Results and Discussion

The SEM images revealed that the first product of hydrothermal alteration is mordenite followed by chabazite, heulandite and stellerite. Secondary electron (SE) images in Figure 2. show rhombohedral chabazite crystals speared by mordenite fibers.

Using high-resolution electron microscopy (HREM) Song (1999) studied mordenite and observed different defect types: dislocations, planar defets and local intergrowth. The two dimensional planar faults with ~1/4 [010] displacement vector yield the possibility of dachiardite presence in the structure.

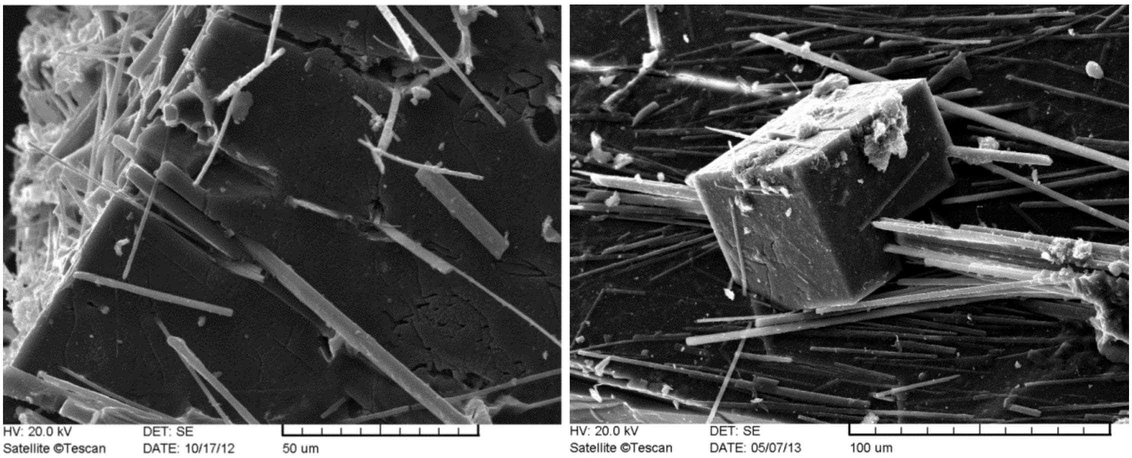

Figure 2. SE images of mordenite and chabazite

Based on SAED patterns and TEM images we also found planar faults indicated by intense streaks and superlattice reflections. Figure 3. shows the [110] mordenite reciprocal lattice where the $l = 2n+1$ reflections are interconnected by intense streaks. This diffuse scattering is interpreted as an evidence of planar faults, where a fault produce a dachiardite type structural slab within the mordenite lattice. As Figure 1. represents the puckered sheets are similar of mordenite and dachiardite, but the connection of these puckered sheets by four-membered rings (light gray shading) differs. The presence of the dachiardite domains affect the mordenite channel capacity.

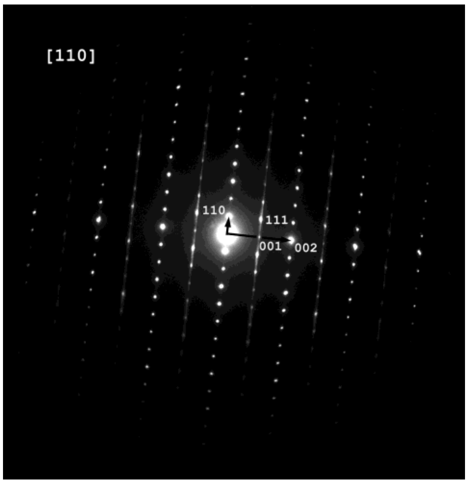

Figure 3. [110] SAED pattern of mordenite

Acknowledgment

The authors gratefully thank Judit Tóthné Király and István Gatter for their kind help in the X-ray diffraction and field work, respectively.

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http://www.iza-structure.org/

Pozzolanic activity of the zeolitic tuffs of Western Turkey Neogene deposits: The controlling parameters

S. Ozen[1], M. C. Goncuoglu[1], B. Liguori[2], B. de' Gennaro[2], P. Cappelletti[3] and C. Colella[2]

[1] *Department of Geological Engineering, Middle East Technical University, Ankara, Turkey;*
E-mail: ozsevgi.ozen@gmail.com
[2] *Dipartimento di Ingegneria dei Materiali e della Produzione, Università Federico II, Naples, Italy*
[3] *Dipartimento di Scienze della Terra, Università Federico II, Naples, Italy*

Introduction

The physical and chemical factors influencing the pozzolanic reaction between zeolites and lime were investigated over a wide range of time. Detailed mineralogical, chemical and physical characterization was performed before testing them as pozzolanic material. Thermogravimetric analyses and Fratini's tests were applied in order to monitor the pozzolanic activity. The experiments showed that the increased specific surface area enhances the pozzolanic activity at the initial stage but has no significant effect on the following reactions. The effect of the Si/Al ratio was observed at the later stages and especially after 28 days. K^+-exchanged clinoptilolite-rich tuffs displayed enhanced reaction rates compared to the Ca^{2+} and Na^+-exchanged ones at longer periods. Kinetic analyses, in accordance with modified Jander equation, showed that the reaction was mainly controlled by the diffusion of reactants through a layer of dense reaction products.

Experimental Methods

The bulk chemical composition of tuffs was obtained by inductively coupled plasma optical emission spectrophotometry (ICP-OES, Perkin-Elmer Optima 2100 DV) under microwave-induced heating (Perkin-Elmer Multiwave 3000 oven). The specific surface area was measured by N_2 adsorption using the BET method whereas the particle size distribution with a Malvern Mastersizer 2000 laser particle size analyser. Quantitative electron microprobe analysis in wavelength dispersive mode (EPMA-WDS) was performed on polished sections of the zeolitic tuffs, using a JEOL JXA 8200 electron microprobe. Quantitative phase analysis was carried out by means of X-ray powder diffraction (XRPD) using a Panalytical X'Pert Pro diffractometer equipped with a silicon-based position-sensitive detector (X'Celerator®) and X'Pert High Score Plus 3.0 software. The operating conditions were: CuKα radiation, 40 kV, 40 mA, 2θ range from 3 to 80°, equivalent step size and counting time 0.0179° 2θ and 120 s per step respectively.

Results and Discussion

The physical properties of the finely ground zeolitic tuffs are given in Table 1.

Table 1: Physical properties of the investigated zeolitic tuffs

	CLI-G	CLI-A	CLI-B	MOR	ANA
Specific Gravity	2.12	2.09	2.12	2.17	2.3
BET surface area, m^2/g	39.9	28.01	17.57	27.3	26.19
Blaine surface area, m^2/g	7436	8209	4769	6328	5076
Fineness					
Passing 90 µm, %	100	100	100	100	100
Passing 45 µm, %	92	99	90	77	95

The scanning electron micrograph of Gördes (Manisa) clinoptilolites is shown in Figure 1. In the micrograph, well-formed clinoptilolite crystals occur as euhedral laths of approximately 1 µm in length and tabular plates.

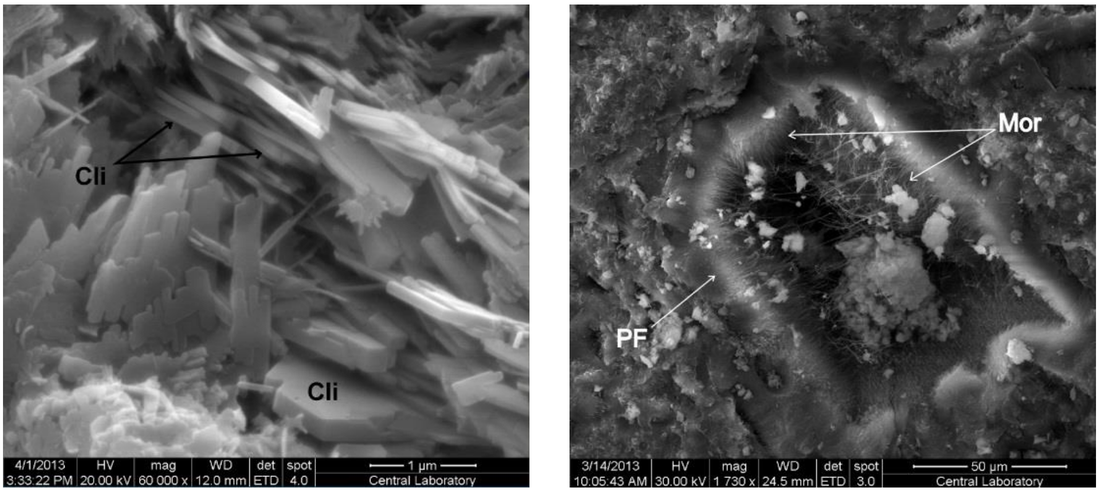

Figure 1. Scanning electron micrograph shows a) clinoptilolite crystals displaying laths and tabular plates (Sample: CLI-G, Cli: clinoptilolite; b) mordenite needles growing on the edge of a volcanic glass shard (Sample: MOR, Mor: mordenite PF: pumice fragment)

The results of Fratini's test, representing the lime concentration of the solutions in contact with the blended cements are presented in Figure 2. Apart from ANA sample, all points fall below the $Ca(OH)_2$ solubility curve, indicating that the contact solutions were found to be under-saturated in portlandite indicating that a part of the Ca^{2+} resulting from the pozzolanic activity was fixed by the zeolitic tuff. Therefore, it was possible to classify all the blended cements prepared using the investigated zeolitic tuffs as pozzolanic.

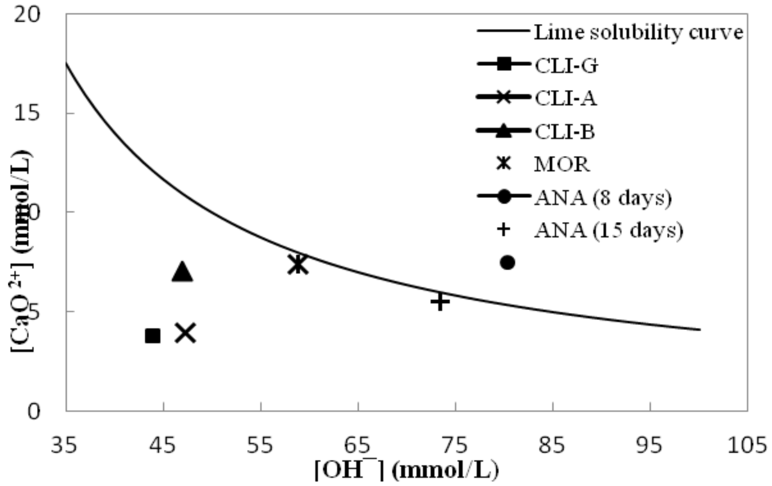

Figure 2. Results of Fratini's test representing the lime concentration of the solutions in contact with the blended cements

Acknowledgment

Thanks are due to Dr. G. Diego Gatta for the microprobe analysis of the zeolites and to Dr. Mustafa Albayrak (MTA) for sharing his knowledge on the zeolite deposits. The supply of the Gördes region zeolite samples Rota Mining Corporation is also thankfully acknowledged.

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Kinetics of dehydration of K- and Na-cation-exchanged forms of clinoptilolite

N. L. Petrova[1], V. Petkova[1, 2] and O. E. Petrov[1]

[1]Institute of Mineralogy and Crystallography, BAS, Acad. G. Bonchev Str. 107, Sofia, Bulgaria;
E-mail:nadia5@mail.bg
[2]New Bulgarien University, Department "Natural Sciences", 21 Montevideo Str., 1618 Sofia,, Bulgaria

Introduction

The nature of the dehydration/hydration process of clinoptilolite is largely controlled by the hydration energy of extra-framework cations (Carry and Bish, 1997; Petrova et al., 2001) and the structural variation during dehydration (Armbruster, 1993). The enthalpy of hydration of cation-exchanged forms of clinoptilolite has been obtained by different calorimetric methods: immersion calorimetry, solution calorimetry and water-vapor calorimetry.

In this study we apply an approach for the evaluation of kinetic parameters by isoconversional methods on DSC data of the endothermic dehydration process of clinoptilolite samples. The method of Ozawa (1970) has been employed for the estimation of kinetic parameters from the DSC data of the dehydration processes of other materials. Ozawa's method is usually performed using the top of the temperature peak (Tp). At this point it is assumed that the frequency factor (A), the conversion degree (α□, and activation energy (E_a) are independent of the scanning rate (β□, while A and E_a are independent of α.

Experimental Methods

Clinoptilolite tuff from Beli Plast, Eastern Rhodopes, Bulgaria, containing about 75 wt.% clinoptilolite was used. This material was purified to obtain almost 98 wt.% clinoptilolite by the following procedure: (1) removal of the clay minerals and crystobalite, and (2) separation of heavy minerals by centrifugation. Then the clinoptilolite material was cation exchanged with 1M Na- and K-chloride solutions following the described procedure in Petrova at al., (2001): by shaking for three days at 60°C changing the solution each day, and finally the material was washed and dried at 40°C. The chemical compositions of these forms are:

Purified: $Na_{0.61}K_{1.90}Ca_{1.32}Mg_{0.35}Fe_{0.06}Al_{5.83}Si_{30.12}O_{72}.24.1H_2O$ (1)
K-exchanged: $Na_{0.64}K_{5.39}Ca_{0.04}Mg_{0.13}Fe_{0.05}Al_{5.76}Si_{30.05}O_{72}.17.3H_2O$ (2)
Na-exchanged: $Na_{4.65}K_{1.05}Ca_{0.06}Mg_{0.18}Fe_{0.06}Al_{5.53}Si_{30.27}O_{72}.21.8H_2O$ (3)

On the charge basis, the cation exchange of the above formula corresponds to 84.8 for K and 75.2% for Na. DSC analyses of clinoptilolite samples were carried out on a Setsys Evolution DSC-TG 2400, SETARAM, France, at three different heating rates: 7, 12 and 15 °C.min^{-1}. The operational characteristics of the TG–DSC system were: sample mass of 19.8–20.0 mg; ceramic sample pan and static air atmosphere. Duplicate runs were made under similar conditions and it was found that the data overlap with each other, indicating satisfactory reproducibility. Thermokinetic software AKTS was used to perform kinetic analyses of the DSC data.

Results and Discussion

The temperature ranges for the dehydration of K- and Na- clinoptilolite, values of peak temperature (Tp) and integrated heats obtained from the DSC at different heating rates are given in Table 1, while the DSC curves are presented on Fig.1.

Table 1. Temperature range for the dehydration of clinoptilolite samples, values of T_p and integrated heats from DSC at different heating rates

Form	Heating rate/° min^{-1}	Temperature range/°C	T_p/°C	Integrated heats/J g^{-1}
K	7	40-250	86.67	502.7
	12	40-250	105.65	624.7
	15	40-250	109.13	892.2
Na	7	40-300	114.50	585.7
	12	40-300	122.20	893.4
	15	40-300	129.32	1055.1

The temperatures of dehydration peaks and integrated heats depend on the hydration characteristic of the exchanged cations: namely, Tp increases and the heats become more endothermic with increasing the hydration energy of the exchanged cations in the sequence: K<Na. The DSC data of the endothermic dehydration process of the clinoptilolite sample were subjected to kinetic analyses through isoconversional methods proposed by Ozawa (1970). Figure 2 shows the dependences of both the reaction progress and reaction rates on temperature at different heating rates. This method gives consistent values of activation energy (E_a) with good correlation. The values of activation energy and correlation coefficient (R) are given in Fig. 3. These values also depend on the hydration characteristics of the exchanged cations, increasing in the order K<Na.

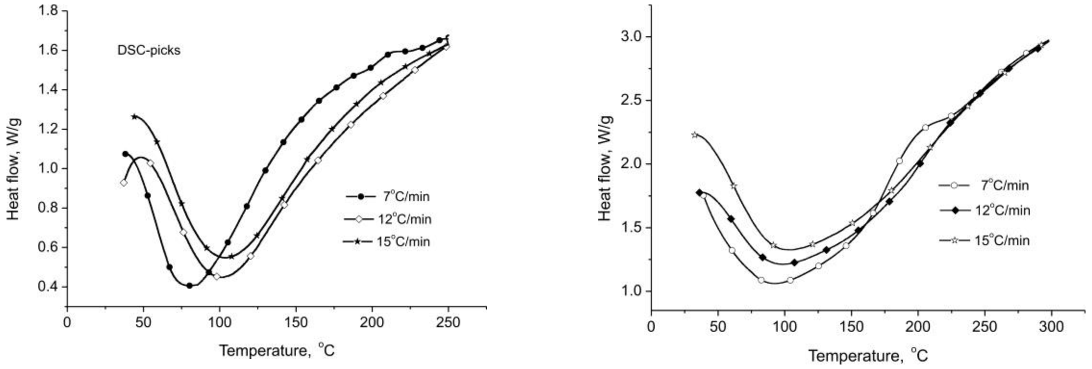

Figure 1. DSC curves of K- (a) and Na-exchanged clinoptololite (b) at different heating rates

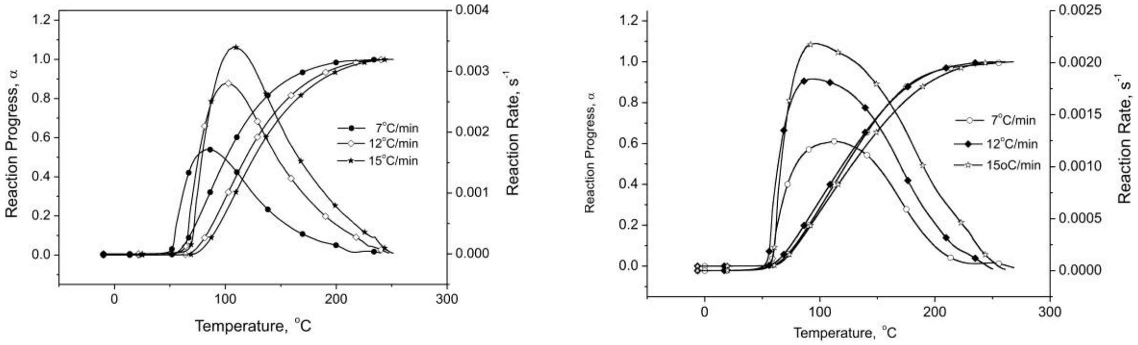

Figure 2. Reaction progress (or conversion degree) and reaction rates *vs.* temperature for K (a) and Na- exchanged clinoptilolite (b) at different heating rates

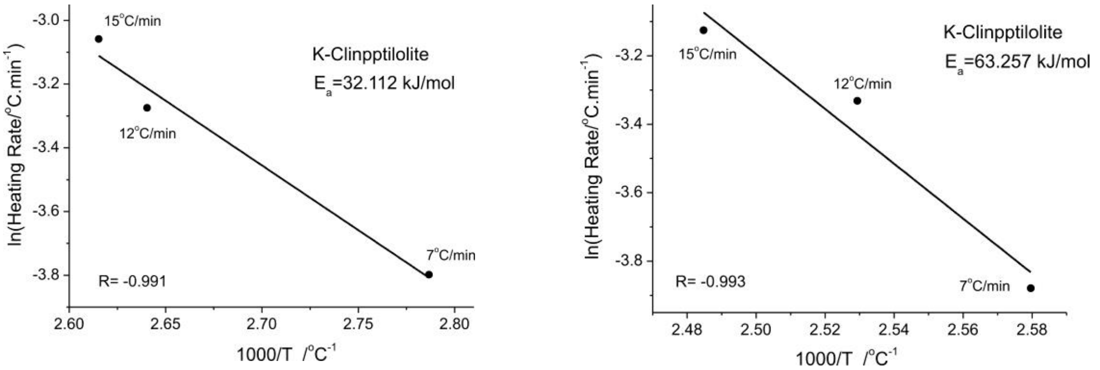

Figure 3. Ozawa plots and values of activation energy for K (a) and Na-exchanged clinoptilolite (b)

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Adsorption of butyl acetate onto modified clay minerals

I. Pliś[1], W. Prokop[1], R. Petrus[2] and J. Warchoł[3]

[1]*OTTO Engineering Polska Sp. z o. o., ul. Połonińska 15, 35-082 Rzeszów, Poland;*
E-mail: ireneusz.plis@ottoindustries.com.pl
[2]*Department of Chemical and Process Engineering, Rzeszow University of Technology*
[3]*Department of Water Purification and Protection, Rzeszow University of Technology, al. Powstańców Warszawy 12, 35-959 Rzeszów, Poland*

Introduction

Volatile organic compounds (VOC) are one of the most common air pollutants emitted from chemical, petrochemical, and allied industries, and include most solvent thinners, degreasers, cleaners, lubricants, and liquid fuels (Dammak et al., 2013). In recent years, the abatement of VOCs has attracted great interest since VOC emission significantly impacts global environment and human health.

New regulations regarding VOC emissions require more efficient and less costly technologies in order to bring down VOC concentrations below the permissible levels before their release into atmosphere (Dammak et al., 2013). Adsorption is widely accepted to be effective for VOC removal, even at low concentration. Yet, for this technique it is important to use adsorbents that are available at tonnage quantities and economical costs, and which are able to be regenerated with minimum damage. This study investigates the adsorption of butyl acetate on natural clay minerals modified by hydrochloric acid (HCl), tetramethylammonium bromide (TMA-Br) and cesium chloride (CsCl).

Experimental Methods

Materials used were glauconite and vermiculite received from BioDrain denoted as GL and VE respectively. Mineral composition is the following for GL: Illite and Smectite 73%, Quartz 21%, K-feldspar 3%, Fluorapatite 2% and for VE: Vermiculite and Biotite 60%, Illite and Smectite 24%, K-feldspar 5%, Calcite 3,5%, Plagioclase 3%, Fluorapatite 2%. The other properties of used materials are shown in table 1.

Modification

1. Selective leaching

Suspensions of VE and GL (15 g) were equilibrated with 2 M HCl at 80°C for 6 hours and 2 hours respectively. Then, 100 ml of cold distilled water was added and the samples allowed to cool. Suspensions were centrifuged, washed with deionized water and dried at 110°C overnight.

2. Cation exchange

A suspension of VE (15 g) was equilibrated with 0.05 M solution of TMA-Br or 0.25 M solution of CsCl under stirring at room temperature for 12 hours. Subsequently, the suspensions were washed with deionized water by dialysis for 5 days and dried at 110°C.

The raw and modified minerals were analyzed by X-ray diffraction (XRD) using Philips X'pert APD diffractometer with PW 3020 goniometer, Cu tube and graphite monochromator. The identification of phases was based on ICDD PDF-2 database and the collection of patterns recommended by International Zeolite Association (Treacy and Higgins, 2001). The cation exchange capacity (CEC) was determined using procedure described by Gillman (1979). All exchangeable cations were exchanged by Ca^{2+} ion and their concentrations were determined by atomic absorption spectroscopy (AAS). The measurement was repeated several times and the average (error <2.5%) CEC values were recalculated per sample weight. The surface area was calculated from the adsorption branch of N_2 isotherm using BET method at −196°C on a Micrometrics ASAP 2420 Analyzer.

Table 1. Properties of raw and modified clay samples

Name	CEC, meq/100g	ECEC, meq/100g	$A_{BET,}$ g/m^2			
			Raw	HCl	TMA-Br	CsCl
GL	27.80	27.69	60.13	128.75	-	-
VE	56.50	48.39	12.24	200.06	13.25	11.48

Adsorption of butyl acetate was determined in dynamic conditions in a home-made system (figure 1) at 25°C and atmospheric pressure. A concentration of butyl acetate (1-30 mmol/m^3) on column inlet and outlet was monitored on-line with a standalone detector PID (Photovac Model 2020 ComboPRO) and a gas chromatograph (Thermo Scientific TRACE 1300 GC with column TR-5).

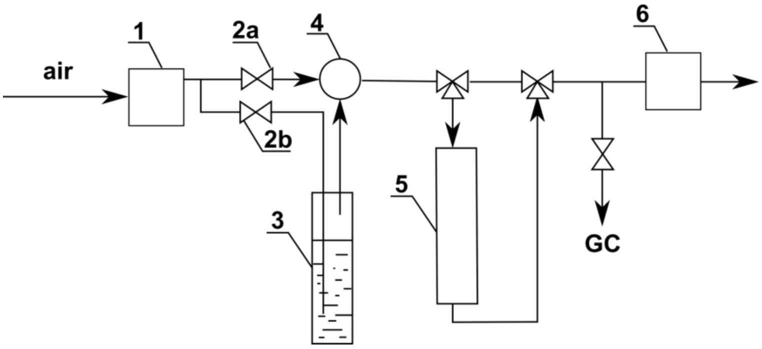

Figure 1. Experimental installation schema; (1) flowmeter, (2) valves, (3) contaminant generator, (4) mixer, (5) fixed-bed column, (6) concentration analyzer

Results and Discussion

The clay minerals modified by HCl show a clear improvement of sorption capacity (figure 2) in comparison to raw materials, which resulted from the increase of surface area (A_{BET}) (table 1). On the other hand, modifications by cation exchange did not increase A_{BET} and decreased the sorption capacity by half. This indicates that big cations such as Cs^+ and TMA^+ actively block large part of active sites which were available for butyl acetate before modification. The experimental data was used for modeling of sorption equilibrium by using empirical equations: Langmuir, Freundlich, Redlich-Peterson, Toth and Langmuir-Freundlich.

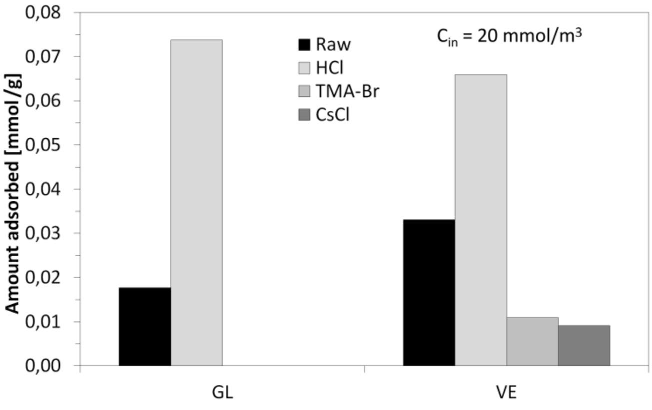

Figure 2. Sorption of butyl acetate by raw and modified forms of GL and VE

Acknowledgment

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Removal of bisphenol-A from water by surfactant modified bentonite and clinoptilolite

V. Rakić[1], V. Rac[1], V. Pavlović[1], M. Krmar[2], Lj. Damjanović[3] and M. Marković[4]

[1]*Faculty of Agriculture, University of Belgrade, Nemanjina 6 11080 Zemun, Serbia.*
E-mail: vesna.rakic@agrif.bg.ac.rs
[2]*Institute "Goša", Milana Rakića 35, 11000 Belgrade, Serbia*
[3]*Faculty of Physical Chemistry, University of Belgrade, Studentski trg 12 11000 Belgrade, Serbia*
[4]*Institute for Technology of Nuclear and Other Mineral Raw Materials, Franše d' Epere 86, 11000 Belgrade, Serbia*

Introduction

Bisphenol A (BPA, CASRN: 80-05-7) is a white solid which is used as an intermediate in the manufacture of epoxy, polycarbonate, polysulfone and certain polyester resins (Y.Zhang et al., 2006). Concerns have recently been raised about the exposure of humans and wildlife to environmental levels of BPA, since it has been shown to have weak endocrine activity (Sohoni *et al.* 2001). Modern analytical methods, which permit detection at low levels, have shown the presence of endocrine disrupting compounds in some environmental samples (Clara et al, 2004). Nanofiltration and reverse osmosis are promising membrane technologies, however adsorption still remains the methods most often used for the remediation of water. The present work focuses on the adsorption of BPA on natural minerals: zeolite clinoptilolite and clay bentonite. These solids were used either in their natural forms or modified by cetylpyridinium chloride (CPC).

Experimental Methods

The starting solid materials used in this work were natural zeolitic tuff (Z) supplied by sedimentary Zlatokop in Vranjska Banja, Serbia and bentonite (B) obtained from the Šipovo deposit in Bosnia. X-ray powder diffraction analysis has shown that the zeolitic tuff contains 72.6 % clinoptilolite phase, 14.6 % feldspar plagioclase and 12.8% quartz while the bentonite contained approximatelly 90% montmorilonite (Rakić et al. 2013). The cation-exchange capacity (CEC) and external cation exchange capacity (ECEC) of the starting zeolitic tuff were determined using the ammonium chloride method (Krajišnik et al. 2011). The total cation exchange capacity of bentonite was determined by the methylene blue adsorption method (Rakić et al., 2013). Cationic surfactant cetylpyridinium chloride (CPC, (Sigma–Aldrich, St. Louis, MO, USA) was used for the preparation of the organominerals (composites). The 10 wt% aqueous suspension of initial zeolitic tuff (Z) or bentonite (B) was treated with surfactant amounts equivalent to 50, 100 or 200% of its ECEC with the purpose of obtain composites with different surfactant loadings (denoted as ZCPC-5, ZCPC-10 and ZCPC-20); while the preparation of the organobentonite (OB), CPC was used in an amount equal to 100% of CEC. All solids were fully characterized by means of relevant techniques (SEM, FTIR, XRD). BPA was purchased from Sigma Aldrich. In this work, its molar volume and van der Waals radius were calculated to be V= 177,66 cm^3/mol and r = 5,05Å, using *ab initio* calculations: The procedure of molecular volumes calculation is based on the Monte Carlo approach, while electron densities were computed using Hartree Fock (HF) wave functions based on HF 6-31G basis set of optimized geometries. Adsorption from aqueous solution of BPA (~ 10^{-3}M) was studied at 303K in the batch system; the suspension of solid and BPA solution was stirred for 60 minutes and then the two phases were separated by centrifugation (MiniSpin from Ependorph, 13400 rpm, during 60 minutes). The equilibrium BPA concentrations in the supernatant were determined by UV spectrophotometry. The results are expressed in the form of adsorption isotherms: the amounts of adsorbed BPA (Na, mol/g) plotted vs. equilibrium BPA concentration (mol/L).

Results and Discussion

The results of FTIR spectroscopy experiments confirmed the presence of CPC in the composite materials obtained in this work. In the IR spectra of clinoptilolite and bentonite, bands characteristic for these structures wereobserved. However, two new bands, centered at ~ 2931 and 2849 cm^{-1} appeared in the spectra of the organomodified clinoptilolites corresponding to the CPC present in the composite; their relative intensities increase with increasing the amount of adsorbed CPC. In the case of bentonite modified by CPC, band at 2919 and 2849 cm^{-1} were observed. Modification by CPC caused the textural changes, which are shown in Figure 1, where SEM images of bentonite and bentonite modified by CPC are presented.

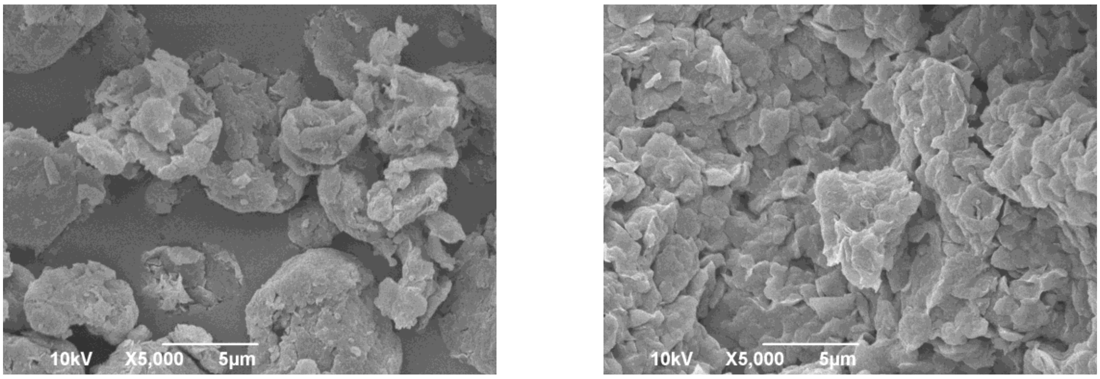

Figure 1. Left: SEM image of bentonite; Right: SEM image of bentonite modified by CPC

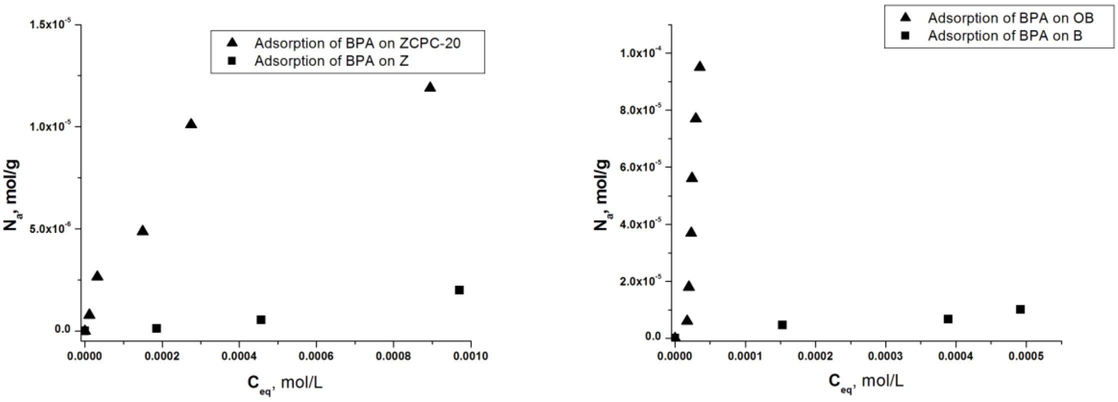

Figure 2. Adsorption isotherms of BPA obtained on clinoptilolite and clinoptilolite modified by CPC (left); and on bentonite and bentonite modified by CPC (right)

The batch adsorption experiments indicate that both natural minerals showed only very low capacities for bisphenol-A adsorption. However, it is evident from Figure 2 that the modification with cetylpyridinium chloride improved the capacities for bisphenol-A adsorption from aqueous solutions significantly in the case of clinoptilolite but particularly in the case of bentonite. The results obtained here indicate the possibility of practical use of the modified materials in the remediation of polluted waters.

Acknowledgment

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Clinoptilolite as a fertilizer carrier: the effect on pasture yield and quality

V. Rakić[1*], A. Simić[1], I. Živanović[1], J. Marković[2], Ž. Dželetović[3] and T. Krogstad[4]

[1]*Faculty of Agriculture, University of Belgrade, Nemanjina 6 11080 Zemun-Belgrade, Serbia;*
E-mail:vesna.rakic@agrif.bg.ac.rs
[2]*Institute for forage crops, Globoder, 37251. Kruševac, Serbia*
[3]*Institute for appliance of nuclear energy, Banatska 31b 11080 Zemun, Serbia*
[4]*Norwegian University of Life Sciences (NMBU), P.O.Box 5003, N-1432 Aas, Norway*

Introduction

Nitrogen is crucially important element which contributes the yield of the majority of crop plants, including forages. Restriction in the use of mineral nitrogen in Europe changed the view on the fertilization of hilly-mountainous grasslands of Serbia. Cattle manure as a fertilizer for pastures is available NH_4^+-source, but ammonia losses through leaching or evaporation significantly reduce the efficiency of manure in crop production. Hence, there is a need for binding agent which can preserve N reserves from manures. Our previous results show that the addition of 10 wt.% zeolite to fresh cattle manure increases retention of realized ammonia by 90 % in comparison to the system without zeolite. Also, preliminary tests indicated that grass herbage yields obtained in pot experiment containing ammonia-loaded zeolite were higher compared to control pots (Simić *et al.*, 2013). Kavoosia (2007) reported that clinoptilolite decreased the NH_4-N loss from the soil and enabled an easier uptake of nitrogen by the plant. The objective of this study was to investigate and launch the sustainable ammonia source for pastures in Serbia, which is based on natural zeolite-clinoptilolite mixed with manure, compared mutually and with mineral N supply. It is expected that the application of zeolite with manure can increase nitrogen usage efficiency.

Experimental Methods

The zeolitic tuff (Zlatokop deposit, Vranjska Banja, Serbia; containing 70% of clinoptilolite: $Ca_{1.6}Mg_{0.7}K_{0.7}Na_{0.3}Al_{5.5}Si_{26}O_{72}\cdot 23H_2O$, grain size in the range 0.063-0.1 mm) was used as the additive to manure in this work. Prior to application, fresh cattle manure was homogenously mixed with the natural zeolite – clinoptilolite and fermented during 3 months. Field plots (5m x 2m) were established on natural pastures in 2012/13 included five different treatments: a) pure manure (30 t ha^{-1}); b) manure+zeolite (30 t ha^{-1} +10 wt.% zeolite); c) pure zeolite (3 t ha^{-1}); d) nitrogen application by mineral fertilizer (50 kg ha^{-1} N) and e) control. The field trial was established in vicinity of Šabac, Serbia by the method of RCB design of plots in 4 replications. The treatments with zeolite, manure and a mixture zeolite+manure were applied in autumn. Spring nitrogen application of mineral fertilizer was performed at the beginning of the vegetation season. The plots were harvested in May and the dry matter (DM) of the harvests was measured. Neutral Detergent Fiber (NDF) and Acid Detergent Fiber (ADF) were determined according to the procedure by Van Soest et al. (1991); protein fractions (true protein and NPN) were determined as described by Licitra *et al*. (1996). The main characteristics of the soils were determined: pH in $CaCl_2$ was 5.07 while pH in H_2O was 5.73; the contents of P_2O_5 and K_2O were 19.8 mg kg^{-1} and 115.1 mg kg^{-1} respectively, total N was found to be 0.16%. Total DM yield and pasture DM quality in each of the two cuts were analyzed by analysis of variance (ANOVA) and LSD test, in order to recognize significant effects of fertilization treatments.

Results and Discussion

Fertilizer treatments affected yield, especially in the case of first cut: the yield was doubled by fertilization, in comparison to control treatment (Table 1). Manure showed some extended effect in second cut, while pure zeolite treatment had a diminishing effect on yield in arid conditions during summer re-growth. The most promising treatments are those with manure (enriched by zeolite or pure manure).

The results obtained in this work indicate that the usage of zeolite based fertilizer lead to increase of true protein content and the decrease of non-protein nitrogen in grasses (Table 1), what can have positive influence on forage digestibility. These findings can be taken as an indication that the high true protein content of the plants can be caused by their ability to raise more nitrogen from soil due to the presence of clinoptilolite enriched by ammonia. It is in accordance with the results of Gevrek *et al* (2009) who found that the high protein content of the rice plants fertilized by clinoptilolite could be caused by their ability to extract more nitrogen from soil. Present results are also in accordance with previously published data on the application of natural zeolite combined with manure, which have been successfully used to remediate soils having unfavourable chemical properties as well as to enhance the crop yield on them (Glisic *et al*., 2009).

Table 1. Pasture dry matter yield and forage quality per cut

treatments I cut	DM yield		CP	CCl	NDF	ADF	TP	NPN	NPN (%solP)
I	1.99c		9.71a	31.9a	62.8a	38.4a	73.6ab	26.4ab	89.4ab
II	2.38c		9.98a	33.0a	63.8a	37.8a	74.2ab	25.8ab	84.6ab
III	4.53a		10.1a	32.7a	63.9a	38.7a	64.8b	35.2a	100a
IV	4.11ab		9.86a	33.3a	63.4a	38.0a	83.5a	16.5b	65.7b
V	3.31b		10.5a	32.0a	62.3a	38.7a	69.6ab	30.4ab	96.2a
treatments II cut	DM yield	Total yield	CP	CCl	NDF	ADF	TP	NPN	NPN (%solP)
I	1.02ab	3.01c	9.04a	25.9a	69.5b	37.1a	84.2ab	15.8ab	79.3a
II	0.91b	3.29c	9.02a	24.4a	66.6ab	41.3a	86.5ab	13.5ab	71.5a
III	1.38a	5.91a	9.72a	25.3a	66.7ab	38.8a	73.9b	26.1a	78.6a
IV	0.97ab	5.08ab	9.05a	25.0a	63.1a	37.9a	91.0a	9.0b	85.3a
V	0.96ab	4.27b	9.77a	27.3a	66.8ab	41.0a	80.7ab	19.3ab	93.8a

NOTE: I treatment-control, II treatment- zeolite (3 t ha^{-1}), III treatment- manure (30 t ha^{-1}), IV treatment- manure+zeolite (mixed) (30 t ha^{-1}), V treatment- mineral nitrogen (50 kg ha^{-1}); DM – dry matter (t ha^{-1}), CP – crude proteins (% DM), CCl - crude cellulose (% DM), TP - true proteins (% of crude proteins), NPN-non protein nitrogen (% of crude proteins), NPN(%solP)-percentage of soluble protein that is non-protein nitrogen

The obtained results show that the use of cattle manure enriched with natural zeolite can be used as a fertilizer for pastures which contributes to a preservation of nitrogen. The application of such a fertilizer may reduce the application of mineral N fertilizers on natural pastures. Based on the results presented here, natural zeolite can be recommended for agricultural purposes in terms of sustainable fertilizing and improving system cattle farm – manure - organic fertilizer for forage crops. Future studies should focus on including additional sites with different soil types in contrasting climatic areas.

Acknowledgment
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Natural clays as drug support system: preliminary studies

A. Rivera[1], L. Valdés[2], A. M. Martínez[3], M. Velázquez[3] and L. C. de Ménorval[4]

[1]*Zeolites Engineering Laboratory, Institute of Science and Technology of Materials (IMRE), University of Havana, 10400 Havana, Cuba; E-mail: aramis@fisica.uh.cu, aramis@imre.oc.uh.cu*
[2]*Department of Basic Chemistry, Institute of Pharmacy and Food (IFAL), University of Havana*
[3]*Research Center for the Miner-Metallurgic Industry (CIPIMM)*
[4]*Laboratoire des Agrégats, Interfaces et Matériaux pour L'Energie(AIME) Institut Charles Gerhardt Montpellier, UMR-5253 CNRS-UM2-ENSCM-UM1.2, Place Eugène Bataillon, CC-1502, 34095 Montpellier Cedex 05, France*

Introduction

Clays are commonly used in the pharmaceutical industry as excipients or active products. Clays intercalated by drug molecules have attracted great interest from the scientific community because they exhibit novel physical chemical properties. In particular, natural clays have been employed as drug delivery carriers (de Sousa Rodrigues et al., 2013); and a good example is the montmorillonite (Park et al., 2008; Joshi et al., 2009). Based on these facts and the experience of our group in the use of modified natural clinoptilolite as drug support (Rivera and Farías, 2005), in the present work two natural clays ─bentonite and palygorskite─ are evaluated for their capacity to incorporate the ciprofloxacin drug. The purpose is the development the drug supports with potential applications as release systems. The raw materials and the clay-ciprofloxacin composites were characterized with different techniques.

Experimental Methods

The natural clays evaluated were sodium bentonite (Bent) and palygorskite (Paly). The model drugs studied were ciprofloxacin, sodium diclofenac and metronidazole, which were obtained from the pharmaceutical industry and used as received. The interaction studies were performed at different drug concentrations (from 3 mg/ml to 9 mg/ml) for 2 h, in order estimate the influence of concentration on drug load in the clay. In all cases, 0.3 g of the clays were placed in contact with 30 ml drug solution. The experiments were carried out at room temperature under magnetic stirring. Then, the supernatant solution was separated by centrifugation. For the assays of drug adsorption in liquid phase, the drugs concentrations in solution before and after the contact with the clays were analyzed and quantified by ultraviolet spectroscopy (UV), according to standard procedures (USP, 2004). The UV spectra were collected by means of a Rayleígh UV-2601 spectrophotometer in the wavelength interval 200-400 nm (adsorption maxima at 277, 275 and 277 nm for the ciprofloxacin, sodium diclofenac and metronidazole, respectively). The experiments were performed by duplicated, and their repeatability was verified. The raw materials and the resulting composites of the interaction drug-clay were characterized by infrared spectroscopy (IR) and X-ray diffraction (XRD).

Results and Discussion

The interaction between the three drugs and the two clays indicated that ciprofloxacin (Cipro) was the drug that showed a true affinity by the clays, sodium bentonite and polygorskite. No clay─drug interaction was observed in the case of sodium diclofenac and metronidazole under the conditions reported in the present work.

The ciprofloxacin (Cipro) incorporation in the clays depended on the initial concentration. For both clays, the Cipro adsorbed per gram of material is comparable; for example, at a Cipro concentration of 6 mg/ml, the amount drug incorporated is ~ 572 and 537 mg/g clay for the Bent and Paly, respectively. The intercalation process of ciprofloxacin in both clays was very fast. Nearly 90% of Cipro was incorporated within 2 h of interaction time.

Fig. 1 shows the XRD patterns for Bent and bentonite-cipro composite (Bent-Cipro). As can be observed the (001) basal reflection of Bent was shitted to lower diffraction angles in the Bent-Cipro composite. It appears at 7.0° for raw clay and at 4.24° for the clay after the incorporation of drug, with basal spacings of 1.26 nm and 2.08 nm, respectively. This increase in the d-spacing indicates that Cipro has been efficiently incorporated into the interlayer of Bent.

The IR transmittance spectra for Cipro, Bent and Bento-Cipro composite are shown in Fig. 2. In the ciprofloxacin spectrum, the most characteristic bands occur in the interval 1800-1200 cm^{-1}. In the Bent-Cipro sample new bands appear which can be attributed to ciprofloxacine present in the clay, in accordance with the XRD results.

Release assays of ciprofloxacine from the composites Bento-Cipro and Paly-Cipro in different dissolution media, following standard pharmaceutical procedures, are in progress (Valdés et al. 2014; Martínez et al. 2014).

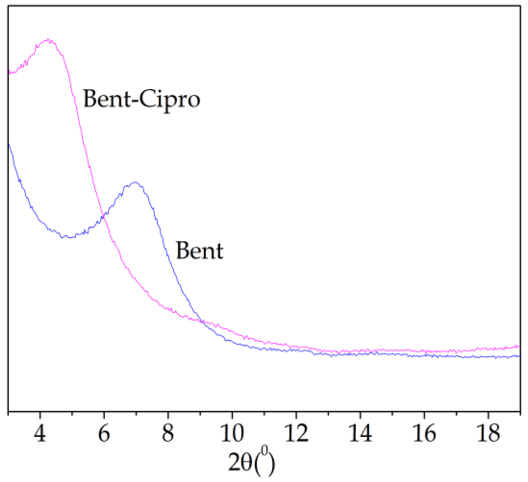

Figure 1. XRD patterns of Bent and Bento-Cipro composite

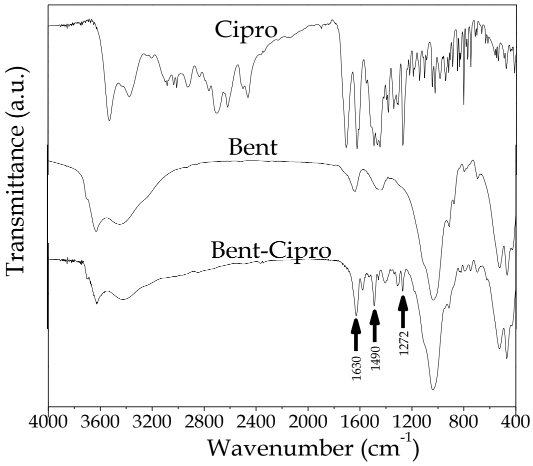

Figure 2. IR spectra of Cipro, Bent and Bent-Cipro composite

Acknowledgment

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ZZ a zinc clinoptilolite for drinking-water treatment

G. Rodríguez-Fuentes and I. Rodríguez-Iznaga

Institute of Material Science and Technology, University of Havana, Zapata y G s/n, Vedado, La Habana 10400, Cuba; *E-mail: gerardo@imre.oc.uh.cu*

Introduction

Disinfection is of unquestionable importance for the supply of safe drinking-water. The destruction of microbial pathogens is essential and it usually involves the use of reactive chemical agents such as chlorine. Recently, several papers have reported the potential of Ag and ZnO nanoparticles in drinking-water treatment to eliminate microbiological contamination. KDF (Kinetic Degradation Fluxion**)** commercial filters release small quantities of Cu and Zn. Some authors have described the use of Ag/Zn zeolite for the same purpose. A zeolite may yield to controlled release of Zn^{2+} ions but two issues should be addressed: 1) The toxicity of the zeolite, and 2) The ability of the zeolite to release the amount of Zn^{2+} required after its incorporation to the drug without creating a health hazard. The design and development of ZZ (a Zn-clinoptilolite) took in account two facts:

a) The introduction of Zinc in clinoptilolite by the exchange of the natural extra-framework cations (Ca^{2+}, K^+, Mg^{2+} and Na^+).
b) The controlled release of Zn^{2+} from the modified clinoptilolite through ion-exchange of the ions present in drinking-water at room temperature.

ZZ is a new material with microbicidal and ion-exchange properties that can be used to purify water for human consumption, as a viable alternative to traditional procedures such as water boiling, and disinfection with chemical substances and physical methods. ZZ makes possible the design of flexible domestic and collective water purification systems, which combine the ZZ properties, the simplicity of the purification systems and their low cost with the peoples' water storage and handling habits.

Experimental Methods

Natural clinoptilolite (HEU Iupac code) from Tasajeras, Cuba, deposit that meets Cuban standard NC 625: 2008 -Annex A, of natural zeolites for human and animal health and nutrition, was used as raw material to obtain purified natural clinoptilolite NZ. The particle size of NZ was 1 - 3 mm. The Zn^{2+}-NZ form was obtained in a pilot plant with capacity 1 ton/day through hydrothermal ion-exchange modification of NZ with 0.5M solution of $ZnSO_4.7H_2O$ USP, at boiling temperature for 10 hours following the procedure described by Rodríguez-Fuentes (1993). The pH, density, sterility and humidity of Zn^{2+}-NZ were adjusted considering the sanitary properties required for products used in water purification treatments recommended by the *WHO Guidelines for Drinking-Water Quality* and Cuban standard NC 827: 2010. The resulting product was denominated ZZ. The ZZ was characterized by chemical analysis and X-ray diffraction. Microbiological tests were carried out to determine possible contamination and the bactericidal properties.

Results and Discussion

The study of the pitcher with ZZ cartridge (140 grams) using home tap water reproduced the exchange of Zn^{2+} by Ca^{2+} as observed in figure 1. The Ca content was reduced by 25% as compared to the initial concentration in tap water while the Zn content is about 2 ppm in the 200L treated during the study. The ZZ water purification systems (figure 1) were evaluated in accordance with existing water quality parameters for human consumption. The results indicate that turbidity in well-water was reduced to 3 units when treated in a ZZ pitcher. In addition to its ion-exchange properties enabling the release of Zn ions through the exchange of Ca ions in the water, ZZ has another important property: the adsorption that reduces excess hardness in water, this being a major cause of sediments in the human urinary tract. Actually, water hardness is reduced by 60%. Heavy metals as Cd, Cr, Mn, Ni and Pb remain at lower levels than the values established for water intended for human consumption. The water purified with ZZ meets the requirements set by the *WHO Guidelines* and the Cuban standard NC 827: 2010.

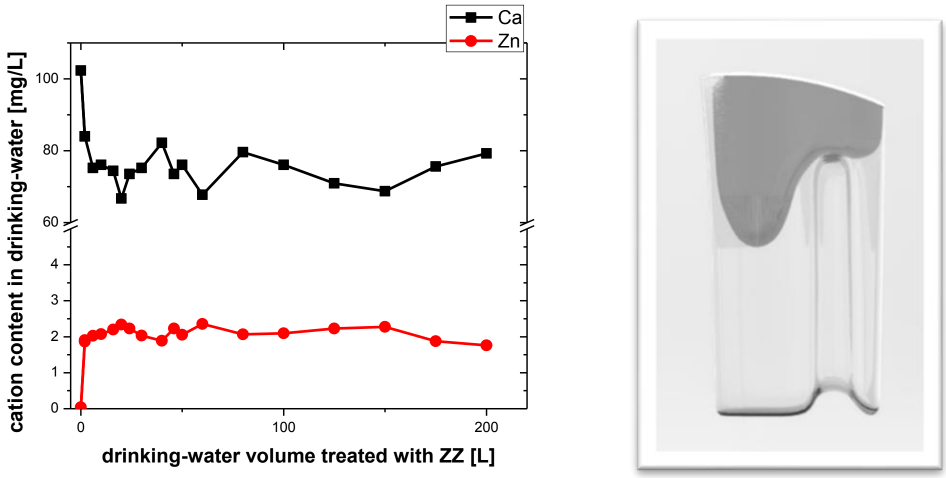

Figure 1. Zinc and Calcium content in tap water (Left) treated in the ZZ pitcher (Right)

The minimum inhibitory dosage of 10% of ZZ was established through a study that used Gram + and Gram - bacteria strains and yeasts. It has been determined that ZZ has a bactericidal effect on a great number of microorganisms. The studies of the microbicidal effect of ZZ show that this material renders absolutely inactive the following microorganisms ordinarily present in drinking-water: *Aeromonas hydrophila ATCC 7614, Plesiomonas shigelloides CNCTC 5132, Escherichia coli O:149 K88 Lt (+), Escherichia coli O:101 K99 St(+), Escherichia coli ATTC 25922, Vibrio cholerae C7258 (Ogawa), Vibrio cholerae C6706 (Inaba), Pseudomonas aeruginosa 5FQ, Pseudomonas aeruginosa O11, Leptospira interrogans M20, Shigella sonnei, Salmonella Typhii* and *Giardia lamblia* cysts.

It has been established that to ensure proper disinfection, water with added ZZ should be left static for at least 30 minutes at room temperature before drinking or placing in the refrigerator. The time should be 3 hours when the contamination of microorganisms is higher than 10^5 CFU (B. Cedre Marrero et al, 2008; L. Bravo, 2008; A. Fernández-Abreu et al, 2009; A. Ruiz Espinosa, 2008).

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Natural clinoptilolite and mordenite forms improved with copper and iron: characterization and catalytic activity in NO reduction

I. Rodríguez Iznaga[1], V. Petranovski[2], F. F. Castillón Barraza[2], A. Simakov[2], B. Concepción Rosabal[1], F. Chávez Rivas[3], D. Tito Ferro[4] and A. Penton Madrigal[5]

[1]*Instituto de Ciencia y Tecnología de Materiales (IMRE) - Universidad de La Habana. La Habana, Cuba.*
[2]*Centro de Nanociencias y Nanotecnología – UNAM. Ensenada, B.C. México.*
[3]*Departamento de Física, ESFM-IPN. UPALM., C. P. 07738. México D.F., México;*
E-mail: fchavez@esfm.ipn.mx
[4]*Centro Nacional de Electromagnetismo Aplicado, Universidad de Oriente, Santiago de Cuba, Cuba.*
[5]*Facultad de Física - Universidad de La Habana. La Habana, Cuba.*

Introduction

The technology for selective catalytic reduction (SCR) of NO_x demands wide variety and important quantities of catalysts. Zeolite catalysts with metal species have attracted great interest. Between other metals, copper and iron have brought attention due to their catalytic properties and low cost (Metka et al., 2013). Natural zeolites such as clinoptilolite and mordenite also draw attention because of their ion-exchange properties, thermal stability, availability and low price. Efficient and low-cost catalysts can be developed from natural clinoptilolite and mordenite modified with copper and iron. The characterization and catalytic activity in SCR-NO of the natural clinoptilolite and mordenite from Tasajeras and Palmarito de Cauto deposits, respectively, modified with Fe^{2+} and Cu^{2+} cations via ion-exchange is the subject of this work.

Experimental Methods

Purified zeolite materials, obtained from the zeolitic rocks of Tasajeras and Palmarito de Cauto deposits (Cuba) with a particle size range of +40-90 μm and +38-74 μm, respectively, were used in this work. The purified zeolites obtained are referred as the natural clinoptilolite (TZ) and mordenite (PZ), respectively. PZ is a mixture of ~ 70% of mordenite with others phases (clinoptilolite-heulandite, montmorillonite, quartz, feldspar and iron oxides). Chemical composition of the sample in oxide form, with the balance as water, is 62.1 % SiO_2; 14.4 % Al_2O_3; 2.59 % CaO; 2,03 % Fe_2O_3; 1,04 % MgO; 0.60 % K_2O; 2,63 % Na_2O; 0.13% P_2O_5; 0.13% SO_3 and 0.22% TiO_2. TZ is a mixture of ~ 78% clinoptilolite-heulandite with others phases (mordenita, montmorillonite, quart, feldspar and iron oxides). Their chemical composition in oxide form, with the balance as water, is 63.7% SiO_2, 14.3% Al_2O_3, 2.49% CaO, 0.93% Fe_2O_3, 0.73% MgO, 0.67% K_2O; 2.73% Na_2O; 0.05% P_2O_5; 0.06% SO_3 and 0.12% TiO_2. Exchanged Fe^{2+} and Cu^{2+} samples were obtained by ion exchange of TZ and PZ with $Cu(NO_3)_2$ (0.5N) and $FeSO_4$ (0.05 N, pH= 2) solutions in a relation of 1 gram of zeolite to 20 mL of solution, for 24 h and agitation, at 80 °C. The Cu and Fe content in the exchanged CuTZ, FeTZ, CuPZ and FePZ samples was 4, 3.7, 4.2 and 4.3 wt %, respectively.

The catalytic activity test of PZ, TZ and exchanged Cu^{2+} and Fe^{2+} samples in NO reduction with C_3H_6/CO was performed in a quartz reactor, using 1000 mg of samples, within a 25-500°C temperature interval with a ramp rate of 5°C/min. The NO(0.09%), C_3H_6(0.22%), O_2(0.46%) and CO(1.179%) reaction mixture was prepared by mixing of individual flows controlled with mass-flow controllers. Before the catalytic test, the samples were pretreated in oxygen flow with temperature increase from 25 to 350°C with ramp rate of 5°C/min. Effluent gases were analyzed by a CAI ZRE gas analyzer. The UV-Vis diffuse reflectance and Mössbauer spectra of the samples exchanged with Cu^{2+} and Fe^{2+}, respectively, were obtained. UV-Vis spectra were obtained with a Varian Cary 300 spectrometer. Mössbauer spectra were obtained in a Halder spectrometer, with ^{57}Co in RH matrix at room temperature. Normos 95 computer program was used for spectra resolution and parameters determination (isomer shifts δ, quadrupole splittings Δ and relative area A; relative to αFe)

Results and Discussion

UV-Vis spectra of CuZP and CuTZ show the characteristic *d-d* transition band of Cu^{2+} centered at 800 - 850 nm and a charge-transfer complex band at 207 nm due to interaction of Cu^{2+} with oxygen from zeolite framework. For Mössbauer spectra resolution and parameters determination were used three and four doublets for FeZP and FeZT, respectively. In FeZP two doublets are associated to Fe^{3+} and one to Fe^{2+}. For FeZT, two doublets were associated to Fe^{3+} and two to Fe^{2+}. To the Fe^{2+} doublets, the δ, Δ and A values in FeZP are 1.20 mm/s, 2.52 mm/s and 17 %, respectively. For FeZT, these values are 1.08 mm/s, 2.23mm/s and 13 % to the first-doublet and 1.30mm/s, 2.53mm/s and 24% to the second-doublet, respectively. The analysis of the values of the Mössbauer parameter and the reported studies (Roque-Malherbe et al. 1990; Tuel et al., 1998) lead to outline that, both for FeZT and FeZP, all Fe^{2+} is found in octahedral coordination. Also that, Fe^{2+} is present in two different positions in FeZT. This Fe^{2+} should be mainly in cationic positions extra-framework as a charge compensation cation. Fe^{3+} in octahedral and tetrahedral coordination is found, too. The obtained results on catalytic activity to NO reduction with CO/C_3H_6 showed that such activity is influenced by the zeolite matrix type and its composition. The catalytic activity of all exchanged Fe^{2+} and Cu^{2+} samples is higher than for PZ and TZ. The catalytic activity of the exchanged Cu^{2+} samples is higher in CuZP (mordenita matrix) than in CuZT (clinoptilolite matrix), while for those Fe^{2+}exchanged such activity is higher in FeZT (clinoptilolite matrix) than in FeZP (mordenita matrix). Such behavior can be due to differences in the cationic positions in that these ions are located in the clinoptilolite and mordenite frameworks, in line with this Mössbauer studies showed that Fe^{2+} is present in two different positions in FeZT (clinoptilolite matrix). The exchanged Fe^{2+} samples have at lower temperature a higher catalytic activity than those of the Cu^{2+} exchanged ones. Among all sample, the exchanged Fe^{2+} natural-clinoptilolite (FeZT) has the higher catalytic activity, which is in line to the higher Fe^{2+} population aforesaid in Mössbauer studies (with A values of 13 % to the first-doublet and 24% to the second-doublet). Additionally, it is observed for all samples that CO_2 concentration is increased during NO reduction. Besides this, at temperature of more than 300 °C the CO concentration is increased in FePZ. In line with this, the CO_2 concentration for FePZ increase very little with respect to the other samples and its catalytic activity at > 300^oC is lower than for CuPZ. This suggests both a partial oxidation of C_3H_6 to CO before final complete oxidation to CO_2 and that active centers to NO reduction associated with iron species are more stable at higher temperature in FeZT (clinoptilolite matrix) than FeZP (mordenita matrix). For the others samples (PZ, TZ, CuZT, CuPZ and FeTZ) an important decrease of the CO concentrations is observed during NO reduction, which suggests a more direct oxidation of CO/C_3H_6 to CO_2.

Conclusions

Natural clinoptilolite (ZT) and mordenite (ZP) from Tasajeras and Palmarito de Cauto deposits (Cuba), respectively, modified both with Fe^{2+} and Cu^{2+} cations via ion-exchange were subject of studies of characterizations and catalytic activity in NO reduction with CO/C_3H_6. UV-Vis spectra showed the Cu^{2+} presence in the exchanged samples by the characteristic band of this cation centered at 800 - 850 nm. Mössbauer spectroscopy studies showed that Fe^{2+} is found in octahedral coordination in the exchanged samples. Fe^{2+} is present in two different positions in FeZT. All exchanged samples have higher catalytic activity to NO reduction than ZP and ZT, and such activity is influenced by the zeolite matrix type and its composition. The catalytic activity of the exchanged Cu^{2+} samples is higher in CuZP than in CuZT, while for those Fe^{2+}exchanged such activity is higher in FeZT than in FeZP. Such behavior can be due to differences in the cationic positions in that these ions are located in the clinoptilolite and mordenite frameworks, in line with this Mössbauer studies showed that Fe^{2+} is present in two different positions in FeZT.

Acknowledgment

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Comparative analysis of zeolite (clinoptilolite) and *Yucca schidigera* extract in diets for adult cats

N. C. Roque[1], F. M. O. B. Saad[2], J. P. F. Santos[3], J. S. Reis[2], A. F. Chizzotti[1], F. S. Ebina[1] and F. Borsatto[4]

[1]*Master in Animal Science; E-mail: nacharleaux@yahoo.com.br*
[2]*Department of Animal Sciences at the Federal University of Lavras – Lavras/MG/Brazil*
[3]*Department of Nutrition and Animal Production in the Veterinary Medicine and Animal Sciences School at the University of São Paulo – Pirassununga/SP/Brazil*
[4]*Industrias Celta Brasil Ltda. – Cotia/SP/Brasil; E-mail: fernandoborsatto@celtabrasil.com.br*

Introduction

Pets enjoy increasingly closer relationship with humans, however, among the drawbacks of this relationship highlights the fecal odor, which is considered a major obstacle in the interaction between humans and dogs and cats inside residences. In this sense, the search for nutritional additives that reduce the odor of feces of dogs and cats are composed by nutritional strategies of great importance, among which stand out the extract of *Yucca schidigera* and zeolites. Thus, this study aimed to evaluate the effects of *Yucca schidigera* and zeolite (clinoptilolite) on reducing the fecal odor of adult cats as well as the fecal score and apparent digestibility of nutrients.

Experimental Methods

The experiments were performed at the Center for Studies on Pet Nutrition, in the Department of Animal Husbandry, at the Universidade Federal de Lavras (UFLA), located in Minas Gerais state, Brazil. Twenty-one adult cats, mongreal with average weighing 3.71 ± 0.84 kg. The experiment was divided into two periods, and in each experimental period the animals were distributed in a completely randomized design, consisting of seven treatments (control wet diet, control wet diet with addition of 125, 250 and 375ppm of *Yucca schidigera* and control wet diet with addition of 0.5%, 0.75% and 1.0% zeolite - clinoptilolite), with the animals being considered an experimental plot, totaling 42 experimental plots, six animals per experimental treatment.

The adaptation stage was consisted of five days, the animals were housed in metabolic cages and the diet amounts of feed supplied to the animals met the recommended by the NRC (2006). The total quantity of feed for each animal was offered once daily at 8h00am and remained available to the animal for 24 hours and the water *ad libitum*. The collection stage was consisted of seven days, in this stage feed leftovers, feces and urine were collected. The feces were available to fecal score, with scale of 1 to 5 (1=watery – liquid that can be poured; 2=soft, unformed – stool assumes shape of container; 3=soft, formed, moist – softer stool that retains shape; 4=hard, formed, dry stool – remains firm and soft; 5=hard, dry pellets – small, hard mass), then they were weighted and packed in plastic bags, taken to the freezer (-20ºC). Diets and feces were analyzed for dry matter, crude protein and crude energy, and crude energy to urine for determination apparent metabolizable energy of their experimental treatments, according to the methodology described by AOAC (1995), in Laboratory Animal Research at UFLA.

Samples of fresh feces were collected for sensory evaluation at the end of the second period, by possible owners and, thus, by cat feed buyers. The analysis was conducted according to information described by Anzaldúa-Morales (1994), with adaptations. Grades were attributed to each sample, as follows: 0=extremely foul, more than the control treatment, 1=more malodorous than the control treatment, 2=similar to the control treatment, 3=less malodorous than the control treatment, 4=considerably less malodorous than the control treatment.

The data was subjected to variance analysis and in order to do so the General Linear Models (GLM) statistical procedure and the Statistical Analysis System (SAS Institute, 2004) statistical package were used. The Shapiro-Wilk test was performed to assess the normality of the residuals and maximum F test for variance homogeneity. Given the assumptions, the means were compared by the Student Newman-Keuls (SNK) test at the 5% significance level, and subsequently the levels of zeolite were deployed in polynomial regressions.

Results and Discussion

There was no significant difference ($p>0.05$) for the coefficient of apparent digestibility of dry matter, crude protein and apparent metabolizable energy between experimental treatments.

With respect to fecal score it was found that the inclusion of *Yucca schidigera* was not effective in altering it ($p>0.05$), since for the zeolite was observed firmer stools in 0.50% and 0.75% levels compared to the control group ($p<0.05$). The fecal odor in turn was altered by both additive ($p<0.05$), reduced fecal odor was observed in the treatments with 125ppm and 375ppm of *Yucca schidigera* and 0.50% and 0.75% of zeolite, while the inclusion of 1.0% zeolite not differ from control treatment and 250ppm of *Yucca schidigera* presented more malodorous than other experimental treatments. Figure 1 shows the behavior of the levels of zeolite for the score and fecal odor.

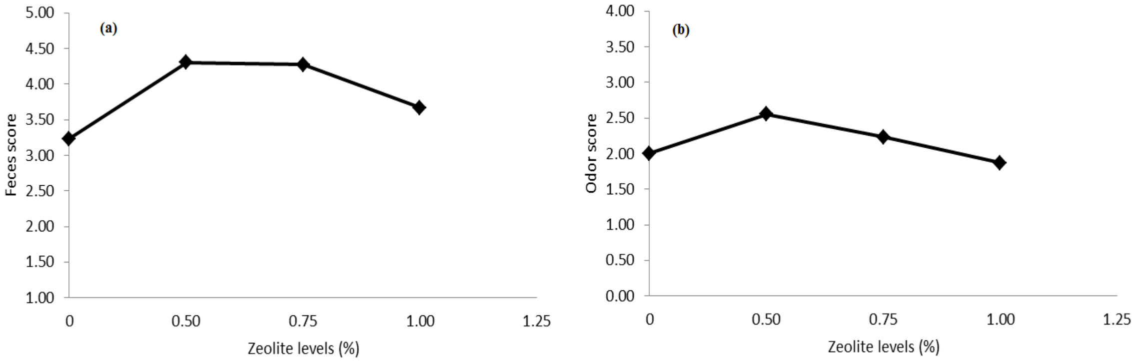

Figure 1. Effects of zeolite levels on feces score (a) and odor score (b)

In this experiment, zeolite presented a quadratic behavior in relation to score and fecal odor, the inclusion of 0.46% zeolite was the level that showed the highest reduction of odor, and to fecal scores the ideal level was 0.56% zeolite. The initial concentration of total ammonia decreases as zeolite is added; however the data behavior presented in this study are supported by the finding of Sonnenholzner (2004), which showed that the adsorbents are more effective when there is high concentration of solute related to the adsorbent. The authors found, by including 1g zeolite, the removal of total ammonia-N at 1.53mg/g, however, by adding 10g zeolite, the removal was 0.91mg/g.

In conclusion, both additives have ability to reduce fecal odor to cats, however only zeolite levels were effective in altering to fecal score of animals.

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An Approach to the Genesis and Mineral Composition of Zeolite in Central Anatolia (Ankara/Turkey)

M. B. Şahin

General Directorate of Mineral Research and Exploration, MTA-06800-Ankara/Turkey;
E-mail: bahadir_sahin@yahoo.com

Introduction

The study area, situated on a suture zone separating the central Anatolian metamorphic massifs in the east from the passive and active margin formations of the so-called Sakarya Continent in the west (Görür et al., 1984) (Dellaloğlu et al., 2001), is located 80 km south of Ankara in Central Anatolia. The Central Anatolian rock formations are collectively called Kırşehir Block which is a microcontinent surrounded by the branches of the Neo-Tethys during the Mesozoic to Paleocene (Şengör et al., 1984). During the Late Maastrichtian to latest Paleocene the Kırşehir Block began to collide with the Sakarya Continent and this juxtaposition triggered formation of two separate sedimentary basins (Haymana and Tuzgölü Basins) on the continents. The collision of the two continental blocks resulted in an ophiolitic melange in between which is generally called the Ankara Melange. The thin ophiolitic melange now constitutes a structural high separating the two basins and is called Samsam Ridge (Görür et al., 1984) on which the studied area is situated. Chabazite-rich zeolitic tuffs have been first termed as *zeolitite* in a volcano-sedimentary lake system in Central Anatolia (Ankara, Turkey). The formation developed during Miocene in a lacustrine environment which formed as a consequence of compressional tectonic events in Central Anatolia. In this lacustrine system, zeolitic-tuff beds represent a portion of intercalated volcanogenic layers, clays, bituminous shales, mudstones and limestones. Mineralogical study was carried out on zeolites in the formation, which are predominantly chabazite and subordinate clinoptilolite and erionite as authigenic zeolites. Zeolitite consist of mainly chabazite, derived from the interaction of volcanic glass with saline-alkaline lake water.

Genesis and Mineralogical Composition of Chabazitolite

Stratigraphically, the basement of the studied area consists of upper Cretaceous ophiolitic melange overlying by upper Cretaceous-Paleocene marine deposits. Forming process of the lake is a thrusting of the melange to the marine deposits. As a result, a small scale trough valley formed as a closed hydrologic basin including a volcano-sedimentary system which corresponds to the depositional environments mentioned as “saline, alkaline lakes” (Hay and Sheppard, 2001). Volcanic material derived from Karacadağ Volcanism (Uğuz et al., 1999). Preliminary volcanic material was volcanic glass in rhyolitic character of zeolitic tuff layers in the study area. Volcanic glass falling into the lake (saline-alkaline) reacted with the solutions. Three different main tuff layers (layer 1, layer 2, layer 3) (40 cm, 65 cm, 1 m, respectively) and lenses (thickness vary between 10–20 cm) deposited at varying average thicknesses in the formation (Şahin, 2007) (Figure 1).

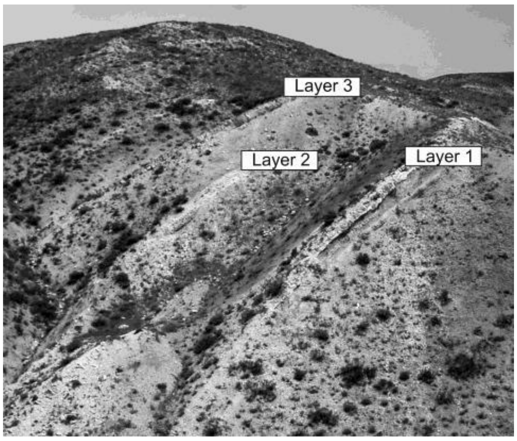

Figure 1. Zeolitite layers in the formation (After Şahin, 2007)

Scanning electron microscopy (SEM) (FEI QUANTA 400 MK2; MTA) and X-ray diffraction (XRD) (Philips XRD; PW 1830: Cu-K_α, 30 kV, 40mA; MTA) were used to analyze the mineralogical composition of the samples. SEM/XRD results indicate that the mineral paragenesis consist of “chabazite + clinoptilolite + erionite” (Figure 2). According to the results of mineralogical determinations of 262 samples from main three different layers, zeolitite consist of zeolite minerals more than % 75 wt of the rock, chabazite is a dominant zeolite mineral in the samples (Figure 3). Unreacted glass, K-feldspar and analcime are also determined in the formation.

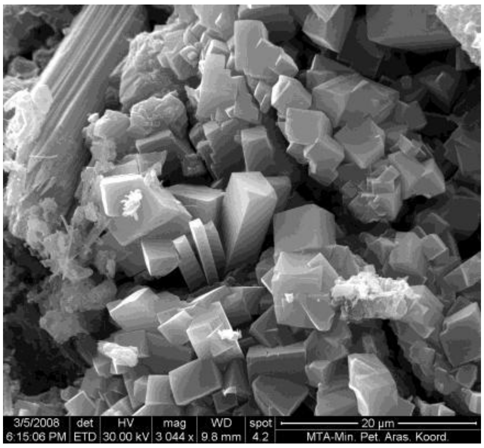

Figure 2. “Chabazite + clinoptilolite + erionite” paragenesis in a sample

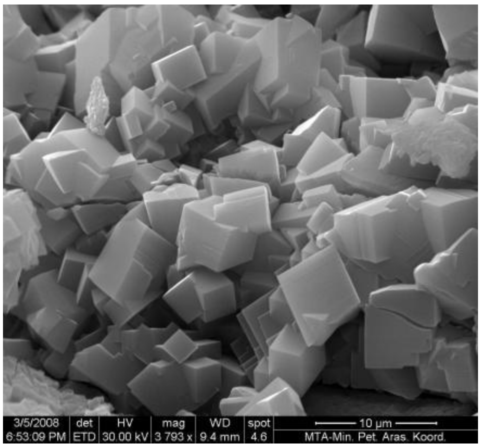

Figure 3. Pseudo cubic chabazite is dominant zeolite mineral

Results and Discussion

Zeolite minerals derived from the interaction between volcanic glass and saline-alkaline lake water. According to the existing zeolite minerals and their distrubution in the basin, probably at the early stage since the medium was less alkaline and at the same time since the Ca concentration of the lake water was higher as suggested by Chipera and Apps (2001), first chabazite was formed, and following this, clinoptilolite crystallized. At the following step, silica activity of the lake water increased, and erionite derived. Mineralogical composition and semi-quantitative data shows that chabazite is the main authigenic phase (about 70-90 % wt of zeolitite) along with minor clinoptilolite (about 5-10 % wt of zeolitite) and erionite (about 1-5 % wt of zeolitite). Nearly monomineralic layers of chabazite occurred in this Miocene lake deposits in Central Anatolia. Chabazite-rich or chabazite-dominant beds termed as “zeolitite” in the study area.

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Effects of zeolite (clinoptilolite) and *Yucca schidigera* extract in cats fed on mineral excretion

J. P. F. Santos[1], F. M. O. B. Saad[2], N. C. Roque[3], R. C. S. Ogoshi[2], M. A. Brunetto[1] and G. A. Igaki[4]

[1]Department of Nutrition and Animal Production in the Veterinary Medicine and Animal Sciences School at the University of São Paulo – Pirassununga/SP/Brazil; Email: joao_paulo@zootecnista.com.br
2Department of Animal Sciences at the Federal University of Lavras – Lavras/MG/Brazil
[3]Master in Animal Science
[4]Industrias Celta Brasil Ltda. – Cotia/SP/Brasil;E-mail: gustavoigaki@celtabrasil.com.br

Introduction

The fecal odours is a factor that causes a lot of discomfort between owners and cats, and many volatile components are involved in this process, such as alcohols, ketones, amines, sulphite, ammonia and volatile fatty acids (Lowe & Kershaw, 1997), which are closely related to the fermentation process performed by intestinal microorganisms. Among the nutritional additives that modulate fecal odour stand out from the extract of *Yucca schidigera* and zeolite, which have been studies in cats (Lowe & Kershaw, 1997; Roque et al., 2011) however, were not found in literature works than considered the effects of these additives on the bioavailability of minerals. Thus, this study aimed to evaluate the effects of inclusion of *Yucca schidigera* and natural zeolite (Clinoptilolite) on the coefficient of apparent indigestibility of calcium, phosphorus, magnesium, sodium, potassium, iron and manganese.

Experimental Methods

The experiments were performed at the Centre for Studies on Pet Nutrition, in the Department of Animal Husbandry, at the Universidade Federal de Lavras (UFLA), located in Minas Gerais state, Brazil. Twenty-one adult cats, mongreal with average weighing 3.56 ± 0.78kg. The experiment was divided into two periods, and in each experimental period the animals were distributed in a completely randomized design, consisting of seven treatments (control wet diet, control wet diet with addition of 125, 250 and 375ppm of *Yucca schidigera* and control wet diet with addition of 0.5%, 0.75% and 1.0% zeolite - clinoptilolite, with 98% purity), with the animals being considered an experimental plot, totalling 42 experimental plots, six animals per experimental treatment.

The adaptation stage consisted of five days in which the animals were housed in metabolic cages and the diet amounts of feed supplied to the animals met the recommended by the NRC (2006). The total quantity of feed for each animal was offered once daily at 8h00am and remained available to the animal for 24 hours and the water *ad libitum*. The collection stage was consisted of seven days in this stage feed leftovers and feces were collected. Calcium, phosphorus, sodium, potassium, magnesium, iron and manganese were analyzed in Laboratory of Nutrition of Institute of Agriculture (Belo Horizonte - MG/Brazil). The determinations were performed by atomic absorption spectrophotometer according to procedures recommended by Cantle (1982).

The data was subjected to variance analysis and in order to do so the General Linear Models (GLM) statistical procedure and the Statistical Analysis System (SAS Institute, 2004) statistical package were used. The Shapiro-Wilk test was performed to assess the normality of the residuals and maximum F test for variance homogeneity. Given the assumptions, the means were compared by the Student Newman-Keuls (SNK) test at the 5% significance level.

Results and Discussion

In Table 1 we show the coefficient of apparent indigestibility of calcium, phosphorus, magnesium, sodium, potassium, iron and manganese to the experimental treatments.

The coefficient of apparent indigestibility of calcium, phosphorus, magnesium, sodium, potassium, iron and manganese there was no significant difference ($p>0.05$) between the experimental treatments. In study with heulandite-type rich tuff, Kantiranis et al. (2011) mention its predilection for NH_4^+, however in the cation exchange by NH_4^+, Ca^{2+}, Na^+ and Mg^{2+} show elevated degree of cation exchange comparing to K^+, but K^+ and Na^+ revealed a rapid release, it is emphasized that there may be differences in natural zeolites. According to Lima et al., (2008), the preference of adsorption of clinoptilolite follows the:

$Cs^+ > K^+ > NH_4^+ > Sr^{2+} > Na^+ > Ca^{2+} > Fe^{3+} > Al^{3+} > Mg^{2+}$, with the K^+ ion as the main competitor of the NH_4^+ ion for the exchange sites, thus the ammonia prevented the adsorption of potassium by competition for exchange sites.

Table 1. Average and coefficient of variation of apparent indigestibility of calcium, phosphorus, magnesium, sodium, potassium, iron and manganese

	Calcium	Phosphorus	Magnesium	Sodium	Potassium	Iron	Manganese
Control	80.82	67.47	73.70	5.94	5.94	82.66	81.41
125ppm YSE	88.23	72.86	79.46	4.48	4.48	71.03	76.35
250ppm YSE	96.04	73.81	94.55	6.40	6.40	89.60	85.18
375ppm YSE	93.57	76.59	77.33	6.75	6.75	97.72	85.70
0.50% ZE	89.01	72.68	85.60	6.60	6.60	94.17	92.75
0.75% ZE	96.06	71.68	85.87	4.51	4.51	94.48	98.66
1.00% ZE	92.36	72.36	93.26	5.57	5.57	84.24	90.84
CV (%)	14.53	15.32	18.15	37.09	41.77	20.40	17.18
p	0.7706	0.9532	0.5483	0.1233	0.4970	0.4077	0.4923

YSE = *Yucca schidigera* extract; ZE = zeolite; CV= coefficient of variation; significance $p<0.05$

This fact takes greater importance when evaluating the work of Roque et al. (2011), when employing the same concentrations of zeolite studied. These authors found a reduction in odour from the feces of cats, possibly by the action of zeolite on ammonia, taking the shield to the adsorption of other cations. In the present study, the action of zeolite on ammonia and the consequent inhibition to the adsorption of other cations in the diet become more important because it is a wet food for cats with high crude protein (34.2% dry matter basis). In sheep, Pond (1989) found no additive action on copper, in animals fed 14% dietary crude protein, the inclusion of aluminosilicate increased gain weight front to animals that received the same amount of crude protein but with absence of zeolite, possibly by the action on the ammonia.

In conclusion, the *Yucca schidigera* extract and zeolite (clinoptilolite) in cats feed in levels used in this study did not affect the coefficient apparent indigestibility of macro and micro minerals.

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Physicochemical characterization and application of wasted fly ashes

Z. Sarbak and M. Kramer-Wachowiak

Adam Mickiewicz University, Faculty of Chemistry, Grunwaldzka 6, 60-780 Poznan, Poland;
E-mail: sarbak@amu.edu.pl

Introduction

Fly ashes are the main combustion by-products of coal fired power plants. Every year the energy utilities in Poland dispose several million tons of fly ashes in landfills causing major environmental problems. Fly ashes make 85 % of the total waste of the power plants.

Fly ashes are oxides whose composition depends on the type of coal subjected to combustion conditions. Analysis of the composition of fly ash enables us to conclude that they are aluminosilicates, whose properties make them similar to vulcanic ash. The physicochemical similarity of the fly ash to aluminosilicates suggests their susceptibility to transformation into zeolite-like crystalline structure materials under the influence of appropriate chemical treatment. It is also expected that the obtained materials may be efficient adsorbents of chemical pollution of the natural environment.

The aim of the present work is to study the synthesis of materials improved via chemical treatment of waste fly ashes from Konin Power Plants (brawn coal) and from Skawina Power Plant (black coal).

Experimental Methods

Modification of fly ashes was combined with NaOH solution and heated under reflux condenser and then filtered and washed with distilled water until pH=7 is reached. The obtained materials were dried at 120^{o}C for 12 h. The same procedure was applied to obtain other modifications of fly ashes using solutions of HCl and water solutions of EDTA. The modified materials were subjected to chemical analysis, elemental analysis, XRD FT-IR, TG/DTA and SEM studies as well as to surface area determination and pore and adsorption characterization.

Results and Discussion

The chemical modification of the initial fly ashes results in a significant increase in their surface area, pore volume and pore size. The shape of hysteresis loop (Fig.1,2) of nitrogen adsorption-desorption indicates the presence of pores in the form of mesoporous capillary tubes open at the ends and with necking. The presence of micropores has also been evidenced.

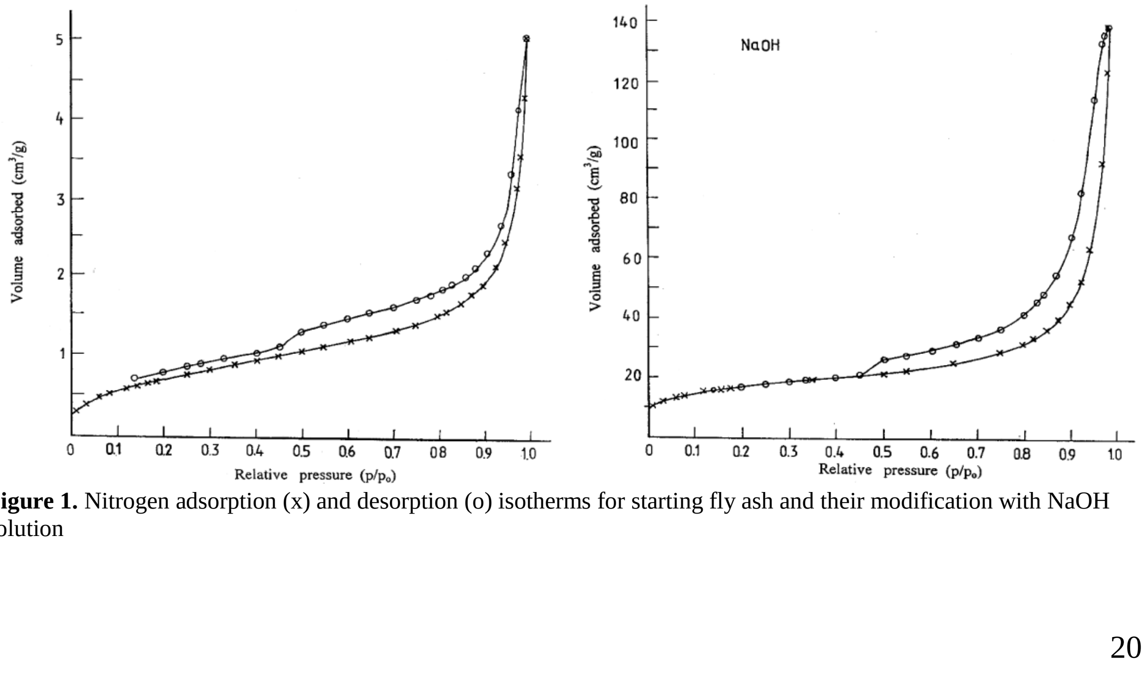

Figure 1. Nitrogen adsorption (x) and desorption (o) isotherms for starting fly ash and their modification with NaOH solution

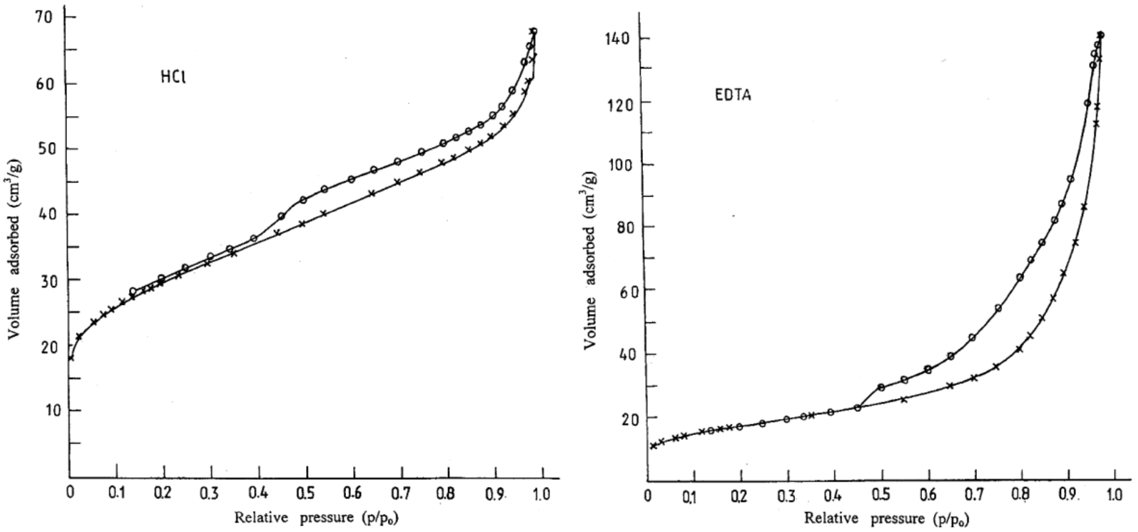

Figure 2. Nitrogen adsorption (x) and desorption (o) isotherms for fly ash modifications with HCl and EDTA solutions

The chemical modifications induce a transformation from a ball-like agglomerations into irregular forms with numerous inclusions in the shape of prisms and irregular elements of needles (Fig. 3). It has been shown that the chemical treatment of the initial fly ashes stimulates the formation of new crystalline structures.

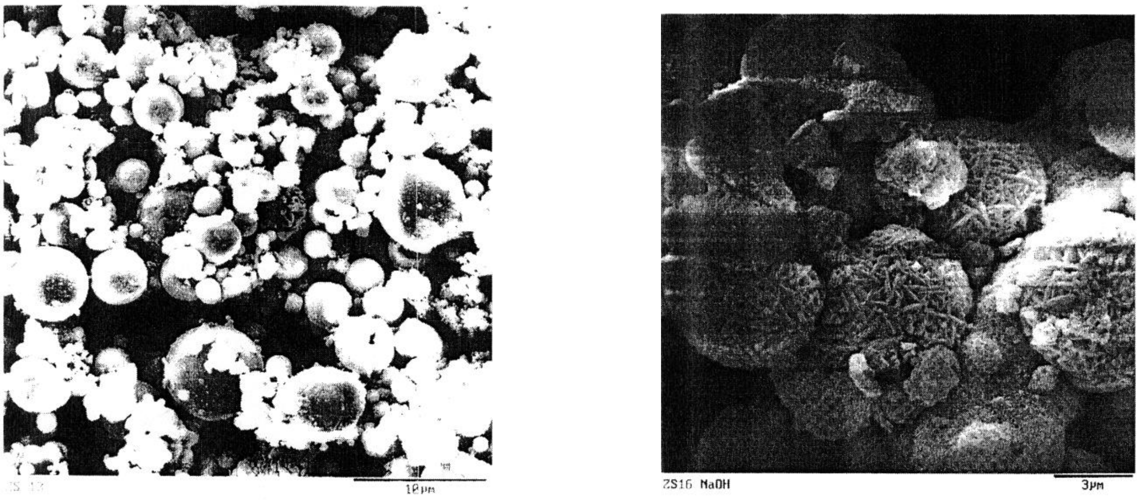

Figure 3. The scanning electron microscopy graphs for starting fly ash and treated by NaOH solution

The fly ashes studied are characterized by high adsorption of n-butylamine, which indicates occurrence of surface acid centers. The fly ashes studied have been shown to remove Cr(III) and Zn(II) ions from the waste of Rolling Bearing Plant (Poznan), and Ni(II) and Cd(II) ions for the sewage waste of CELAKO plant producing nickel-cadmium batteries. Moreover, the fly ashes have been proved to totally stabilize the Zn(II) and PO_4^{3-} ions from the post-galvanic slime of the PRESTA plant. The solidification of the above slime has been an effective method of the ions inhibition. A general conclusion following from the results presented is that the fly ashes studied are a cheap material capable of efficient adsorption of chemical pollutants. Their chemical modification usually increases their adsorption abilities.

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Mechanical performance, durability and aluminosilicate chain structure of high volume zeolitic natural pozzolan - portland cement based systems

A. Sassani[1], L. Turanli[2], A. H Emwas[3] and C. Meral[4]

[1] Middle East Technical University (METU), Ankara 06800, Turkey. E-mail:alireza.sassani@metu.edu.tr
[2] Middle East Technical University (METU), Ankara 06800, Turkey. E-mail: turanli@metu.edu.tr
[3] King Abdullah University of Science and Technology (KAUST), Thuwal, Kingdom of Saudi Arabia
E-mail: abdelhamid.emwas@kaust.edu.sa
[4]Middle East Technical University (METU), Department of Civil Engineering, K1-235, Ankara 06800, Turkey. E-mai: cmeral@metu.edu.tr.

Introduction

The carbon dioxide (CO_2) emissions due to concrete production accounts for more than 6% of the anthropogenic CO_2 emissions (Mehta & Monterio, 2006). The majority of PC concrete production-related CO_2 emissions are ascribed to production of PC. Approximately 60% of these emissions come from the calcination of limestone (Gürsel & Meral, 2012; Gursel, Meral, Horvath, & Monteiro, 2013) and is not related to energy consumption during the processes. Therefore, adopting energy efficiency policies is not solely enough to make the PC concrete industry sustainable. An effective way to manage the CO_2 emission associated with calcinations of Limestone is partial or complete replacement of PC by low-carbon alternative materials such as fly ash, slag or natural pozzolans (K. Celik et al., 2014; Kemal Celik, Meral, & Mancio, 2013; Erdem, Meral, Tokyay, & Erdoğan, 2007). The effectiveness of this policy is assured by high-volume replacement of PC (PC replacement ≥ 50 wt.%) by supplementary cementitious materials (SCMs). Natural zeolites cover a very wide range of minerals rich in aluminium silicates; and some natural zeolitic materials have been observed to possess pozzolanic properties.

Clinoptilolite is one of the most abundant natural zeolite minerals. The crystal structure of clinoptilolite is characterized by a framework of three 2D-view channels formed by layers of 8- and 10- membered tetrahedral rings. Herein a clinoptilolite-rich NP source of volcanic origin, located in Turkey was chosen. The NP was taken from Balikesir-Bigadic quarry in Turkey. The material was received in the form of crushed rock of volcanic tuff and it was then ground in a ball mill in order to obtain a fine powder. Since Zeolites in tuffs occur as fine-grained aggregates, generally x-ray based characterization techniques are needed for their identification. Therefore, the selected NP was characterized by x-ray fluorescence spectroscopy (XRF) in order to determine the major oxide compositions and by x-ray diffraction (XRD) to determine the mineralogical composition. Laser diffraction analysis was performed to determine the particle size distribution within the pozzolan powder. Once the NP was fully characterized, the strength activity index of the NP was determined according to ASTM C 311. The engineering performances of the high-volume NP - PC systems (50 wt. % NP – 50 wt. % PC) were evaluated in terms of compressive and flexural strength development, heat evolution during hydration, and expansion due to alkali silica reaction. Powder XRD was used to identify the phases within the hydration products of HVNP-PC systems. ^{29}Si solid-state NMR and ^{27}Al solid-state NMR spectroscopy techniques were utilized to investigate the silicate and (alumino)silicate species present in the hydration products, especially in the calcium silicate hydrate (C-S-H) phase which is the main binder of hydrated PC.

Experimental Methods

Strength activity index: Strength activity indices of the finely ground zeolitic NP were determined in accordance with ASTM C 311 standard to evaluate the performance of the selected NP in practice.

Compressive and Flexural Strengths: The strength performance of a cementitious system can be evaluated by following the evolution of compressive and flexural strengths. In this case, for HVNP-PC systems 3, 7, 28, 90 and 180-day strengths were measured. The mortar mixtures consisted of 50 wt. % NP and 50 wt. % white PC. The sample preparation and measurements were performed according to ASTM C 348 standard with minor unconformities.

Isothermal calorimetry: In order to monitor the heat evolution during the hydration of the blended cements, *isothermal calorimetry* experiment was performed on the pastes containing 0 and 50% NP blended with white portland cement.

Powder X-ray Diffraction: There are some crystalline or semi-crystalline phases present in the hydration products of cementitious materials which can be detected and characterized by ordinary XRD, e.g. $Ca(OH)_2$, ettringite (AFt) and monosulfate (AFm).

Laser Diffraction: Due to the nano-porous nature of the clinoptilolite-rich NP which was under study the results of the Blaine air permeability test did not present explicit and meaningful information about the fineness of the NP. Therefore, in order to establish a relation between the pozzolanic reactivity and the fineness of the cementitious materials, the particle size distribution (PSD) of PC and the selected NP were determined by laser diffraction method.

Alkali-silica Reaction(ASR): The effect of the selected NP on the alkali-silica reaction-induced expansion of mortar prisms were investigated according to the ASTM C289-07 standard. For this purpose blends of 50%NP and 50%PC were used to make mortar samples with reactive aggregates.

^{29}Si NMR spectroscopy: HVNP-PC pastes were examined by ^{29}Si NMR spectroscopy technique. This technique is applicable for detection of various silicate species with various degrees of anion condensation and consequently various degrees of silicate polymerization, namely Q^0, Q^1, Q^2_B, Q^2_P, Q^3, Q^4 , their substituted forms such as Q^2(1Al) and their hydrated forms such as Q^0(H). The data obtained by NMR spectroscopy were utilized to determine factors such as the mean silicate chain length in the C-S-H , the quantity of different silicate species in the hydration products of the cementitious system and the incorporation of guest ions namely Al^{3+}, OH^- and Ca^{2+}, in C-S-H structure and their location.

^{27}Al NMR spectroscopy: This technique is proved to be a very useful tool to probe Al sites in cement-based materials, and it can be used to detect, distinguish, characterize and quantify different Al species and their accommodating sites. By difference in ^{27}Al chemical shift we can observe and distinguish between various coordination of Al in C-S-H.

Results and Discussion

The zeolitic material herein studied showed an acceptable performance with respect to compressive and flexural strengths to be used as a high volume cement replacement. The most significant problem associate with its application was the considerable reduction of workability due to excessive water absorption by the pozzolanic material. In the ASR test, the HVNP-PC mortar prisms showed a better performance. In HVNP-PC systems, Lower density was observed in the microstructure of the hydration products; however, the morphology and existing phases were not significantly different from control samples without NP. According to the NMR results, the reactant species in the NP material were significantly different from the reactant species in the PC. However, the hydration products in the HVNP-PC systems detected by ^{29}Si and ^{27}Al NMR spectroscopy were very similar to PC samples, the difference being principally in the relative mount of the species.

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Properties of Portland cement with addition of Pb-zeolite

Ž. Sekulić[1], M. Kragović[1], A. Terzić[2], S. Mihajlović[1], V. Kašić[1] and M. Petrović[1]

[1]Institute for Technology of Nuclear and Other Mineral Raw Materials, 86 Franchet d'Esperey st., 11000 Belgrade, Serbia; E-mail: z.sekulic@itnms.ac.rs
[2]Institute for material testing, Vojvode Mišića Blv. 4., 11000 Belgrade, Serbia

Introduction

It is well known that various materials that exhibit latent hydraulic properties can be used as SCM's (Supplementary Cementitious Materials) in Portland cement (Opoczky and Beke 1967, Knape et al., 1967). The quantity of these SCM's is strictly limited. The SCM's which are often used in cement production are: composition by decreasing the calcium hydrate products and improving the chemical, acidic and sulphate stability. They can be milled before or milled together with the clinker. Zeolite may be considered as natural pozzolanic material in accordance with the (EN 197-1). Like other pozzolanic materials, being mixed with water, it does not harden, but if it is smoothly grinded it reacts in the presence of water at ambient temperature with the soluble hydroxide of calcium to form the silicates and aluminates of calcium, which are responsible for the increased hardness (Janotka and Krajci 2000). The aim of the present work is the investigation of the influence of the combination of the Pb-zeolites on the properties of Portland cement type PC42.5R-BFC. The aim of this investigation was to imitate the procedure of Pb removal from the water by application of zeolite. Namely, a question has been raised concerning possibility of reapplication contaminated filter, i.e. zeolite which has been saturated with lead.

Exsperimental Metods

In this investigation, natural zeolites originating from Vranjska Banja, Serbia and Portland cement PC 42.5R from Beočin, Serbia have been used. In Table 1 chemical compositions of starting raw materials are given.

Table 1. Chemical composition of starting raw materials

Oxide, Wt. %	SiO_2	Al_2O_3	CaO	MgO	Fe_2O_3	K_2O	Na_2O	TiO_2	LoI	SO_3	MnO	PbO
PC42.5R	24.02	6.03	59.60	2.03	1.48	0.76	0.34	0.346	1.89	3.4	0.087	0.0065
Zeolite	65.15	13.58	4.15	0.62	2.27	1.26	1.60	-	11.37	-	-	-

Natural zeolite was milled to reach the grain size - 100% of 43 μm, and afterwards mixed with $PbNO_3$ under following procedure: 400 g of $Pb(NO_3)_2$ was dissolved in 120 l of distilled water. The initial pH was set to 4.24. Then, 3.5 kg of natural zeolite was added in lead contaminated water. Reaction time was 7 days with occasional mixing. After 7 days of the samples curing; dewatering, filtration, drying and disintegration subsequently followed. Thus, by means of the "batch" procedure dry zeolite contaminated with lead (PbZ) was obtained. The sorbed amount of lead was ~60 mgPb^{2+}/g which is very close to the maximum sorption capacity of natural zeolite used in this study (Kragović et al. 2012).

Afterwards, mixing of Portland cement with 10% of Pb-zeolite (PC10PbZ); 30% of Pb-zeolite (PC30PbZ) and 50% of Pb-zeolite (PC50PbZ) in laboratory mill without balls was performed in duration of 10 minutes. On such obtained samples of cement with addition of zeolite and on starting sample (cement PC42.5R) standard physico-mechanical testing have been performed according to European Normative EN197:

- Determination of the specific surface according to Blaine (EN 196-6) (Blaine apparatus was used).
- Determination of standard consistency (EN196-3) (Vicat apparatus was used).
- Determination of the setting time of the cement dough (EN 196-3) (Vicat apparatus was used with the rod replaced by a needle)
- Determination of the compressive strength (EN 196-1).

Results and Discussion

In Table 2, the results of physico-mechanical properties testing of PC and PC with addition of Pb-zeolite, in various mass ratio, are given. Since the grain size of initial zeolite sample is 0.043 mm, when zeolite is mixed with Portland cement, the mixture specific surface area (Sp) is significantly increased, as it can be seen in Table 2. Namely, the Sp for PC42.55R has value of 3940 cm^2/g, while the cements with addition of Pb-zeolite shows values of Sp in the range from 4880 up to 9840 cm^2/g.
The longest setting time was found for the PC30PbZ sample (Table 2), since this cement requires 70 minutes more to finish the setting procedure than cement without addition, i.e. PC42.5R.

With increasing of the PbZ content in the PC mixtures, the initial flexural strength, measured after two days of hardening, is decreasing (from 6.4 MPa to 2.4 MPa), as well as the final flexural strength, measured after 28 days of hardening (from 9.6 MP to 6.9 MPa) (Table 2). The compressive strength, as the main characteristics of the cement, follows the same pattern. Namely, value of compressive strength after two days for PC is 33.0 MPa, and for PC50PbZ the compressive strength is 10.0 MPa. Also, after 28 days of hardening compressive strength for PC amounts up to 61.1 MPa for PC, and 44.9 MPa for PbZ (Table 2).

Table 2. Results of physico-mechanical properties

Sample	Fineness, %	Sp, cm^2/g	SK, %	Setting time, min	
				Start of the setting	End of the setting
PC42.5R	0.6	3940	29.0	220	270
PC10PbZ	0.05	4880	31.6	190	250
PC30PbZ	0.06	6960	37.0	270	340
PC50PbZ	0.1	9840	36.8	190	250

Sample	Flexural strength, MPa			Compressive strength, MPa		
	2 days	7 days	28 days	2 days	7 days	28 days
PC42.5R	6.4±0.8	8.4±0.6	9.6±0.8	33.0±0,7	49.0±0.8	61.1±1.4
PC10PbZ	6.2±0.4	7.5±0.7	9.2±0.2	25.2±0,8	41.2±0.9	63.3±2.1
PC30PbZ	4.3±0.1	5.9±0.2	8.5±0.5	17.0±0.4	31.3±0.7	57.3±0.6
PC50PbZ	2.4±0.1	4.2±0.6	6.9±0.3	10.0±0.6	23.4±0.1	44.9±1.5

Having in mind mechanical characteristics of the investigated cements it can be concluded that due to the significant decreasing of the flexural and compressive strength, it is not recommended that more that 30 % of the zeolite contaminated with lead is added to PC. Namely, compressive strength which shows cement PC30PbZ is 57.3±0.6 MPa which is acceptable from the application aspect. Also, it has to be investigated if this cement contains free lead which could negatively affect the properties, performance and application of this cement.

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Comparison of ammonium removal between Natural and Sodium modified Clinoptilolite

R. M. D. Serio[1] and F. Borsatto[2]

[1]*Industrias Celta Brasil Ltda; Brazil; E-mail: tecnico@celtabrasil.com.br*
[2]*Industrias Celta Brasil Ltda; Brazil; E-mail: fernandoborsatto@celtabrasil.com.br*

Introduction

Nowadays water is a natural resource which is becoming increasingly scarce because natural sources are contaminated by anthropogenic action. One of these contaminants is ammonia (NH_3), which can be derived from natural decay of organic matter or agricultural inputs (NPK). In aqueous solution the ammonia, which is a gas, can also be solubilized in its ammonium ionic form (NH_4^+). When it is present in high concentrations in drinking water, it can cause serious damages because it interfere in oxygen's transport by hemoglobin (CETESB). Natural zeolites, principally clinoptilolites, are used as granular media filters due to ease of operation. In Brazil it is applied the Ordinance 2914 (Ministry of Heath, 2011) which establish potability parameters for drinking water – Regarding [NH_3] the parameter is <1,5 mg/l. The objective of this study is to compare the removal of ammonium ion using natural clinoptilolite (ZN) and a sodium modified clinoptilolite (ZS).

Experimental Methods

These experiments were conducted at Industrias Celta Brasil, São Paulo, Brazil, using a natural clinoptilolite (from Cuba) and sodium modified clinoptilolite (made in Celta Brasil's plant) It was used also two acrylic columns and two metering pumps(each pump to realize this experiments,. Each product, in an amount of 260g, was deposited inside an independent acrylic column. The flow used was 1 l/h (flow rate = 3,35 m³/m².h). Ammonium chloride was used to contaminate the water samples in three concentrations: 80, 40 and 10 mg/l. Neutral pH was adopted – this is a maximum pH value where the concentration of ammonium ion (NH_4^+) begins to decrease and ammonia (NH_3) to rise. To determinate the concentration of ammonium ion was used a spectrophotometer (Smart Spectro/Policontrol); to determinate the pH was utilizate a pH meter (Mettler Toledo).

Results and Discussion

A spectral quantitative analysis of X-Ray fluorescence (XRF-1800/Shimadzu) was made to determine some elements present in the samples of clinoptilolite used. These results are shown in Table 1. In this study natural clinoptilolite was named by ZN and sodium modified clinoptilolite by ZS. After the water samples passed through the columns there was a change in pH, which was higher when the concentration of ammonium was higher (this can be seen in Figures 1, 2 and 3). The pH was more raised after passage by ZS than ZN.

Table 1. Spectral quantitative analysis of X-Ray fluorescence

Clinoptilolite	Content, %						
	SiO_2	Al_2O_3	Na_2O	K_2O	CaO	MgO	LOI
ZN	69.87	11.33	0.86	1.36	2.78	0,53	10,50
ZS	66.82	11.62	5.14	1.40	1.64	0,61	11,15

Figures 4 and 5 show the removal efficiency of ZN and ZS, respectively, demonstrating that ZS is more efficient compared to ZN. This difference is inversely proportional to the ammonium concentration in the samples; in other words, the higher the ammonium concentration in water, the closer will be the efficiency values.

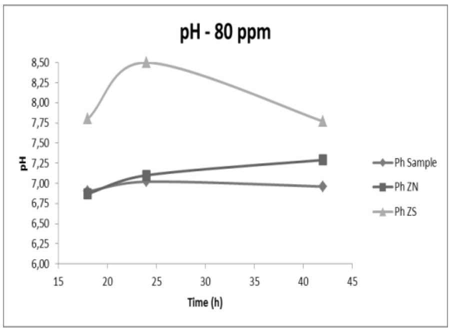

Figure 1. Variation of pH in the solution with 80 mg/l

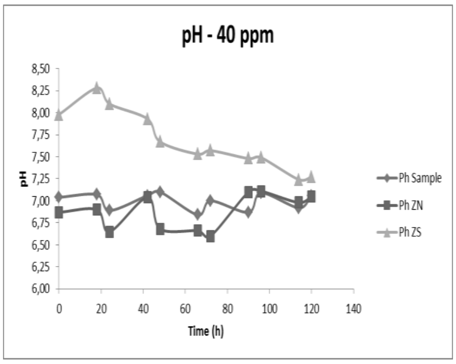

Figure 2. Variation of pH in the solution with 40 mg/l

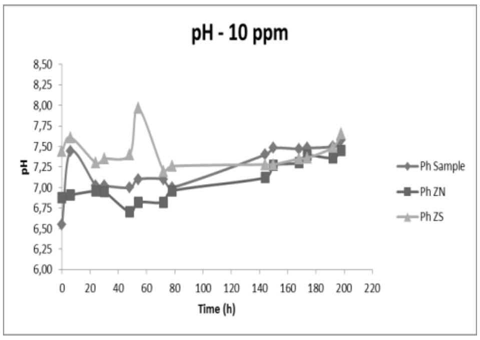

Figure 3. Variation of pH in the solution with 10 mg/l

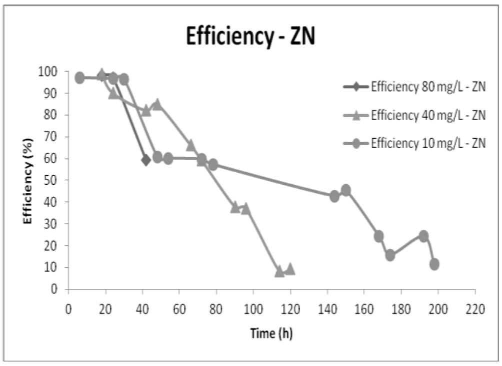

Figure 4. Ammonium removal efficiency with natural clinoptilolite

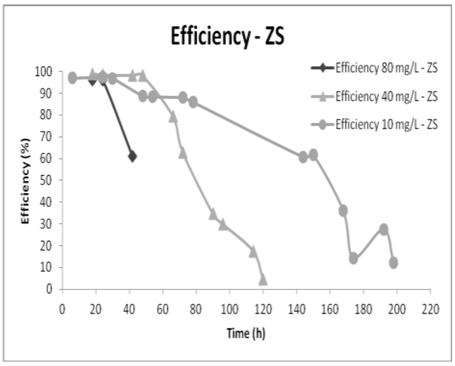

Figure 5. Ammonium removal efficiency with sodium clinoptilolite

It was concluded that the pH is raised, after passage by both columns (ZS and ZN). Sodium modified clinoptilolite raised more pH than the natural clinoptilolite because during the process of cation exchange with the ammonium presented in the water sample, the sodium exchanged increase the pH of the water

Sodium modified clinoptilolite is more efficient than natural clinoptilolite because it has more sodium in its structure and enhances the removal, since the ion Sodium performs the cation exchange with ammonium ion Although, for high concentrations of ammonium in water, natural clinoptilolite obtained a similar efficiency comparing with sodium modified clinoptilolite.

Acknowledgment

Thanks for Indústrias Celta Brasil the opportunity to conduct this study, providing space, material and equipment. I also thank my colleagues who cooperated with me during this study.

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Applications of Zeolites for Bioenergy Production: A Review

I. V. Sezgin and H. Merdun

Akdeniz University, Faculty of Engineering, Dept. of Environmental Engineering, 07058, Antalya, Turkey;
E-mail: merdun@alumni.clemson.edu

A zeolite is a crystalline, hydrated aluminosilicate of alkali and alkaline earth cations having an infinite, open, three-dimensional structure (Mumpton, 1999). Zeolite types include Amorphous Silica Alumina (ASA), H-Mordenite, HY, ZSM-4, ZSM-5, ZSM-11, ZSM-12, H-ZSM-5, KA, LiA, NaA, NaX, CaA, and there are many others. In contrast to zeolites A and Y, ZSM-5 type zeolites have a uniform channel structure which has larger cavities. Zeolites are porous in nature, and their structures can accommodate a wide variety of cations that can be easily exchanged for others. Zeolites are solid catalysts with the following properties: a) high surface area; b) molecular dimensions of pores; c) high adsorption capacity; d) partitioning of reactant/products; e) possibility of modulating the electronic properties of active sites; and f) possibility for preactivating the molecules when in the pores by strong electric fields and molecular confinement (Corma, 2003). The structure, Si/Al ratio, particle size, and nature of the (exchanged) cation all impact catalytic properties. Zeolites have been widely used in heterogeneous catalysis because of their well-defined pore structures, extremely high surface areas and surface acidity (Yung et al., 2009).

The advantages of the zeolites over conventional catalysts include: a) precisely defined arrangement of SiO_4 & AlO_4^- tetrahedra (crystallinity), resulting in reproducibility in production; b) shape selectivity, meaning that only molecules that are smaller than the pore diameter of the zeolite undergo reaction; c) controlled incorporation of acid centers in the intracrystalline surface is possible during synthesis and/or by subsequent ion exchange; d) catalytically active metal ions can be uniformly applied to the catalyst by ion exchange or impregnation; e) zeolites are thermally stable up to 600°C and can be regenerated by combustion of carbon deposits; and f) zeolites are well suited for carrying out reactions > 150°C (Mumpton, 1999). Different catalysts are used in a variety of industrial applications. Tanabe and Hölderich (1999) reviewed statistics on industrial applications of different catalysts and found that zeolites were used in 74 out of 180 studies, and the remainder included oxides and complex oxides (54), ion-exchange resins (16), and clays (4).

Zeolites have a wide range of commercial uses (Mumpton, 1999; InterSun 2007), and general applications include: a) aquaculture (ammonia filtration in fish hatcheries, biofilter media); b) agriculture (odor control, confined animal environmental control, livestock feed additives); c) horticulture (nurseries, greenhouses, floriculture, vegetables/herbs, foliage, tree and shrub transplanting, turf grass soil amendment, reclamation, revegetation, and landscaping, silviculture, medium for hydroponic growing); d) household products (household odor control, pet odor control); e) industrial products (absorbents for oil and spills, gas separations); f) construction (dimension stone, cement and concrete, lightweight aggregate). Environmental applications include: a) radioactive waste isolation (site remediation/decontamination); b) water treatment (water filtration, heavy metal removal, swimming pools); and c) wastewater treatment (ammonia removal in municipal sludge/wastewater, heavy metal removal, septic leach fields).

Biomass conversion has attracted tremendous interest, and zeolites have the potential to play a role in a thermochemical biomass conversion scenario. One of the ways for upgrading pyrolysis oil is to convert bio-oil to gasoline using a zeolite catalyst. When vapors of pyrolysis oil are passed through a bed of zeolite catalyst at 300-500°C they are converted to hydrocarbons along with the formation of H_2O, CO_x, and coke. Oxygen is removed over the zeolites in the form of H_2O, CO or CO_2 (Taarning et al., 2010). Many catalytic applications in biomass conversion and bio-oil upgrading processes involve zeolitic catalysts, such as zeolites Y and ZSM-5 (Bridgwater, 1996; Williams and Nugranad, 2000; Thring et al., 2000; Bulushev and Ross, 2011). Several researchers have tested zeolite catalysts for the conversion of biomass to aromatics (Pattiya et al., 2008; Pattiya et al., 2010; Valle et al., 2010). The influence of faujasite, which is the active ingredient in fluid catalytic cracking (FCC) catalyst, on the conversion of lignocellulosic biomass to various organic components was investigated for establishing a catalytic pyrolysis process for a green refinery (Nguyen et al., 2013). When compared with hydrodeoxygenation, zeolite upgrading of bio-oils offers significant processing and economic advantages, as no hydrogen is required and the reaction can be carried out at atmospheric pressure and moderate temperatures, 623-773 K (Serrano-Ruiz and Dumesic, 2012). Samolada et al. (2000) used ZSM-5 zeolites as catalysts for pyrolysis of biomass and found a decrease in the concentration of liquid products and an increase in the quantity of gaseous products. Aho et al. (2008) compared non-catalytic and catalytic pyrolysis of pine chips in the presence of different zeolites in a fluidized bed reactor. The composition of the bio-oil after fast pyrolysis of cellulose, cellobiose, glucose, and xylitol mixed with different catalysts was compared by Carlson et al. (2009). The effects of temperature and time on the transformation over a HZSM-5 zeolite catalyst of several model components of the liquid product obtained by the flash pyrolyAsis of vegetable biomass (1-propanol, 2-propanol, 1-butanol, 2-butanol, phenol, and 2-methoxyphenol) were studied (Gayubo et al., 2004).

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Zeolite deposits and occurrences in Serbia – an overview

V. Simić[1], D. Životić[1], N. Andrić[1], A. Radosavljević-Mihajlović[2] and V. Kašić[3]

[1]*University of Belgrade, Faculty of Mining and Geology, Đušina 7, 11000 Belgrade, Serbia;*
E-mail: simicv@rgf.bg.ac.rs
[2]*University of Belgrade, Belgrade, Institute of Nuclear Science „Vinča“,11000 Belgrade, Serbia*
[3]*Institute for Technology of Nuclear and Other Mineral Raw Materials, Franche d'Esperey Street 86, 11000 Belgrade, Serbia*

Introduction

Zeolite deposits and occurrences in Serbia are mostly related to subaqual alteration of ash-fall tuffs of Miocene age, but also to alteration of tuffs of Eocene age. So far, all known commercially interesting zeolite tuff deposits in Serbia are related to Miocene volcanic activity and are of high quality, with zeolite content of over 70 % (Fig. 1). The term "tuff" is here used in a non-genetic sense meaning that it delineates fine-grained material with volcanogenic particles irrespectively of their fragmentation and depositional mechanism. Due to their industrial significance, zeolite tuffs were subject of many studies in Serbia (Stojanović, 1968; Nikolić et al., 1975; Obradović, 1977; Obradović, 1988; Simić, 1999; Simić et al, 1999, 2013; Mihajlović-Radosavljević et al, 2013). This paper aims to review the actual zeolite mineral base in Serbia.

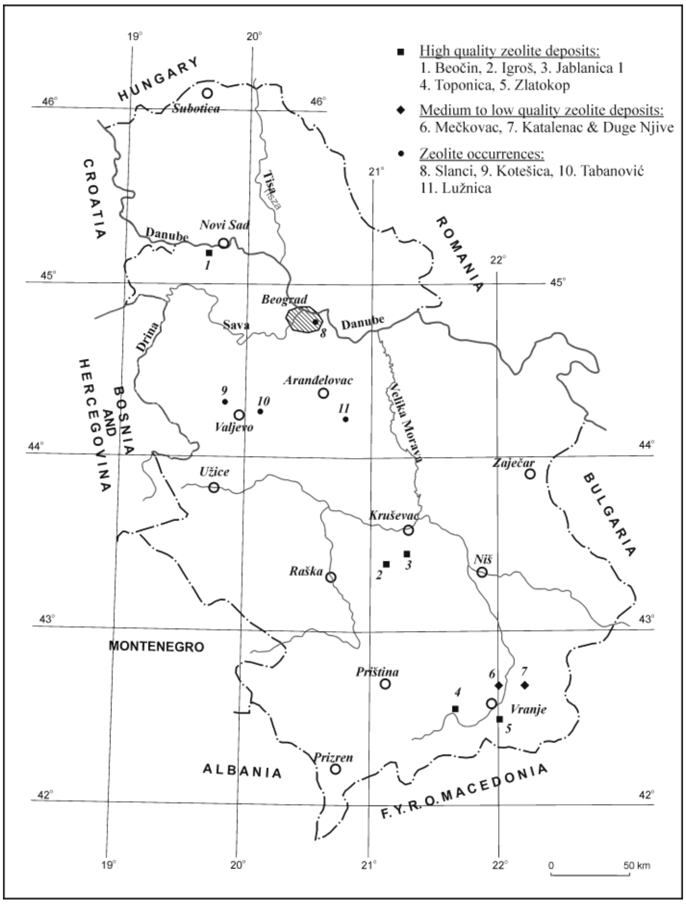

Figure 1. Zeolite deposits and occurrences in Serbia

Experimental Methods

The usual methods used to characterise zeolite tuffs are: geochemical, optical, structural and physical. Chemical analyses were done mostly by classic wet silicate analysis. Optical microscopic analyses were done by polarisation microscope in transmitted light. Scanning electron microscopy was used for imaging and collecting chemical data using a Jeol JSM – 6610 LV Scanning Electron Microscope equipped with energy-dispersive spectrometer (EDS). XRPD analyses were performed on APD2000, Ital Structure usually in the range from 4^o to 60^o 2θ. Cation exchange capacity (CEC) of the examined samples was determined by standard procedure with CH_3COONH_4.

Results and Discussion

The most important parameters of zeolite deposits in Serbia (Table 1) reveal that those deposits are relatively small in term of reserves and/or average thickness. Clinoptilolite is the most abundant zeolite mineral, while mordenite occurs in several deposits. There are considerable differences in zeolite tuff quality within the same deposit. Geological and technological knowledge on the Katalenac, Duge Njive, and Mečkovac deposits is rather low because previous exploration campaigns were oriented towards utilisation in cement industry, so the data on zeolite quality are just indicative.

Table 1. Basic parameters of zeolite deposits in Serbia

Deposit	Age	Depth of zeolite (m)	Zeolite thickness (m)	Resources (Mt)	Reserves (Mt)	CEC (meq/100g)	Exploitation method
Beočin	Miocene	2-28	14.2	2	0.26	157	Open pit
					0.15	108	
Igroš	Miocene	5-20	1.5	0.1	0.05	145	Open pit
Jablanica 1	Miocene	0-15	18.5	2.2	0.20	168	Open pit
Toponica	Miocene	2-25	2,4	0.5	0.50	140	Underground
Zlatokop	Miocene	20-30	2	1.3	0.67	164	Underground
Katalenac	Eocene	At surface	110	3.4		70	Open pit
Duge Njive	Eocene	At surface	> 50	1.1			Open pit
Mečkovac	Miocene	At surface	38	1.0			Open pit

Nevertheless, even this brief overview indicates that Serbia has a potential to develop zeolite industry, but based on much more detailed geological and technological characterization of the resources.

Acknowledgment

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The remediation of toxic metal polluted sediment by natural zeolite

N. S. Slijepčević[1], D. D. Tomašević[1], M. B. Dalmacija†[1], Dj. V. Kerkez[1], B. D. Dalmacija[1], M. Kragović[2] and S. D. Rončević[1]

[1]*University of Novi Sad, Faculty of Sciences, Department for Chemistry, Biochemistry and Environmental Protection, Trg Dositeja Obradovica 3, 21000 Novi Sad, Serbia; E-mail: dragana.tomasevic@dh.uns.ac.rs*
[2] *Institute for Technology of Nuclear and Other Mineral Raw Materials, P.O. Box 390, 11000 Belgrade, Serbia*

Introduction

One of the major environmental problems is polluted sediment which constitutes reservoir of potentially bioavailable metals that can lead to a bioaccumulation of toxic elements in the food chain, and induce perturbation of the ecosystem and adverse health effects. It is now widely recognized that the toxicity and the mobility of these pollutants depend strongly on their specific chemical forms and on their binding state. The solidification/stabilization (S/S) techniques have been widely applied to treat soils with heavy metal contamination. Natural materials like zeolite have been investigated as potential adsorbents for this purpose. The capability of zeolites to exchange cations is one of their most useful properties, and it determines their ability to remove heavy metals from industrial wastewaters (Kocaoba et al., 2007). The degree of effectiveness of the S/S products is defined basically by two parameters: strength and leach resistance. The performance of S/S treated wastes is generally measured in terms of leaching tests. The mechanisms governing heavy metals leachability of contaminants from monolithic solidified waste forms and evaluation of the long-term behaviors of S/S wastes can be effectively examined using the American Nuclear Society's (ANS) semi-dynamic leaching test (ANS, 1986). The main goal of this study was to investigate the possibility of applying the solidification/stabilization technique for treatment of toxic metal contaminated sediment using zeolite in the mixture as a stabilization agent.

Experimental Methods

The treated sediment samples were prepared by mixing with natural zeolite according to standard method ASTM D1557-00. Specimens were designated by the capital letters, followed by a number indicating the percent weight of the given attribute. Additionally, the amount of S/S agents present was varied in order to evaluate its relative contribution to toxic metal immobilization. The zeolite (clinoptilolite) composition was as follows (% wt.): SiO_2 (66.9), Al_2O_3 (13.5), Fe_2O_3 (0.98), MgO (0.69), CaO (3.85), K_2O (0.54), Na_2O (0.37), SO_3 (1.18) and ignition loss (11.4). Samples were cured at 20°C in sealed sample bags for 28 days and then subjected to ANS 16.1 leaching tests.

Results and Discussion

Pseudo-total concentrations of metals were: for Cr 1335 mg kg^{-1}, for Ni 1048 mg kg^{-1}, for Cu 506.9 mg kg^{-1}, for Zn 1962 mg kg^{-1}, for As 63.94 mg kg^{-1}, for Cd 26.85 mg kg^{-1} and for Pb 2255 mg kg^{-1}, respectively, which according to the Serbian regulation standards (Ministry of Natural Resources, 2011), is above intervention value and such sediment is considered severely polluted with analyzed metals (class 4) and needs dredging, disposal in special reservoirs and, if possible, sediment clean-up measures.If the percentage of the leached metals were observed as the efficiency criteria, then treatment with zeolite is very efficient for all tested metals with the percentage of leaching less than 3%. With increasing the share of zeolite, naturally, the percentages of metals leached are reduced. Mean values of diffusion coefficients ($\overline{De}$) ranged from 1.2E-11 to 9.4E-14 cm^2s^{-1} are presented in Table 1. According to Nathwani and Philips (1980), the diffusion coefficients of metals from the S/S mixtures generally range from values for highly mobile metal 1E-5 cm^2s^{-1} to 1E-15 cm^2s^{-1} for metals that are immobilized in the S/S mixtures. Based on this it can be concluded that the metals in the S/S mixtures when using zeolite as an immobilization agent are practically immobilized. According to the Canadian Agency for Environmental Protection, it can be seen that LX values are above 9 for all metals leached, which means that the mixtures are suitable for controlled utilization.

The controlling leaching mechanisms were evaluated by using a diffusion model developed by de Groot and van der Sloot (1992) (Figure 1).

Most of the treated sediment samples slope values were in the range of 0.40 to 0.60 which indicates that the dominant leaching mechanism is diffusion.

Table 1. Mean effective diffusion coefficient D_e ($cm^2 s^{-1}$) and leachability index (LX)

	De, cm^2s^{-1}				LX			
	Z5	Z10	Z20	Z30	Z5	Z10	Z20	Z30
Cr	6.8E-12	1.1E-13	3.4E-13	4.4E-13	12.7	12.3	12.3	12.5
Ni	5.2E-11	4.4E-11	8.8E-11	5.3E-12	10.5	10.7	10.8	10.6
Cu	2.3E-11	2.9E-11	3.6E-11	3.9E-11	10.9	10.8	10.9	10.9
Zn	3.7E-12	7.1E-12	8.3E-12	9.4E-13	11.8	11.5	11.0	11.8
As	6.8E-12	8.9E-12	9.5E12	9.7E-12	12.1	12.1	11.3	11.7
Cd	1.2E-11	1.7E-11	2.5E11	3.2E-11	11.4	11.1	10.5	11.2
Pb	7.8E-12	8.0E-12	8.3E-12	1.7E-12	12.7	12.2	12.1	12.8

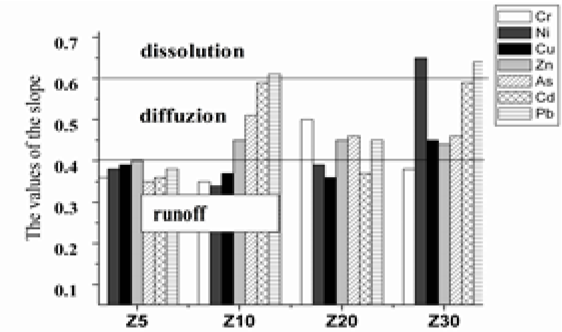

Figure 1. The controlling leaching mechanisms based on the slope values of the cumulative fraction release logarithm, log(Bt), vs. the logarithm of time, log(t)

Zeolite used as immobilization agents have a high efficiency for solidification/stabilization of toxic metals in sediment based on all the applied criteria. The great majority of S/S specimens were viable for controlled utilization, indicating that this treatment is sustainable from both environmental and economic aspects.

Acknowledgement

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Phonolite-hosted zeolite deposits in the Kaiserstuhl Volcanic Complex, Germany

S. Spürgin[1], T. B. Weisenberger[2], N. Rosing-Schow[2] and M. Vasilopoulos[2]

[1]*Hans G. Hauri Mineralstoffwerke, Bötzingen, Germany; E-mail: s.spuergin@hauri.de*
[2]*Department of Geosciences, University of Oulu, P.O. Box 3000, 90014 University of Oulu, Oulu, Finland; E-mail: tobias.weisenberger@oulu.fi*

Introduction

Zeolite mineralisation in the Miocene Kaiserstuhl Volcanic Complex (KVC) results from alteration of alkaline volcanic and subvolcanic rocks. The types of zeolite species formed depend on rock composition (Weisenberger and Spürgin, 2009). The KVC is located in the central-southern segment of the Upper Rhine Graben, which is part of the European Cenozoic Rift System. Several subvolcanic phonolite intrusions occur within the KVC (Fig. 1). Hydrothermally altered phonolitic rocks are of economic interest, due to the high (>40 wt%) zeolite content, which accounts for the remarkable zeolitic physicochemical properties of the ground rock. Currently there is active mining in the Fohberg phonolite, the largest phonolite intrusion in the eastern KVC. The Endhale phonolite marks a further deposit currently under exploration. Both phonolites are hosted in Tertiary sedimentary units. In contrast the zeolite-poor Kirchberg phonolite intrusion in the western KVC is hosted by volcanic rocks of tephritic composition.

The aim of this study is to carry out new mineralogical and geochemical data a) to evaluate the hydrothermal alteration of the phonolitic bodies, b) to constrain the physical and chemical properties of the fluids, which promoted hydrothermal replacement of primary igneous minerals and c) to outline the influence of geologic setting to alteration.

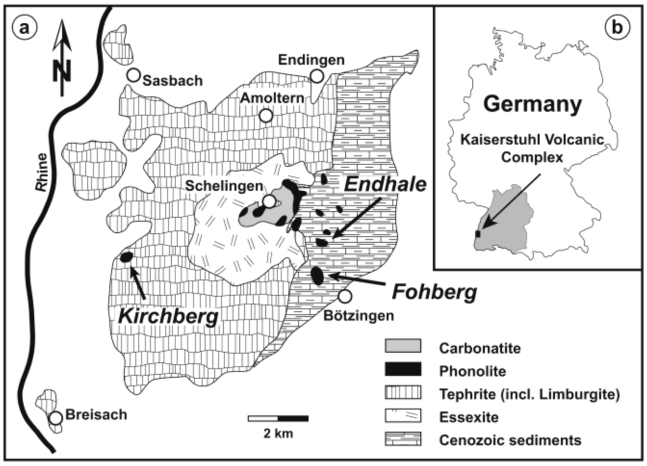

Figure 1. (a) Simplified geologic map of the Kaiserstuhl volcanic complex (after Wimmenauer, 1963). Studied phonolites are shown with arrows. (b) Outline of Germany and Baden-Württemberg (grey) showing the location of the KVC

Results and Discussion

The high degree of alteration in the Fohberg and Endhale phonolites is in contrast to the only slightly altered Kirchberg phonolite in the western KVC. The alkaline intrusive bodies are characterized by the primary mineralogy: feldspathoid minerals, K-feldspar, aegirine-augite, andradite, and wollastonite occurring only in the Fohberg and Endhale phonolites. Additional various Ti-, Fe-, and REE-minerals (e.g. götzenite) occur.

Fluid-induced re-equilibration of feldspathoid minerals and wollastonite caused breakdown to a set of secondary phases in the Fohberg and Endhale phonolites. Feldspathoid minerals in the rock matrix are totally replaced by secondary phases including various zeolite species, calcite, and barite during subsolidus hydrothermal alteration under alkaline conditions. Wollastonite breakdown results in the formation of various zeolites, calcite, pectolite, sepiolite, and quartz. The large variability of secondary minerals indicates a heterogenic fluid composition throughout the phonolitic intrusions and through time. A sequence of Ca-Na-zeolites (gonnardite, thomsonite, mesolite) is followed by pure sodium endmember species (analcime, natrolite). These sequence reflects an increase in log[aNa$^+$)/(aH$^+$)] of the precipitating fluid.

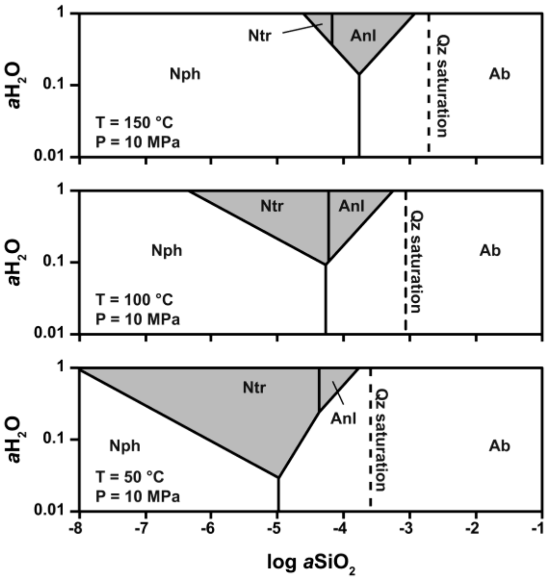

Figure 2. Quantitative $aSiO_2$-aH_2O diagrams for selected Na-Al silicates at constant pressure (10 MPa) and different temperatures. Gray areas are stability fields for zeolite species. Dashed lines represent the lower limits of quartz saturation. Mineral stabilities were calculated using the program SUPCRT92 (Johnson et al., 1992), employing the slop98 database (http://geopig.asu.edu/sites/default/files/slop98.dat) and thermodynamic data from Helgeson et al. (1978) and Neuhoff (2000). Mineral abbreviations: Ab: albite, Anl: analcime, Nph: nepheline, Ntr: natrolite, Qz: quartz

The Fohberg phonolite only contains natrolite-group minerals, whereas the Endhale phonolite additionally contains analcime as pure Na zeolite species. The appearance of analcime is caused by higher silica activity during fluid-rock interaction, which favours the formation of analcime over natrolite (Fig. 2).

In contrast, the Kirchberg phonolite exhibits the primary minerals including preserved feldspathoid minerals. Sodalite-group minerals show only a slight sign of alteration to natrolite.

Phonolite intrusions rich in easily decomposing feldspathoids are good candidates for the generation of zeolite deposits. A major factor controlling the degree of zeolitization is the nature of the country rock in which phonolitic magmas are emplaced: The Fohberg and Endhale phonolites in the eastern KVC intruded water-rich sediments which is critical for the generation of local hydrothermal systems, and suffered complete reaction of feldspathoid minerals to zeolites. The Kirchberg phonolite in the western KVC intruded dry tephritic lavas and pyroclastics and preserved its primary mineralogy with only minor zeolitization. The geologic setting significantly affects the fluid-rock interaction and finally causes the differences in the degree of alteration.

Acknowledgments

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Experimental studies on the effect of particle size on the performance of zeolite fixed beds

M. A. Stylianou[1] and V. J. Inglezakis[2]

[1] *University of Cyprus, Department of Civil & Environmental Engineering, NIREAS-International Water Research Center, Subsurface Research Laboratory, Nicosia, Cyprus; E-mail: stylianou.a.marinos@ucy.ac.cy*
[2] *Nazarbayev University, School of Engineering, Chemical Engineering Department, Astana, Republic of Kazakhstan; E-mail: vasileios.inglezakis@nu.edu.kz*

Introduction

Natural minerals are often used as packing materials in fixed bed columns for the removal of metal ions in ion exchange processes due to their high ion exchange capacity (Tsitsishvili *et al*., 1992; Helfferich, 1995). In the present study natural clinoptilolite from northern Greece was used. Most ion-exchange processes, both at laboratory and plant scale, are performed in columns (Inglezakis and Poulopoulos, 2006). A solution is passed through a bed of ion-exchanger material where its composition is modified by ion exchange or sorption. The composition of the effluent and its change with time depends on the properties of the ion exchanger, the composition of the feed and the experimental conditions. The influence of the experimental conditions, i.e. particle size and volumetric flow rate on exchange rates is theoretically expected and experimentally verified in several studies for removal of metals and other cations using several materials (Inglezakis and Grigoropoulou, 2004; Stylianou *et al*., 2007). In the present work the effect of particle size on the removal of Pb^{2+}, Cu^{2+}, Mn^{2+}, Zn^{2+} and Cr^{3+} was studied and compared to results of similar experimental studies found in the related literature.

Experimental Methods

The zeolite used was supplied by S&B Industrial Minerals SA and IGME (Institute of Geology & Mineral Exploration). The chemical composition of the material was obtained through XRF and XRD analysis was also performed. CEC of clinoptilolite is 188.40 mequiv./100g.

Fixed bed experiments were conducted in order to examine the Pb^{2+}, Cu^{2+}, Mn^{2+}, Zn^{2+} and Cr^{3+} uptake by clinoptilolite, using the same experimental conditions. Mineral samples were used in three granular sizes of 0,250-1mm; 1,4-2mm and 2-5mm. Metal solutions were passed through the packed column at a relative volumetric flow rate of 10 BV/h (where BV is a volume of liquid equal to the volume of the empty bed), under a total normality of 0.01N and initial pH value equal to 4 and ambient temperature (25°C). The ion exchange process was conducted in 0.7m long plexiglass columns of 0.02m internal diameter (V_{bed} = 216.6 mL, H_{bed} = 0.69 m, $M_{clinoptilolite}$= 215 g). The solution was introduced at a constant volumetric flow rate (Q) and concentration (C), using a peristaltic pump in up-flow mode in order to assure complete wetting of the mineral particles. Liquid samples were withdrawn at the exit of the bed at specific time intervals, acidified with HNO_3 at pH 2 and analyzed for heavy metal cations. By plotting the exit metal concentration versus time, the breakthrough curves can be obtained.

In the present study the breakthrough point" or "breakpoint" was used for comparative reasons. Breakpoint is set at 10% and the total volume of the treated solution until this point (*V*BR, expressed in terms of Bed Volumes) is used as a measure of the operation's removal efficiency.

The samples were analyzed for heavy metal cations by atomic absorption spectrometry (Perkin-Elmer model 2380 spectrophotometer).

Results and Discussion

The effect of particle size on V_{BR} was examined for concentration of 0.01N and volumetric flow rate of 10 BV/h and the results are shown in Figure 1. It can be seen that lowering the particle size from 2-5mm to 0,250-1mm, V_{BR} is increased. More specifically the series in relation to BV is 0,25-1mm>1,4-2mm>2-5mm.

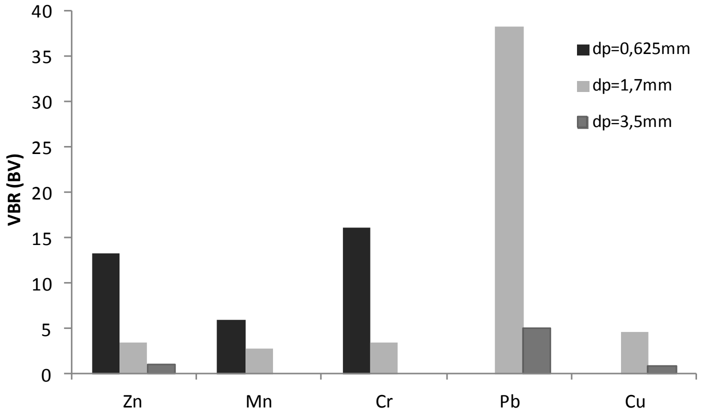

Figure 1. Effect of particle size on breakpoint for the ion exchange of heavy metals on natural clinoptilolite (C = 0.01 N, Q = 10 BV/h)

In table 1, the results of the present study are compared with similar studies in the literature. Inglezakis and Grigoropoulou (2004) showed that by lowering the particle size of zeolite from 1.4–1.7 to 0.8–1 mm, V_{BR} is increased by a factor near to 2 in the cases of Pb^{2+}, Cu^{2+} and Cr^{3+}.

The dependence of the performance on particle size is leading to the conclusion that diffusion (either particle or film) is the rate-limiting step of the overall ion exchange (Inglezakis and Grigoropoulou, 2004). It is well known that by decreasing the particle size, the performance of adsorption and ion exchange processes is improved (Helfferich, 1995). However small particle sizes result in high flow resistance of the column and should be avoided. It has been found that smaller particle sizes may exhibit lower rates, due to lower effective diffusion coefficients, resulting from structural problems or pore clogging (Inglezakis and Grigoropoulou, 2004). Consequently, V_{BR} should be increased as it can be viewed as an indication of exchange rate, since it is well known that the shape of breakthrough curve (and thus the location of V_{BR}) is influenced by the rate of ion exchange process.

Table 1. Bed Volumes (BV) in relation to particle size for the ion exchange of heavy metals on natural clinoptilolite

Flow, BV/h	d, mm	d_p, mm	V_{BR}, BV					Reference
			Zn	Mn	Cr	Pb	Cu	
10	0,250-1	0,625	13,3	6,0	16,2	--	--	Present study
5	0,8–1	0,9	--	--	7,4	21,3	5,3	Inglezakis and Grigoropoulou, 2004
5	1,18–1,4	1,29	--	--	6,1	13,7	3,4	Inglezakis and Grigoropoulou, 2004
5	1,4–1,7	1,55	--	--	3,7	10,6	2,5	Inglezakis and Grigoropoulou, 2004
10	1,4-2	1,7	3,5	2,8	3,5	38,3	4,7	Present study
10	2-5	3,5	1,1	--	--	5,0	0,8	Present study

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Removal of chromium(VI) from aqueous solutions using zeolites modified with HDTMA and ODTMA surfactants

B. Szala, T. Bajda and A. Jeleń

AGH University of Science and Technology, al. A. Mickiewicza 30, 30-059 Kraków, Poland;
E-mail: bszala@geol.agh.edu.pl

Introduction

Numerous studies have confirmed that zeolites have proven to be excellent materials for removing metal cations from wastewater (Bowman, 2003; Apreutesei et al., 2008). To improve the sorption properties of Zeolites in terms of their anionic forms, surface modification is necessary. Replacement of K^+, Na^+, Ca^{2+} and Mg^{2+} ions in the zeolite's exchangeable positions by organic cations improves the hydrophilicity of the crystallites' surface and produces a material with a positively-charged surface (Bowman 1995). The modification takes place only on the outer surface of the crystallites as the ammonium salt molecules are too large to enter the zeolite's channels. Therefore, external cation exchange capacity (ECEC) is an important property in the synthesis of organo-zeolites. Many studies have indicated that organo-zeolites can be used to remove anions, such as phosphates (Onyango et al., 2007), arsenates (Swarnakar et al., 2011) and chromates (Bajda, Kłapyta 2013) from aqueous solutions.

The aim of this study was to compare the chromate adsorption capacities of natural and synthetic organo-zeolites modified with hexadecyltrimethylammonium bromide (HDTMA) and octadecyltrimethylammonium bromide (ODTMA) surfactants. Interest is mainly focused on: The impact of zeolites' source order on the sorption capacity; the sorption mechanism; the pH effect and the immobilization durability. Another objective was to select the most efficient sorbent which could be used in water purification.

Experimental Methods

A natural zeolite (clinoptilolite from Ukraine) and zeolite Na-P1 synthesized from fly ash after combustion of coal were modified with HDTMA and ODTMA surfactants at 100% (1.0 ECEC) and 200% (2.0 ECEC) of their external cation exchange capacity. Batch and column studies were conducted to evaluate the influence of pH and the initial Cr(VI) concentration on the efficiency of removal of chromates. The chromate concentration in the supernatant was determined spectrophotometrically (UV–VIS Hitachi U-1800) using the biphenylocarbazide method (ASTM, 1992). For solid characterization, powder XRD patterns were recorded using a Philips APD PW 3020 X'Pert instrument with Cu Kα radiation and a graphite monochromator.

Results and Discussion

The resulting mole ratios for organo-zeolites modified with HDTMA are almost identical to the organo-zeolites modified with ODTMA (**Tab. 1**). Therefore, it can be concluded that the carbon chain length of the surfactant used for modification has no impact on sorption efficiency. The resulting molar ratios indicate that in the case of the synthetic organo-zeolite, only half of the sorption capacity is utilized (assuming an ion exchange mechanism).

Table 1. The molar ratio of adsorbed Cr(VI) to HDTMA and ODTMA

	Molar ratio $Cr(VI)_{sorbed}/HDTMA$		Molar ratio $Cr(VI)_{sorbed}/ODTMA$	
	1.0 ECEC	2.0 ECEC	1.0 ECEC	2.0 ECEC
Natural zeolite	0.71	0.77	0.75	0.75
Synthetic zeolite	0.49	0.58	0.47	0.51

After modification with the HDTMA and ODTMA surfactants, the zeolites used in this work showed a significantly improved ability to remove chromium(VI) contamination from aqueous solutions. These experiments showed that the amount of Cr(VI) removed by organically modified natural zeolites (ZN) is higher at low pH (2-3), whereas the synthetic zeolites (ZS) sorbed more efficiently at pH 5.7-7.0. Sorption of chromate is more efficient by the organo-zeolites modified with HDTMA than ODTMA surfactant (**Fig. 1**). All experiments have shown that the synthetic zeolite is a better sorbent for anionic forms of chromium(VI) than natural zeolites (**Fig. 1**). The results of this research can be used in environmental protection as well as for further study into the properties of surfactant-modified zeolites (SMZ) and their potential applications in environmental protection.

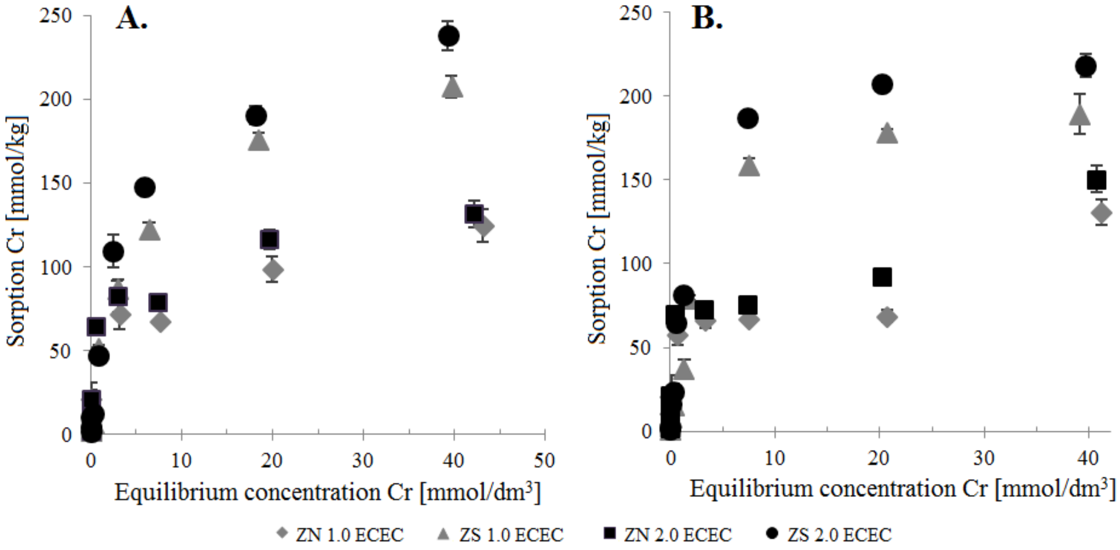

Figure 1. Sorption of chromium (VI) by natural zeolites (ZN) and synthetic zeolites (ZS) modified with HDTMA (A.) and ODTMA (B.)

Acknowledgment
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Removal of Reactive Black 5 from Wastewater by using Apolaccase Modified Zeolite

E. Tasgin[1], H. Nadaroglu[2], E. Kalkan[3], N. Celebi[2] and E. Karaman[4]

[1]Bayburt University, Faculty of Education, Chemistry Department, 69000 Bayburt, Turkey;
E-mail: esent25@atauni.edu.tr
[2]Ataturk University, Erzurum Vocational Training School, 25400 Erzurum, Turkey
[3]Ataturk University, Oltu Erath Sciences Faculty, Geological Engineering Department, 25240 Oltu-Erzurum, Turkey
[4]Akdeniz University, Engineering Faculty, Geological Engineering Department, 07000 Antalya, Turkey

Introduction

The wastewater disposed by textile industry is causing major hazards to the environment and drinking water due to presence of a large number of contaminants like acids, bases, toxic organic, inorganic, dissolved solids and color. It is now a well-established fact that the coloration of water is mainly caused by dyes, which are generally toxic, non-degradable and stable. The stability of dyes towards light and oxidizing agents also creates a problem for their removal by different waste treatment procedures (Abdel-Aal et al., 2006; Lambert et al., 1997; Guivarch et al., 2003). This paper describes the use of laccase modified-zeolite for removal of Reactive Black 5 (RB5) dye from aqueous solutions. The adsorption of RB5 dye has been investigated as a function of contact time, pH, temperature and adsorbent dose. The RB5 dye has been adsorbed by laccase modified-RM from RB5 dye polluted-wastewater (Ngah and Hanafiah 2008). Adsorption isotherm, kinetic and thermodynamic studies have been performed to describe the adsorption process.

Experimental Methods

Reactive black 5 dye was purchased from Sigma-Aldrich Co. Ltd. The natural zeolite was collected from open pit mine in Gordes (Manisa) Region (West Anatolia). It was first sieved through sieve and then washed with distilled water. The washed material was heated at 100±5 °C for 24 h. The solid fraction was washed five times with distilled water following the sequence of mixing, settling, and decanting. The last suspension was filtered and the residual solid was then dried at 105ºC, ground in a mortar, and sieved through a 200-mesh sieve. The product was used in the study. Synthetic wastewater was prepared by dissolving Reactive black 5 (RB5) dye. The absorbance of the solutions was measured at 597 nm with spectrophotometer (PG Instrument T80 Spectrophotometer). A calibration curve was prepared in the range 0-40 ngmL^{-1} of RB5 dye according to the general procedure.

Results and Discussion

RB5 dye is dissociated anionic sulfonate in aqueous solution. It has two sulfonate groups and two sulfatoethylsulfon groups that have negative charges in an aqueous solution (Greluk and Hubicki, 2010).The chemical structure and the general characteristics of RB5 are summarized Table 1.

Table 1. General characteristics of RB5 dye

Chemical formula	Molar mass	Color index number	λ_{max}
$C_{26}H_{21}N_5Na_4O_{19}S_6$	991.82 g/mol	20505	597 nm

In the study, Laccase was purified from *Lactarius volemusin* two steps. Firstly, it was partially purified by precipitation in $(NH_4)_2SO_4$. Secondly, ion exchange chromatography on DEAE-sephadex was used (Nadaroglu and Tasgin 2013). Then, laccase enzymewas dialyzed against 0,2 M phosphate buffer (pH: 7,0) which contains 0,075 M dipicolinic acid. By this was almost 100% pure apoenzyme was obtained (Demir et al. 1993).

The effect of apolaccase immobilized on zeolite was studied by varying surface material concentration (0.0125-0.2 mg). The activity of this catalyst to decolorize RB5 was tested by different parameters such as contact time 0-360 min (Fig 1).The amount of the removal increased with the increase of the contact time and reached a constant value. This may be due to the attainment of equilibrium condition at 60 min of contact time, which is fixed as the optimum contact time. It was observed that removal of dye by laccase modified-zeolite is optimum pH in the range 3-9, optimum temperature in the range of 20-80 ^{o}C (Fig. 1).

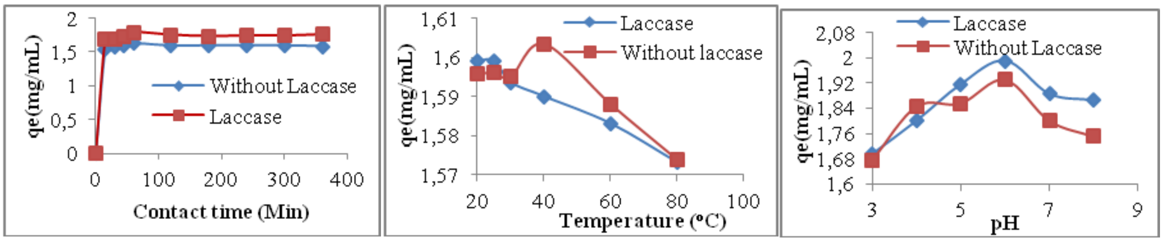

Figure 1. Effect of contact time, temperature and pH on the removal of dye by laccase modified-zeolite

In the all the study runs, as described above, other parameters were kept stable and samples were taken at regular time (an hourly) for the analysis (Nadaroglu et al., 2013: Noroozi et al., 2007).

In this study, the suitability of the Langmuir and Freundlich adsorption isotherm models to the equilibrium data were investigated for removal of RB5 dye using laccase modified-zeolite. For adsorption of RB5 dye on the modified zeolite surface, values of the Langmuir and Freundlich adsorption isotherms were shown in Table 2.

Table 2. Values of the Langmuir and Freundlich adsorption isotherms

Adsorption isotherm	With Laccase Value	Without laccase Value
Langmuir constants		
q_{max}(mg/g)	500.00	500.00
b (L/mg)	176.5	263.0
R^2	0.986	0.991
Freundlich constants		
K_F	0.759	0.241
n	0.93	0.799
R^2	0.999	0.9826

Based on the results, laccase modified-zeolite can be used as a relatively efficient and low cost absorbent for the removal of RB5 dye from textile wastewater.

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Kinetic and successive sorption/desorption study of Zn and Cd uptake onto iron-modified zeolite

M. Ugrina, N. Vukojević Medvidović, J. Perić and M. Trgo

Faculty of Chemistry and Technology, University of Split, Teslina 10/V, 21000 Split, Croatia;
E-mail: mugrin@ktf-split.hr

Introduction

The process of heavy metal ions binding on zeolite is a complex transfer process effected by diffusion of metal ions through the solution, diffusion through the liquid film, diffusion through the zeolite particle and sorption/desorption reaction. The aim of this paper is to determine the rate limiting step of Zn and Cd sorption onto iron-modified zeolite (IMZ), as well as the possibility of multiple reuses of IMZ in sorption/desorption cycles.

Experimental Methods

The iron-modified zeolite (IMZ) was prepared from natural zeolite, originating from the Zlatokop deposit (Serbia), according to the procedure published previously (Ugrina et al., 2013). The particles zeolite size was 0.6-0.8 mm.

The kinetic study of Zn or Cd sorption on IMZ was carried by the batch method with solutions of initial concentration in the range 5.647-14.821 mmol Zn/l and 6.147-14.510 mmol Cd/l at a constant S/L ratio of 10 g/l and in the time interval of 24 h. Batch sorption and desorption studies were performed in two steps. In the first step IMZ was saturated with a solution of the initial concentration of 10.515 mmol Zn/l and 10.063 mmol Cd/l. In the second step desorption of metal saturated IMZ was performed with different concentrations of NaCl, $NaNO_3$ and KCl solutions in the range of 0.1-5.0 mmol/l. The consecutive sorption/desorption of heavy metal ions was repeated four times with the highest concentration of NaCl, $NaNO_3$ and KCl.

Results and Discussion

The results of the kinetic study of Zn and Cd uptake on IMZ are shown on Fig 1. Two kinetics stages are evident, an initial rapid stage within 240 min followed by a slower stage up to 1440 minutes, indicating the change in the kinetic mechanism. Thus, the experimental results were tested according to different diffusion kinetic models, such as Homogeneous, Vermeulen, Parabolic, Weber-Morris and film diffusion (Apiratikul et al., 2008, Sparks, 1998). For both metal ions, the results show that intra particle diffusion is the rate limiting step. From the proposed models corresponding parameters have been calculated. The calculated diffusion coefficients are of the same order of magnitude for the investigated concentration range.

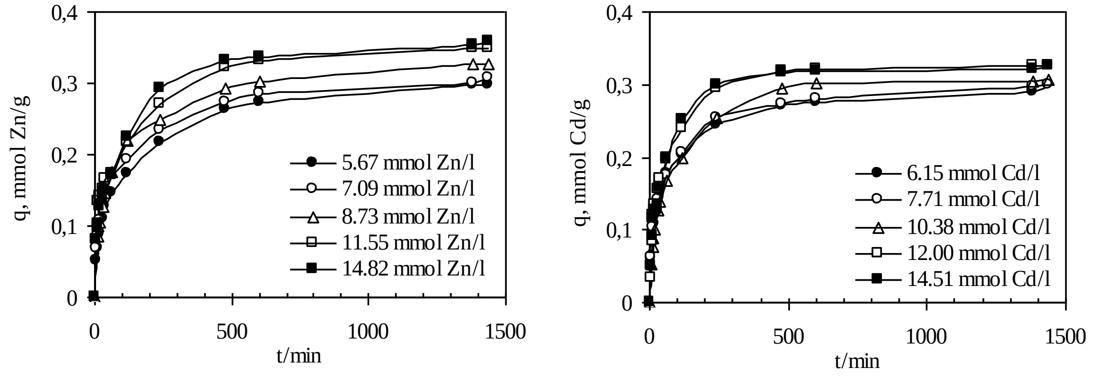

Figure 1. The amount of Zn (left) and Cd (right) uptake per gram of zeolite vs. time

The results for amounts of Zn and Cd sorbed and desorbed during four consecutive cycles are presented in Fig. 2. Results indicate that saturated IMZ can be easily desorbed with a sodium solution, while desorption with a potassium solution is less effective. This is probably due to higher ion exchange affinity of Na compared to K towards saturated IMZ. It is also evident that the anion does not significantly influence on desorption of Zn and Cd. The results show that Cd is easily desorbed in the first cycle, while Zn is mostly retained in the IMZ. This is probably connected with higher reversibility for the exchange couples Na/Cd, than Na/Zn which is a consequence of higher selectivity of IMZ towards Zn (Pabalan et al., 2001). In the following cycles, the amount of desorbed Zn and Cd increased and reached the values of sorbed Zn and Cd already in the second cycle. A small difference between the amount of sorbed/desorbed Zn and Cd from the second to the fourth cycle indicates excellent sorption/desorption abilities of zeolite. Moreover, the zeolite was not completely exhausted and still had abilities for additional cycles.

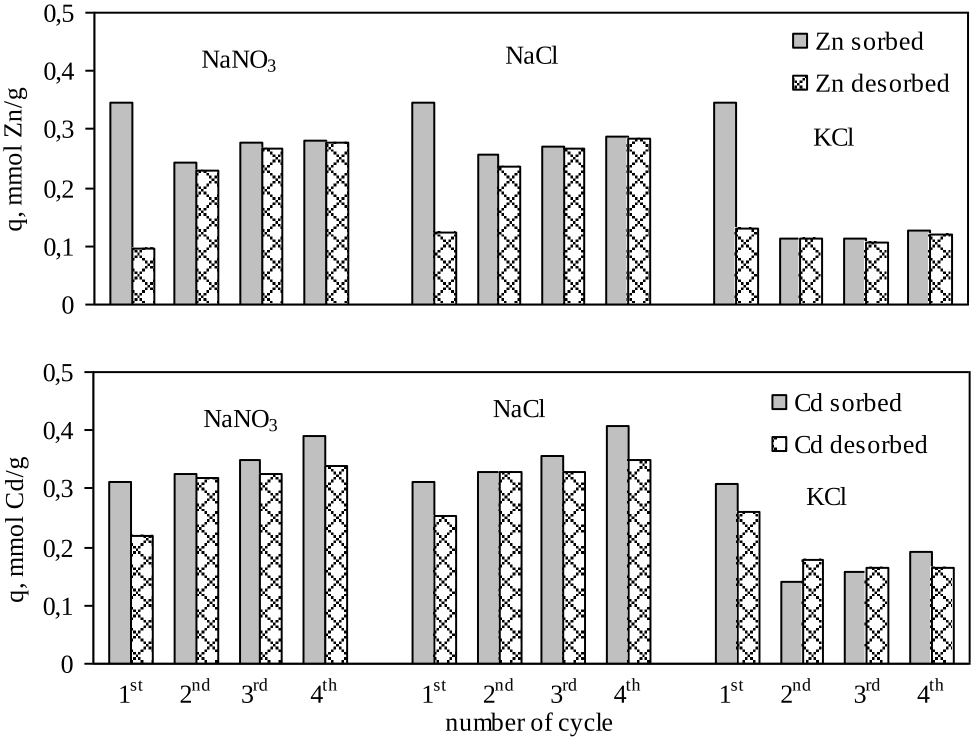

Figure 2. Quantity of sorbed and desorbed of Zn and Cd ions per gram of IMZ

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Activated natural zeolitic tuff – applicability in vegetable production

M. Ugrinović[1], V. Verbić[2] and D. Vojnović[2]

[1] *Institute for vegetable crops, 11420 Smederevska Palanka, Serbia; E-mail: milan.ugrinovic@gmail.com*
[2] *I-Zeolit Ltd.; 11000 Belgrade, Serbia*

Introduction

Zeolites represent very wide group of natural aluminosilicate minerals. They are characterized by a large specific surface area and a high value of the cation exchange capacity that is derived from isomorphic substitution of triple charged aluminum with double charged cations (Mg^{2+}, Ca^{2+}), making the surface negatively charged (Mojić, 2006, Xu et al,. 2009). The use of natural zeolites is very diverse. They are used in various technological processes (Wang and Peng, 2009) and also in the agricultural production (Damjanović et al., 2005, Damjanović et al., 2006, Ugrinović et al., 2012). Clinoptilolite is the most abundant in the zeolite group of minerals. Clinoptilolite-heulandite group is the only type of zeolite that emerges in Serbia. Several tests were performed in order to determine biological nutritive value of plant nutrition product and soil enhancer (acitvated natural zeolitic tuff), as well as its applicability in vegetable production.

Experimental Methods

A natural zeolitic tuff from the „Jablanica 1" deposit near Krusevac, was used in this experiment, which was performed in protected area with additional heating. Natural zeolitic tuff (71% of clinoptilolite, 24% of mica – phyllosilicate minerals and less than 5% of quartz, calcite, feldspar and amphiboles) was activated using high temperatures (400-550 °C) for 75 minutes and then enriched with ammonia solution, NH_4OH and mono-ammonium phosphate, $(NH_4)H_2PO_4$. Containers for seedling production with 104 holes, made of styrofoam, were used in this experiment. Containers were filled with standard commercial substrates Klasman (TKS 2) and Floragard (B Fine) with the application of enriched zeolite (EZ). Phy (Table 1).

Table 1. Physical and chemical properties of comercial substrates and enriched zeolite

Substrates	Water Absorption (ml/100g)	CEC meq/100 g	Density kg / m^3	pH		N (%)	(kg / m^3)	
				H_2O	KCl		P_2O_5	K_2O
TKS 2	87,1	125	141,0	6,4	4,9	0,21^{t}	0,217^{a}	0,208^{a}
B Fine	88,5	na	128,0	6,7	5,1	0,17^{t}	0,128^{a}	0,144^{a}
EZ	28,4	168	1243,0	7,2	na	1,0^{a}	18,788^{t}	48,84^{t}

CEC - cation exchange capacity; na - not available; ^{a} - available; ^{t} - total;

Treatments (substrates and mixtures), which were used in the experiment, are shown in the volumetric ratio (v/v):

1. TKS 2 100% (control)
2. TKS 2 75% + enriched zeolite 25%
3. B Fine 100% (control)
4. B Fine 75% + enriched zeolite 25%

Tomato variety Balkan F1 and pepper variety Romana were sown in the above-mentioned substrates, two seads in each cell. After emerging, the number of plants was reduced to one plant per cell. Additional nutrition and fertilizing hasn't been performed.

The experiment was set up in three replications. At the seedlings maturity stage samples were taken (10 plants per replication). Plant height, number of leaves per plant, plant mass, percentage of plants with flowers, and percentage of plants with fruits were measured. The differences between treatments were assessed with one-way ANOVA. Duncan's multiple range test was used when differences were significant ($p < 0{,}05$).

Results and Discussion

Significantly higher values of height, number of leaves per plant and plant mass are noted in the treatments with the enriched zeolite (TKS 2 75% + enriched zeolite 25% and B Fine 75% + enriched zeolit 25%) as opposed to control treatments (TKS 2 100% and B Fine 100%), at the 0,05 level of probability (Table 2.). The percentage of plants with flowers was significantly higher in the treatments with the enriched zeolites. Significantly higher percentage of plants with fruits is noted on pepper, in the treatment B Fine 75% + EZ 25%.

Table 2. Mean values of tested characteristics of tomato and pepper seedling in Klasman substrate TKS 2 (100%), combination of Klasman substrate TKS 2 (75% v/v) with enriched zeolite (25% v/v), Floragard substrate B Fine (100%), and combination of Floragard substrate B Fine (75% v/v) with enriched zeolite (25% v/v)

Treatments	Average plant height (cm)	Average number of levaes per plant	Average plant mass (g)	Plants with flowers (%)	Plants with fruits (%)
		Tomato			
TKS 2 100%	27.677^{c}	6.067^{b}	5.58^{c}	0^{b}	0^{a}
TKS 2 75% + EZ 25%	37.22^{b}	7.73^{a}	9.12^{b}	23.3^{a}	0^{a}
B Fine 100%	21.3^{d}	4.567^{c}	2.97^{d}	0^{b}	0^{a}
B Fine 75% + EZ 25%	41.913^{a}	8.3^{a}	11.2^{a}	36.7^{a}	0^{a}
		Pepper			
TKS 2 100%	23.59^{c}	8.63^{a}	2.29^{b}	0.167^{b}	0^{b}
TKS 2 75% + EZ 25%	31.933^{a}	8.467^{a}	5.157^{a}	0.8^{a}	0.0333^{b}
B Fine 100%	13.633^{d}	5.7^{b}	1.553^{c}	0^{c}	0^{b}
B Fine 75% + EZ 25%	28.483^{b}	8.433^{a}	5.196^{a}	0.867^{a}	0.4667^{a}

$^{a, b, c, d}$ - values within the same column signed with same letter do not differ significantly at the 0,05 level of probability, according to Duncan's test

Based on the results it can be concluded that the enriched zeolite had an impact on the improvement of tomato and pepper seedlings quality. Application of enriched zeolite in the amount of 25% (v/v) increased plant height, plant mass, number of leaves per plant and promoted appearance of flowers and buds. These results are in accordance with results of other researchers and preceding data (Damjanović et al., 2005, Damjanović et al., 2006, Ugrinović et al., 2012).

The use of enriched zeolite minimized the need for additional nutrition of the plants. Its application is possible in greenhouse vegetable seedlings production.

Acknowledgement
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Influence of pH on the adsorption of phenol and nitrophenols by Na clinoptilolite-rich tuff

L. Valle[1], S. Martinez-Vargas[1], M. T. Olguín[2] and M. Abatal[1]

[1]*Fac. Ing. Universidad Autónoma del Carmen, C.P. 24180, Cd del Carmen, Campeche, México;*
E-mail: mabatal@pampano.unacar.mx
[2] *Dep. Química, ININ, A.P. 18-1027, Col. Escandón Miguel Hidalgo, C.P. 11801, México, D.F., México*

Introduction

In this work, the adsorption of phenol (Phen), 2-nitrophenol (2-NPhen), 3-nitrophenols (3-NPhen) and 4-nitrophenol (4-NPhen) from aqueous solutions on sodium natural zeolite (ZCh-Na) was investigated at pH values 2 to 10 at T = 25 °C. The zeolitic material was characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). A batch system was used to evaluate the kinetic of the phenol and derivatives adsorption processes. Results by XRD and SEM techniques indicate that the clinoptilolite is the major phase in the zeolitic rock. The kinetic experimental data were well fitted by the pseudo second-order model. It was found that the pH is an important parameter which influence phenol and nitrophenols adsorption behaviour by the ZCh-Na due to the point of zero charge of the zeolitic material, of phenolic compounds in solution.

Phenols are classified as high-priority pollutants due to their carcinogenic effects on humans, and they have been found to be harmful to wildlife (Takahachi et al. 1994). Based on regulations by the US Environmental Protection Agency (US EPA), the concentration of phenol and its derivatives in wastewater should be less than 1 mg/L (Min et al. 2007). The use of activated carbon is limited due to its cost-effectiveness and difficult regeneration for reuse (Lin and Juang 2009). Many alternatives are very attractive from a cost standpoint. Zeolites are very attractive options for the removal of pollutant compounds from water due to their accessibility and low cost, high availability, high specific surface areas and high cation exchange capacity (Bosch et al. 2011).

Numerous researchers have reported the use of natural zeolites as clinoptilolite to remove organic compounds (Ayse 2007), including derivatives of phenol, from wastewater (Rushdi and Bassam 2009). However, no investigations have compared the removal efficiency of phenolic compounds at different pH values using the clinoptilolite-rich tuff from a new deposit located in the state of Chihuahua (Mexico). Therefore, the main objective of the present study was to evaluate the effectiveness of Mexican clinoptilolite-rich tuffs for Phen, 2-NPhen, 3-NPhen and 4-NPhen removal from aqueous solutions at pH values from 4 to 10. The adsorption kinetics, equilibrium adsorption, and adsorption mechanism were also considered.

Experimental Methods

Raw material and Sodium- clinoptilolite-rich tuff: The raw material was clinoptilolite-rich tuff from the recently discovered deposit of "Cerro Prieto", in the state of Chihuahua, México. The sample was washed with distilled water and then dried in an electric oven at 60 °C for 12 h. This sample is referred as "ZCh". This simple was treated with NaCl solution according with. This material was labeled "ZCh-Na".

Point of zero charge: The value of the pHpzc of each material was determined using the modified pH drift method (Faria et al. 2004).

Effect of pH: The effect of pH on the amount of phenols removal was analyzed over the pH range from 4 to 10. 10 ml of Phen, 2-NPhen, 3-NPhen and 4-NPhen with a concentration 20 mg.L^{-1} was taken in stoppered conical flask and agitated with 0.1 g of ZCh-Na at room temperature for 24 h. The samples were centrifuged, and the left out concentration in the supernatant solution were analyzed using a UV-VIS spectrophotometer by monitoring the absorbance changes at a wavelength of 270 nm.

Results and Discussion

Characterization: The SEM analysis of ZCh-Na showed the present of two phases: clinoptilolite crystals with monoclinic symmetry and mordenite fibers (Figure 1 and Figure 2, respectively). This result confirms those obtained by XRD.

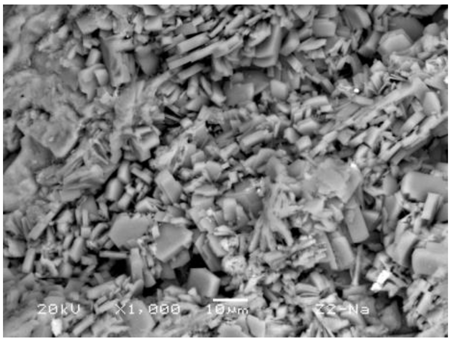

Figure 1. SEM image of ZCh-Na (clinoptilolita phase)

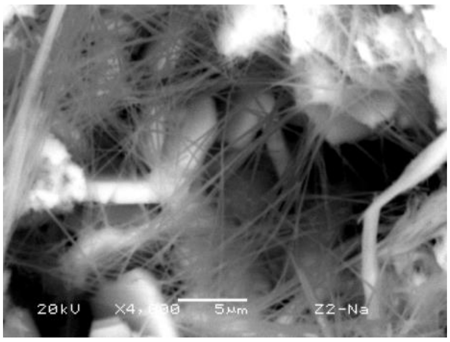

Figure 2. SEM image of ZCh-Na (mordenite phase)

Point of zero charge: The pH of the point of zero charge, pHpzc, is the pH at which the curve crosses the straight line that fits the points $pH_{Initial} = pH_{Final}$. ZCh have a pHpcz of 7.60 (Figure 2). When the pH is lower than these values, the material has positively charged sites and sorbs anions, and when the pH is higher, the surface has negatively charged sites and predominantly sorbs cations.

The adsorption capacity of phenols is influenced most by the pH of the solution. The pH of the solution affects the surface charge of the adsorbent, degree of ionization and speciation of the adsorbate species, which may lead to change in kinetics and equilibrium characteristics of the adsorption process. Fig. 4 shows the effect of pH on the adsorption of Phen, 2-NPhen, 3-NPhen and 4-NPhen.

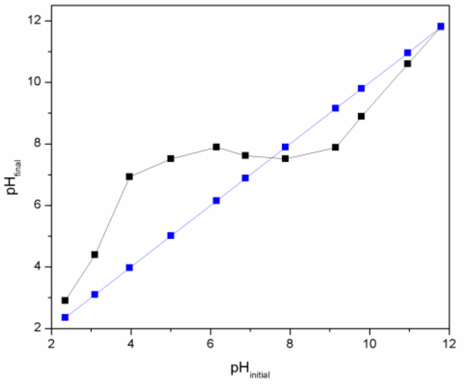

Figure 3. pH drift method to obtain pHpzc

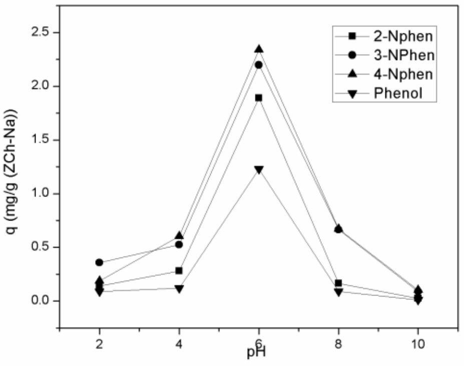

Figure 4. Effect of initial pH on Phenols uptake

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Jablanica 1 – perspective zeolite deposit

D. Vojnović[1], D. Križak[2] and M. Maksimović[3]

[1]I-Zeolit Ltd.; 11000 Belgrade, Serbia; E-mail: office@i-zeolit.rs
[2] Betec Resources Ltd.; 11000 Belgrade, Serbia
[3] Contractor Ltd.; 11000 Belgrade, Serbia

Introduction

On the slopes of Jastrebac mountain, on the west side, near Krusevac, geologists of the company Contractor Ltd., determined three deposits of zeolitic tuffs, of which the largest, „Jablanica 1“, was geologically explored in details. The totally identified reserves of deposits amounted to 1,613,000 t of dry ore. Contractor Ltd. owns about 1/8 of the total reserves, i.e., 206,000 t. The deposit covers around 8 hectares and it represents a layer of zeolite, with the average thickness of about 18.5 m. The ore varies in quality, and consequently in final application. It can be used in pharmacy, cosmetics, water protection, agriculture and remediation. Contractor Ltd. established, during the investigation, that the selective exploitation of zeolite will give the maximum utilization of the deposit.

The region of Krusevac is promising, according to rough estimates of Contractor's geologists, because these three deposits have reserves of about 2.2 million tons of zeolite. Given that the need for natural zeolite in Serbia is around 7000 t/year, the perspective of this region is exceptional. The quality of zeolitic tuff is reflected in the high content of clinoptilolite, which contributes to high market price of mineral raw material and finished products.

„Jablanica 1“ deposit is located in a micro-location of the Jablanica village. Two varieties of tuff are distinguished in the deposit: white massive tuff and banded sandy tuff. The bright white tuff builds the largest part of the deposit and they are in the upper layer, while the sandy tuff is in the basal section. The basic colour of white massive tuff is white, and the colour of sandy tuff is gray to dark gray.

Experimental Methods

Determination of the zeolitic tuffs' chemical composition in the „Jablanica 1“ deposit was done by making partial and complete analyses of individual and composite sample. Chemical analysis of individual and composite sample were performed by classical methods, as well as by methods of instrumental analytical chemistry - AAS. In the first stage of the research complete chemical analyses were carried out. Several representative samples of white and gray tuff were examined, and mixtures thereof, obtained by sampling several old excavations. In order to control the previous results, in 2006, two old strenches were tested (R -1 and R-2). The results are shown in Table 1.

X-ray analyses were performed on a total of 23 samples (1964) and 10 samples (2006).

Sorption capacity tests were performed on samples of white tuff (Table 2). Adsorption tests of engine oil SAE 15-40, euro diesel, heating oil and gasoline were carried out in order to implement zeolite to petrol stations, for rapid intervention in the sorption of hazardous liquids. The tests have given excellent results.

Cation exchange capacity test was performed in three independent laboratories that operate with various methodologies and standards, and the conclusion is given only on the basis of test results of composite samples (Table 3).

Results and Discussion

By microscopic examination, all samples are determined as pyroclastic structure tuffs, made up of tiny fragments and core mass. The primary mass of tuff, as a major component (70 - 95%), is completely altered volcanic glass. Based on the results of microscopic tests and chemical composition, tested rock is defined as fine-grained diagenetically altered dacite tuff with heulandite group minerals where clinoptilolite is dominant. Complete analyses of individual samples of white and gray tuff from the surface point to some differences in the chemical composition of raw materials.

The dominant phase in the investigated tuffs is zeolite from the heulandite/clinoptilolite group. Mica, quartz, amphibole and calcite are present in minor scale. Identical results were obtained in two stages of testing 1964/2006 (Figure not shown).

The results from sorption capacity tests show that the adsorption sensitivity of zeolite is extremely high, especially in the first two hours. Based on the adsorption capacity, zeolite from "Jablanica 1" deposit is classified as high-quality adsorbent. In particular, the zeolite has a high adsorption of substances at low concentrations.

Table 1. The results of individual samples of white and gray zeolite

Type of tuff		Chemical composition of the composite samples, %						
		SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O
		1	2	3	4	5	6	7
white	1.	62.47	13.03	2.90	2.80	2.81	1.43	3.84
white	2.	60.79	12.42	2.22	3.60	2.03	1.68	1.80
white	3.	62.20	13.98	4.22	3.11	2.42	-	-
white	4.	62.22	9.63	4.87	4.42	1.59	-	-
white	5.	59.01	12.27	3.52	2.66	2.07	0.12	0.76
C_{sr}	6.	61.34	12.27	3.55	3.32	2.18	1.08	2.13
gray	7.	61.50	12.38	2.37	3.49	1.99	-	-
gray	8.	62.14	11.58	2.37	2.42	3.66	-	-
gray	9.	59.50	11.80	3.20	2.80	1.84	0.05	0.96
C_{sr}	10.	61.05	11.92	2.65	2.90	2.50	0.05	0.96
white+gray $_{50:50}$	11.	62.20	13.98	4.22	3.11	2.42	-	-

Table 2. Test results of natural zeolite's sorption capacity

No.	Parameter	Unit	Result
1.	max C_{NH3}	meq u NH_3/g	1.01
		mg NH_3/g	17.22
2.	max C_{etanol}	%	7.58
3.	max C_{H2O}	%	10.00

Table 3. Test results of cation exchange capacity of two composite samples

Sample		Test results				
		Ca	Mg	Na	K	CEC, meq/100g
		1	2	3	4	5
K-I	1.	121	20.4	4.5	45.1	191
K-II	2.	86	16.1	4.0	40.0	146

Comparing the results of CEC values of zeolite from „Jablanica 1“ deposit with the results of zeolite from Igroš deposit (140-160 meq/100g) and from Zlatokop deposit (150-196 meq/100g), it can be concluded that the CEC values of the "Jablanica 1" deposit are larger than Igroš and approximately the same as in Zlatokop near Vranje. CEC values of zeolitic tuff varies from 146 to 191 meq/100 g.

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The effect of S/L ratio, pH and initial concentration on mercury ion capture by the iron-modified zeolite

N. Vukojević Medvidović[1], M. Macherzynski[2], L. Uruski[2] and M. Ugrina[1]

[1]University of Split, Faculty of Chemistry and Technology, Teslina 10/V, 21000 Split, Croatia;
E-mail: nvukojev@ktf-split.hr
[2]AGH University of Science and Technology, Faculty of Energy and Fuels, al. Mickiewicza 30, 30-059 Krakow, Poland

Introduction

Natural zeolites have already been recognized as a sorbent for mercury ion capture (Campbell et al., 2006). Recently, many authors have tried to modify natural zeolites in order to increase their sorption properties. One of modifications is the preparation of iron-modified zeolite which has shown better removal of heavy metals (Ugrina et al., 2013). This study has examined the effect of the S/L ratio, pH values and initial concentration on mercury ion capture by iron-modified zeolite.

Experimental Methods

Zeolite samples preparation - The iron-modified zeolite (IMZ) was prepared from natural zeolite originating from the Zlatokop deposit with particle size fraction of 0.6-0.8 mm, according to the procedure published previously (Ugrina et al., 2013).
Isothermal batch experiments - Mercury capture on IMZ was examined using a batch incubator shaker in the period of 24 h at room temperature. One set of experiments was performed with initial mercury solutions of 777.2 and 80.24 mg Hg/l prepared from $HgCl_2$ with adjusted initial value of pH_o=3.19. Different amounts of zeolite, in the range from 0.2 g to 7 g, were shaken with 50 ml of mercury aqueous solutions (S/L=4-140 g/l). The second set of experiments was performed with mercury solutions of γ_o(Hg)=29.46 mg/l adjusted at initial pH values in range pH_o= 1.27-3.19 at S/L=1-120 g/l, in which the lowest value of pH_o was adjusted at the highest S/L ratio. The third set of experiments was performed with γ_o(Hg)=14.79 mg Hg/l of acetate buffer solution at pH_o=4.63-6.31 and S/L=1-120 g/l (the lowest value of pH_o was adjusted at the highest S/L ratio). After equilibrations, the concentration of remaining mercury in supernatants was determined by Automated Mercury Analyzer MA-2 (NIC). Also, concentrations of released Na, Ca, K, and Mg ions in supernatants were determined by ion chromatography, and the concentration of Fe was checked by the complexometric method.

Results and Discussion

Figure 1 shows the mercury equilibrium concentration (γ_e), released exchangeable cations and equilibrium pH_e values in solutions versus the S/L ratio for two initial concentrations of mercury of 777.2 mg/l and 80.24 mg/l. In both cases, the mercury content in the solution decreased with increasing S/L ratios, while a sharp increase of pH_e is followed by increasing concentrations of released exchangeable cations (mainly Na, while K, Ca and Mg are present in smaller amount). At S/L=12 g/l, there is the evident appearance of a yellow precipitate which probably corresponds to HgO (indicated by the shaded area in Figure 1a). In order to avoid precipitation, the same experiment was performed at the initial γ_o(Hg)=80.24 mg/l with lower S/L ratios (Figure 1b). After 4 hours the pH value in the solution increased above 6. By addition of 1 drop of 6 M HCl, except in points 1 and 2 (S/L <2), the pH of suspensions was reduced. However, after the addition of HCl, the pH values increased again. In the experiment with S/L >7, the equilibrium pH values were higher than 7, and a slight clouding was visible. Our experiments revealed that we should avoid the precipitation phenomenon during sorption studies with IMZ. Thus, the pH of solutions during mercury uptake should be maintained below 7.0. Also the initial Hg concentrations were fixed to values that may be encountered in industrial wastewaters (15-30 mg/l).

The following experiments have been performed with the solution of γ_o(Hg) = 29.46 mg/l adjusted at pH_o =1.27-3.19, and with γ_o(Hg) = 14.79 mg/l prepared in the acetate buffer solution with the initial pH in the range pH_o=4.63-6.31. The results are expressed as the equilibrium amount of mercury capture on zeolite (q) and removal efficiency versus S/L ratio, and are given in Figure 2 together with the results obtained with γ_o(Hg) = 80.24 mg/l.

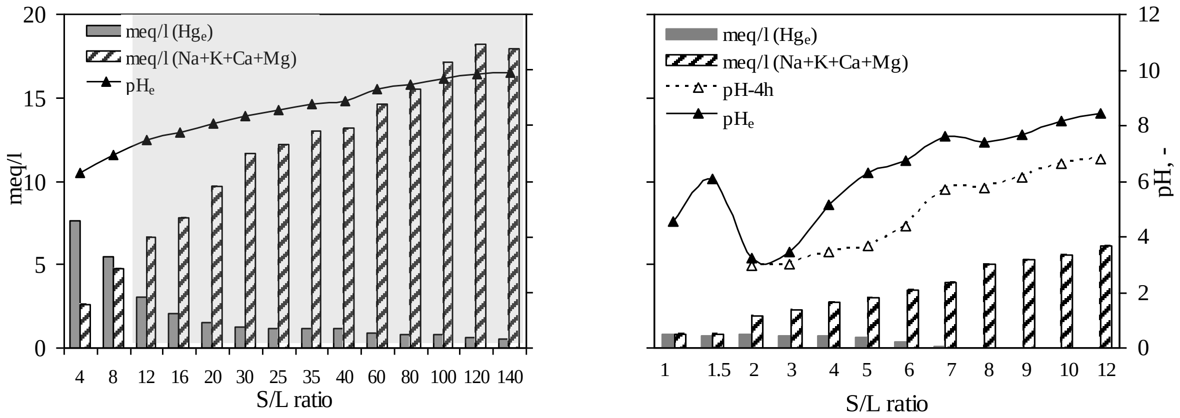

Figure 1. Relations between equilibrium concentrations of Hg, released exchangeable cations in the solution and pH as a function of the S/L ratio for: Left - $\gamma_o(Hg)$ = 777.2 mg/; Right - $\gamma_o(Hg)$ = 80.24 mg/l

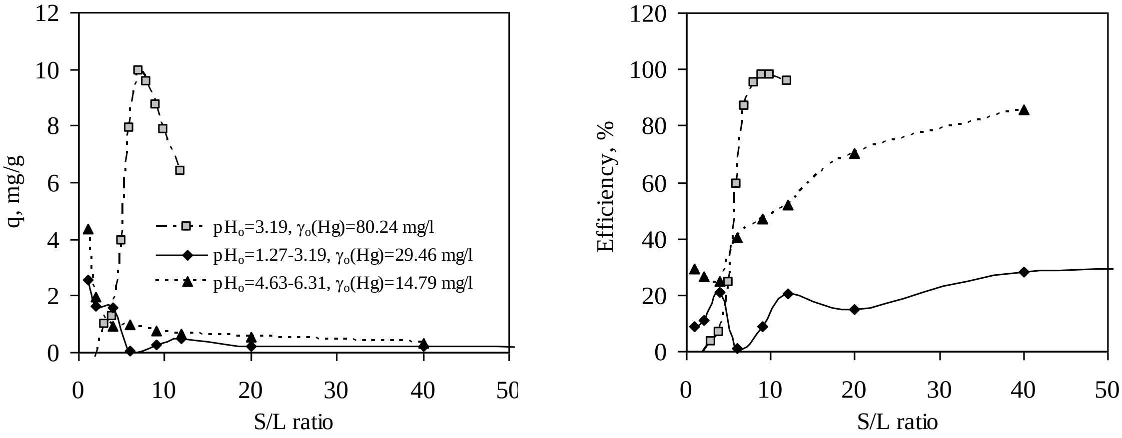

Figure 2. Equilibrium amount (q) of mercury capture on zeolite and efficiency versus S/L ratio

It is evident that with increasing S/L ratio for experiments with pH_o= 1.27-3.19 and with pH_o= 4.63-6.31 (acetate buffer) q values decrease. For experiments with pH_o=3.19, q values rapidly increased up to 10 mg/g. With further increase of S/L ratios, q values rapidly decreased, while efficiency increased, even these experiments are performed with highest mercury concentration of $\gamma_o(Hg)$=80.24 mg/l. In these last five points, in which slight clouding was visible, mercury removal efficiency was > 86 % for S/L> 7 g/l. As the equilibrium $pH_e > 7$, it indicates that mercury ions capture on IMZ was competing with precipitation. In experiments with pH_o=1.27-3.19, the equilibrium pH reached the values of pH_e=2.51-4.02. The obtained removal efficiency was low (< 30 %) even for high S/L ratios. This is probably a consequence of competition between H^+ and mercury ions. In experiments with pH_o=4.63-6.31 (acetate buffer), precipitation was avoided even at high S/L=40 g/l. The obtained removal efficiency increased with the S/L ratio, and reached the values of 80 %.

Acknowledgement

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Host-guest interactions in zeolites: insights from the NAT-topology system

H. W. Wang[1] and D. L. Bish[2]

[1]Lujan Neutron Scattering Center, Los Alamos National Laboratory, MS H805, Los Alamos, NM 87545, USA; E-mail: wanghw@lanl.gov
[2]Department of Geological Sciences, Indiana University, 1001 E. 10th Street, Bloomington, IN 47405, USA; E-mail: bish@indiana.edu

Introduction

Porous materials that exploit host-guest interactions are extremely important in Nature and in technology. The host framework structure of natural and synthetic zeolites, possessing specific void geometries (size/shape), are applied in the refining industry, as molecular sieves, catalysts, adsorbents, and ion exchangers (Davis, 2002). Despite the myriad of applications for zeolites, understanding why such materials show wide compositional and structural diversity is one of the challenging questions in modern zeolite sciences. A detailed knowledge of the interaction of guest molecules with the host framework provides a direct tie to the molecular-level mechanisms responsible for zeolite crystallization and their design for specific applications. As the field is broad, this abstract does not provide an overview of zeolite syntheses, design and related applications, but rather it presents a snapshot reflecting the insights gained from our experimental work on the effects of host framework flexibility (i.e., structural changes) on guest molecule motions/uptake and vice versa.

Natural zeolites of the NAT-type topology (T_5O_{10} building unit), including natrolite, scolecite, and mesolite, were used as the prototypical framework for the study of structural changes leading to disordering of extraframework cation-H_2O (as guest) arrangements within the pores. The small-pore NAT-type channels provide an extreme case of pronounced host-guest and guest-guest interactions as well as of the confinement of the guests in the channels. The compressibility and expansibility of the NAT framework are amplified by changing pressure (P), temperature (T), or guest chemistry, all of which have been investigated experimentally and theoretically over the past several decades. Two of the more-intriguing properties are emphasized here, a flexible structural window and a comparatively specific cation-H_2O arrangement. Like most of the known zeolite frameworks, the nearly rigid tetrahedra with freely rotating spherical joints through shared oxygen atoms possess a flexibility window over the range of structural densities. Geometric simulations using idealized stress-free SiO_4 units have predicted such structural deformations, but most of the simulated configurations inside the flexibility window are not accessible in real zeolites due to their high energies (Sartbaeva et al., 2006; Kapko et al., 2010). Natural zeolites tend to occur at the low-density edge of the window, towards maximum pore/volume extension, due to Coulomb repulsions between framework oxygens (a conclusion drawn from simulations as in Sartbaeva et al., 2006) and more importantly to the presence of guest cation-H_2O species. Second, the NAT framework expands in accordance with the size of guest species. The resulting compounds, however, have a specific catio-H_2O arrangement. It has been shown that small/medium-size cations (e.g., Li^+, Na^+, Ca^{2+}, Sr^{2+}, Cd^{2+}, Pb^{2+}, Ag^+) tend to occur near the ‘center’ of the elliptical channels, whereas larger cations (e.g., K^+, Rb^+, Cs^+, Ba^{2+}) tend to occur near the ‘wall’ of the channels at the joint of two [T_5O_{10}] chains (Lee et al., 2011). Concomitantly, H_2O molecules swap positions from near-the-‘wall’ locations in the former case to central locations in the latter case. A tendency for larger guest species (cation or H_2O) occupying the ‘wall’ location suggests that the internal flexibility of the NAT framework serves as a coupling force that governs guest complex arrangements (i.e., host frameworks do *not* play a passive role in their accommodation to guest complexes), and this is what we have explored through the structure and dynamical investigations.

Experimental Methods

To determine how framework flexibility affects host-guest interactions, the structures of the NAT frameworks in natrolite, scolecite, and mesolite were altered through a change of their hydration states (by applying temperature and relative humidity (RH) control). With systematic T-RH investigations using static structure probes, including in situ X-ray diffraction (Cu Kα and high-resolution synchrotron X-ray measurements for average structure) and pair distribution function (PDF) analysis of total scattering data (for local host-guest geometry), a sequence of RH-dependent dehydration and accompanying structural transitions was observed. Experimental details can be found in Wang and Bish (2012, and references therein). Parallel observations on the dynamic interactions of cation-H_2O complexes with host NAT frameworks were made using *in situ* diffuse-reflectance infrared Fourier transform spectroscopy (DRIFTS). The combined methodologies with controlled T-RH variables allowed us to determine not only where atoms are but also what they are doing in the study system.

Results and Discussion

In all three studied zeolites, temperature-induced dehydration caused a sequence of structural transitions from hydrated to dehydrated states in which the host framework transformation path was coupled primarily with the thermal motion of guest Na^+/Ca^{2+} and H_2O molecules. The observation of different transformation phases (Figure 1) and interactions of H_2O and Na^+/Ca^{2+} with host NAT frameworks under high- and low-RH conditions indicated the development of different local strains, arising from the thermal motion of cation-H_2O complexes. These induced local strains influence energetically feasible T-O-T angles, which can be significantly reduced (to ~120º) with the increased coordinations of the hinge oxygens by guest cations (i.e., similar to the case in feldspars). Framework flexibility in the host and Coulomb repulsion of framework oxygens, however, serve as opposite driving forces where the host has the ability to remain in its stress-free state (ideally with T-O-T angles at ~130º to 160º). It is the balance between the cost in Coulomb energy (when bringing framework oxygens closer together) and the strength of interactions between the guest cations and framework oxygens that determines the overall structural states under a given T-RH condition (details in Wang and Bish, 2012). We argue that, regardless of the applied variables (such as increasing T or P), two cooperating factors, namely short-range host-guest interactions and long-range host-host Columbic repulsions, are the fundamental mechanisms governing the overall structural stabilities/changes in the NAT-topology system. In a survey of cation-exchanged NAT-topology compounds and their relative stabilities in response to pressure-induced hydration (as opposed to temperature-induced dehydration), the onset pressure of structural transitions can be lowered by simply using different extraframework cations (e.g. Lee et al., 2013). Interactions among the host topology and guest chemistry apparently play a critical role in the NAT-type zeolites. A clear understanding of atomic factors controlling structural behaviors is important and requires further investigation (for both natural and synthetic zeolites) because these host-guest interactions influence host structure stabilities under particular physical or chemical environments. Predictive understanding of a material's macroscopic behavior can (only) be obtained from a detailed knowledge of its microscopic or atomistic nature. Understanding host-guest interactions is essential for determining and predicting the structural stabilities of zeolites and their future applications (e.g., use of zeolites for energy storage relies largely upon on a detailed knowledge of structural breakdown mechanisms).

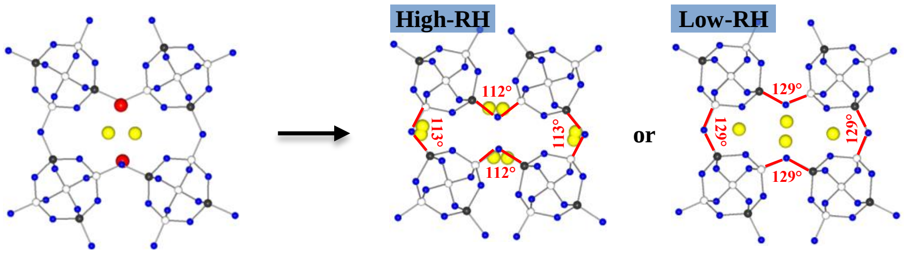

Figure 1. Different transformation paths and disordering of Na^+ cations (yellow) during thermal dehydration of natrolite

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Surface-water mineral composition adjustments of Alpine stilbite

T. B. Weisenberger[1] and K. Bucher[2]

[1]*Department of Geosciences, University of Oulu, P.O. Box 3000, 90014 University of Oulu, Oulu, Finland; E-mail: tobias.weisenberger@oulu.fi*
[2]*Institute of Earth and Environmental Sciences, Albert-Ludwigs-University, Albertstrasse 23b, 79104 Freiburg, Germany*

Introduction

Stilbite is locally present as late mineral on fractures and fissures of granitic basement in the Central Swiss Alps. The studied stilbite samples have been collected in the Central Swiss Alps, an orogenic belt that formed during Late Cretaceous and Tertiary time. The late collision stage of the orogeny caused a complicated tectonic structure and a late Barrovian-style regional metamorphism in the Central Swiss Alps. Collision was followed by uplift and erosion beginning in the late Tertiary. It continuously exhumes deeper structural elements and brings them to the erosion surface (Engi et al., 2004). Alpine zeolites occur predominantly in the fracture porosity of the Aar and Gotthard massifs These so-called external massifs represent parautochthonous units of the European plate, forming a 115-km-long and 23–40-km-wide SW–NE trending outcrop of pre-Alpine basement. The massifs represent erosional windows and expose typical continental crust, predominantly granites and gneisses. This pre-Alpine basement has been overprinted by the Tertiary Alpine metamorphism. Alpine peak metamorphic grade in the Aar- and Gotthard Massif region increases from lower greenschist facies in the north to lower amphibolite facies in the south. During post-orogenic uplift and erosion, the Central Swiss Alps underwent extensive late brittle deformation that created a complex multistage network of fractures. The produced fracture porosity is normally occupied by an aqueous fluid that is in thermal equilibrium with the rock matrix. If the connectivity of the fracture network is high, it also will permit fluid advection. Migrating fluid may not be in chemical equilibrium with the rock matrix and may react with the rocks exposed along the fissure walls to form secondary vein or fissure minerals (Bucher et al., 2012). In particular, characteristic sequences of fissure minerals precipitate from fluids with decreasing temperature. Zeolites and apophyllite are the youngest silicate mineral formed in Alpine fissures of the massifs.

We collected and analyzed zeolite and water samples from surface and subsurface localities in the Central Swiss Alps. Subsurface samples derive from two major Alpine tunnels: The Gotthard road tunnel, which was built in the 1970’s and the Gotthard rail base tunnel (NEAT), which is currently under construction. We report on compositional changes of fissure stilbite in response to changes in fluid composition caused by cooling and exhumation. Reported fluid and solids phases are in equilibrium before and after the cation exchange process on Alpine stilbite.

Results and Discussion

Subsurface and surface stilbite show specific chemical variation with respect to framework and extraframework cations. Specific chemical characteristics of surface and subsurface stilbite are inherited during primary mineralization. During exhumation and cooling subsurface stilbite reacted with surface- or near-surface waters and created distinguishable chemical pattern in surface stilbite minerals (Bucher and Weisenberger, 2013).

All tunnel stilbite samples show a compositional variation that can be described by the exchange reaction:

$$Ca_4Al_8Si_{28}O_{72}.{\cdot}28H_2O \text{ (stellerite)} + NaAlO_2.{\cdot}4H_2O \Rightarrow NaCa_4Al_9Si_{27}O_{72}.{\cdot}32H_2O \text{ (stilbite)} + SiO_2 \qquad (1)$$

The $Si^{4+} \Rightarrow Al^{3+}$ substitution increases the extraframework occupancy with [ ] => Na^+. Fridriksson et al. (2001) related this substitution with increased Na occupancy in the stilbite–stellerite solid solution to decreasing temperature during zeolite formation. In the tunnel samples, Na increases from the core to the rim in a single stilbite crystal suggesting that the zeolites formed in a cooling environment in accord with the geological context.

Stilbite collected at surface outcrops contains significant amounts of potassium. This is a fundamental difference to the tunnel samples. All other compositional variations in surface stilbite are similar to those of the tunnel samples. However, because of the presence of potassium in surface stilbites calcium and sodium is lower than in the tunnel samples, suggesting the extraframework cation exchange reaction Ca^{2+} => $2K^{+}$.

From the place, temperature, and depth where the stilbite originally formed, it is a long-lasting and protracted process to reach the erosion surface. Uplift, erosion, cooling, and denudation are the processes that finally make the fissure minerals to appear at the earth surface where they can be collected at an outcrop and studied by the baffled geologist. The chemical composition of the sample material is typically assumed to reflect the circumstances and conditions of rock- and mineral-forming processes.

It has taken a minimum of 2 million years for the stilbite crystals to reach the erosion surface and ‘‘see’’ the sunlight for a geologically very short moment of their total existence (Weisenberger et al., 2012). As the rocks slowly move upward during the late stages of Alpine orogeny (about 1 mm/a average) at some stage, the rocks get under the influence of near-surface groundwater. Precipitation reacts with exposed rocks and modifies its composition as described above. The typical high-Alpine surface waters with an unusually low Na/K ratio finally infiltrate the fractured near-surface rocks. The Ca–K exchange reaction inevitably modifies the composition of the million years old stilbites and makes them distinctly K-enriched. The K-enrichment is, however, not a primary feature of the stilbites and relates to late near-surface processes involving surface waters.

Our study demonstrates cation exchange in a natural system based on data for primary zeolite and fluids in equilibrium during crystallization and secondary cation-exchanged zeolite, including fluid data for the fluid that caused cation exchange in the zeolite. The composition of subsurface and surface waters that are in contact with stilbite shows a potassium pattern analogous to the stilbites. We suggest that stilbite found at the present day erosion surface originally precipitated as a K-absent phase at depth. Exhumation brought the stilbite-bearing rocks in contact with K-rich surface water and cation exchange reactions modified the original stilbite composition introducing a significant amount of K.

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Thermal energy storage by zeolitic tuffs

E. Yorukogullari

Anadolu University Physics Dept.26470 Eskisehir/Turkey, E-mail: eyorukog@anadolu.edu.tr

Introduction

Heat storage properties of zeolitic tuffs from the northwestern part of Turkey. It was found that these minerals were better than that of the other conventional storage materials such as water and gravels, etc. The particle sizes of zeolitic tuffs have been investigated in using them as heat storage materials. Calcium-exchang experiments were carried out to increase the energy density of the zeolitic tuffs samples (Tchernev, 2001; Yörükoğulları, et al. 1997; Edem N'Tsoukpoe et al., 2009).

Experimental Methods

Several physical and chemical properties of the materials have been determined by doing twenty – one different experiments on zeolitic tuffs and the other materials. These measurements consisted of adsorption heat (ΔH_{ad}), density (d), specific heat (c_s), pH, chemical analysis, IR, DTA etc. Measurements on the storage system have been realized in order to determine the required parameters in the case where it could be used for space heating and air -contitioning in house, locomotive,car and the other closed areas.

Results and Discussion

The adsorption and desorption of H_2O molecules –the HO in zeolites is not water, which a hydrogen-bonded liquid in zeolites are reversible processes. As large enthalpic effects are associated with these processes, zeolites may be used for the purposes of energy storage. Energy stored in such a system can be described as:

$Q=\Delta H_{ad} + Q_s + Q_l$

Where ΔH_{ad} is the integral adsorption heat. This heat, as a function of adsorbed H_2O, can be calculated using isosters and the Clausius-Clapeyron equation. Q_s is the energy stored by the solid part of the material and can be calculated by the relation:

$Q_s = m_s c_s \Delta T$

Where m_s is the mass of the material, c_s is its specific heat and ΔT is the temperature difference.

Q_l is the energy stored by the remnant H_2O after the heat is given to the material. The stored energy in the remnant water is

$Q_l = m_l c_l \Delta T$

Where m_l is the mass of remnant H_2O and c_l its specific heat.

The calculated volume heat capacity of the clinoptilolite tuff from the Bigadiç-Balıkesir region of Turkey and the other heat – energy storage materials are given in Table 1.

Table 1. Volume heat capacities of several energy storage materials at 20-80 °C temperature range(*)values are taken from Scarmazzino et al (1980)and (**)values are taken from Sadek et al(2000)and(***)Günerhan, et al (2005)

Material	Volume heat capacityx10^8, J/m^3
*Water	2.51
*Granite	1.29
*Marble	1.42
*Dry earth	0.59
*Chabazite tuff	2.68
Ca- Clinoptilolite tuff	4.34
*** Basalt Stone	2.52
**Ca- Montmorillonite(250°C)	4.68
**Na-Montmorillonite(250° C)	7.61

Our results suggest that clinoptilolite tuff samples fom the Balıkesir, Turkey region were superior to conventional thermal energy storage materials - but you don't show results for any conventional storage materials. Given the factors that are effective in the selection of storage materials, zeolitic tuffs appear to be promising. However, one drawback of heat storage systems using zeolitic tuffs may be their design and cost in comparison with conventional systems - but shouldn't zeolitic tuffs be much less expensive? We anticipate that heating and cooling systems using zeolitic tuffs may replace conventional systems in some applications if these drawbacks can be eliminated.

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Structural and spectroscopic characterization of air-calcined zeolitic tuff from Etla, Oaxaca, México

G. Zacahua-Tlacuatl[1], C. D. Hernández Zapiain[2], A. Manzo-Robledo[3], G. Berlier[4], F. Chávez-Rivas[5], V. Petranovskii[6] and S. Coluccia[4]

[1]*Laboratorio de Posgrado- ESIQIE-IPN, UPALM., C. P. 07738. México D.F., México.*
[2]*Departamento de Física, UANL, 66450 San Nicolás de Los Garza, Nuevo León, México.*
[3]*Laboratorio de Electroquímica y Corrosión, ESIQIE-IPN, UPALM., C. P. 07738. México D.F., México.*
[4]*Dipartimento di Chimica and NIS Centre of Excellence, Università di Torino, Via P. Giuria 7, 10125 Torino, Italy.*
[5]*Departamento de Física, ESFM-IPN, UPALM., C. P. 07738. México D.F., México;*
E-mail: fchavez@esfm.ipn.mx
[6]*Departamento de Nanocatálisis, Centro de Nanociencias y Nanotecnología (CNyN) – Universidad Nacional Autónoma de México. Carretera Tijuana-Ensenada, Km 107. Ensenada, B.C. México*

Introduction

Zeolitic tuff from Etla Oaxaca, Mexico has been successfully used in the remission of iron and manganese in residual waters (Simenova and Mintchev, 2001), however the main application in México of this zeolitic tuff mineral, ZTM, is by far in the building and construction industry (Bosh and Bulbulian, 1992). With the purpose of a potential application of this mineral in photocatalysis and electrocatalysis, in this work we present the characterization of ZTM samples ball milled for 3h (Zacahua-Tlacuatl et al., 2010) and air-calcined at 250, 350, 500, 700 and 900 °C using XRD (X-ray diffraction), UV-Vis-DR (diffuse reflectance spectroscopy), FMR (Ferromagnetic Resonance), and CV (cyclic voltammetry) spectroscopies. The structural and spectroscopic results on the set of the milled-calcined ZTM samples show the presence of iron oxide/hydroxides nanoparticles probably attached on the surface of the zeolitic material contained in the tuff mineral which under the process of calcinations in air atmosphere evolve in the formation of hematite-like nanoparticles with the collapse of the zeolitic structure around 700 °C. It was found that the redox processes attributed to iron species are strongly linked with heat-treatment of the samples, as demonstrated using cyclic voltammetry.

Experimental Methods

XRD patterns were recorded in a Phillips X' Pert powder diffractometer equipped with a curved graphite monocromator, using CuKα (λ = 0.154 nm) radiation. UV-vis diffuse reflectance spectra were measured using a Perkin Elmer Lambda 20 UV-Vis spectrophotometer with a diffuse reflectance attachment. Room-temperature FMR spectra were recorded using the standard electron paramagnetic resonance spectrometer Jeol Jes-Re3x working at 9.25 GHz. Powder samples, were put inside quartz rods of 4 mm in diameter and accommodated in the centre of the cavity. Modified carbon paste electrodes (MCPE) were prepared mixing graphite powder (99.9995%, Alfa Aesar), silicon oil (Aldrich) and the zeolite samples (50 % wt of ZNM and 50 % of graphite). The mixture was mechanically homogenized and inserted in 2 mm diameter cylinders (0.0314 cm^2). The surface contact on the MCPE was made with a copper wire. Electrochemical characterization was performed in a conventional three electrodes cell. Carbon rod and saturated calomel electrode (SCE) served as a counter and references electrode, respectively. CV technique was employed in acid conditions. Electrode potentials were controlled using a Potentiostat-Galvanostat (Autolab PGSTAT30).

Results and Discussion

The XRD patterns of ZTM and its calcined samples up to 700 °C shows a high degree of crystallinity. The more characteristic lines of clinoptilolite ($2\theta = 22.43°$, and 30.50°) are observed. Other intense lines can be identified as the main reflections of mordenite ($2\theta = 25.8°$) and α-quartz ($2\theta = 20.8°$) which are present in a lower concentration (patterns not shown). The structural changes due to the calcinations treatments are manifested by the decrease of the intensity lines and the appearance of a broad low baseline, facts indicative of the transformation of the structure into an amorphous phase, quite clearly seen when the crystalline structure collapse for calcinations at 900 °C. No lines related with iron oxides are present in the XRD pattern of ZTM sample neither in the set of calcined samples implying that the iron oxides are amorphous or with sizes below the detection limit of the XRD technique.

Figure 1 shows UV-Vis diffuse reflectance spectra of ZTM and all calcined zeolites. The UV-Vis spectrum of ZTM present broad absorption bands at 365, 410, 500 and a broad absorption around 750 nm (curve (a) of Fig.1). Samples calcined at 250 and 350 °C show the disappearance of the absorption around 750 nm and the increase of the absorptions below 550 nm. For samples calcined at 500, 700 and 900 °C signals at 350, 415, 550 and 650 nm significantly grow in intensity. The analysis of the second derivative allows assigning the absorptions above 350 °C to hematite-like nanoparticles.

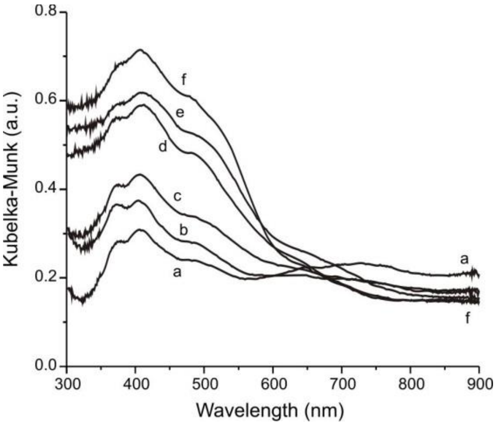

Figure 1. UV-Vis spectra of (a) uncalcined ZTM and samples calcined at 250 (b), 350 (c), 500 (d), 700 (e) and 900 °C (f)

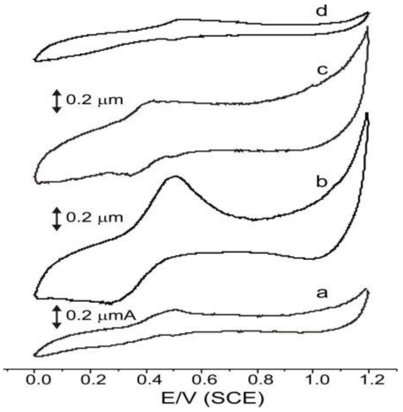

Figure 2. Cyclic voltammograms of ZTM/MCPE electrode (a) and of MCPE with materials calcined at 250 (b), 350 (c) and 500 °C (d)

FMR spectra (not shown) measured at 300 and 77 K of the untreated and calcined samples show that for samples calcined up to 350 °C the FMR signal have characteristics of ferromagnetic nanoparticles of maghemite/magnetite-like type and for samples calcined above 500 °C the FMR spectra can be assigned to antiferromagnetic nanoparticles of iron oxides of hematite type (Fischer et al., 2007).

The i-e profiles obtained by cyclic voltammetry of ZTM/MCPE (Fig. 2a), put in clear an anodic peak at ca. 0.45 V and a weak cathodic peak at ca. 0.3 V. The same redox processes can be observed at the MCPE sample calcined at 250 °C (Fig. 2b) although the current magnitude is more intense. These redox processes might be attributed to the presence of iron oxides of hematite-type on the surface of the zeolitic particles (Capek et al., 2005). However, the interaction of such species at the electrode surface decreases as heat-treatment temperature increases, putting in evidence that iron-oxidation states are highly modified with temperature.

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A preliminary study on the effect of the natural zeolite and bentonite on the tomato “Nemo Netta” growth

C. Živković and J. Kokot

Geological Survey of Serbia, Belgrade, Serbia; E-mail: jelena.kokot@gzs.gov.rs

Introduction

The increasing demand on environmental protection and the production of healthy food leads to many investigations in the production of ecologically acceptable materials for use in agriculture. In Serbia, an excessive and usually uncontrolled use of mineral fertilizers has lead to an undesirable effect on the quality of fruits and vegetables. Regeneration of soil is not only expensive but also is a long-term process. As an example, renewal of soils affected by uncontrolled use of mineral fertilizers and pesticides could take more than 20 years (Tian et al., 2000). Accordingly, minerals such as natural zeolites and bentonites, which are cheap, non-toxic and environmentally suitable materials, attract great attention in the remediation of soils, also for the agricultural use (Misaelides et al., 2004, Rehakova et al., 2004). Positive effect of the use of zeolites and clays in improving plant productivity has been attributed to their influence on physico-chemical properties of soil (creating of favorable air and water regime close to the plant root system), as well as to an increase of the ion-exchange capacity of soil, leading to a regular and rational plant nutrition (Henderson et al., 2000). The present paper deals with the agricultural use of the natural zeolite (clinoptilolite) from the Igroš deposit near Brus (Serbia) and bentonite from the Mečji Do deposit near Vlasotince (Serbia) on the tomato growth at an agricultural field near Novi Sad.

Experimental Methods

The zeolitic tuff from the Igroš deposit with a grain size of 60-100 μm and bentonite from the Mečji Do deposit with a grain size of about 80 μm were used for the preparation of two types of natural based substrates. The first substrate, marked as G1, was obtained by mixing of bentonite (30 wt. %), zeolite (30 wt. %) and peat (40 wt. %). The second one, marked as G2, contains bentonite (30 wt. %), zeolite (20 wt. %) and peat (50 wt. %).

Experiments were carried out in three variants on a small field in the village of Mošorin near Novi Sad from January to October, 2007. Substrates G1 or G2 were compared with and control samples containing peat without nonmetallic materials. The “Nemo Netta” tomato type was chosen for the growth monitoring.

Results and Discussion

Until now, the zeolitic tuff from the Igroš deposit mainly has been investigated as an adsorbent (Hrenović et al., 2009). The tuff contains approximately 75% clinoptilolite and in small quantities calcite, analcime, plagioclase, feldspars, mica (biotite and/or celadonite) and quartz (approximately 5% of each) (Rehakova et al., 2004). A qualitative X-ray powder diffraction analysis of bentonite indicates that it consists approximately 90% of montmorillonite with a small amount of quartz and calcite.

In this experiment we have found that the simple use of a mixture of two minerals - zeolite and bentonite - (substrates G1 and G2) positively effects the vegetable growth and yield. The mixture is easily applied at the beginning of the vegetation period and it seems that shows positive effect throughout the whole period (Živković & Kokot, 2008-2013).

Table 1. The effect of substrates on the vegetative growth and yield of the tomato "Nemo Netta"

Monitored feature	G1	G2	Control
Number of productive branches (floors)	12-15	12-15	10-13
Number of products on productive branches	5-8	5-8	5-7
Produce weight, kg	0.16-0.22	0.16-0.22	0.16-0.20
Yield per productive branch, kg	0.9-1	0.9-1	0.7-0.8
Yield per plant, kg	12.4	12.8	8.3
Plant height, m	5.2	5.3	4.8

Preliminary results indicate that addition of the clinoptilolite-rich zeolitic tuff and bentonite in substrates has a positive effect on the tomato growth and yield. That means that these natural and non-toxic minerals could improve the physical properties of soils. These minerals are investigated in the Republic of Serbia and with some other nonmetallic minerals (carbonates, dolomites, phosphates, diatomites, sepiolites, etc.) could have important role in future agricultural (organic) production (Vakanjac, 1988).

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