

Cation exchange tests of natural zeolites with rare earth elements

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ABSTRACT

The present work aims to analyze the effectiveness of natural zeolites for the concentration of certain elements in the rare earth group, as well as some associated cations. The work has been centered on four samples of natural zeolites from Cuba that are characterized by physical, chemical and mineralogical methods, which confirm their membership to the mordenite zeolite family, except one that was discarded in the exchange tests because it belonged to the heulandite family. The elements exchange tests were carried out over a period of 168 hours with the cations: Y^{3+} , Eu^{3+} , Yb^{3+} , Ba^{2+} , Pb^{2+} , Cu^{2+} y Ni^{2+} . Initial concentrations were set based on the average cation exchange capacity of the zeolite samples. It was concluded that this family of zeolites did not have the utility sought, because its composition contained some of the selected elements, resulting in a leaching of these cations.

1. INTRODUCTION

Natural zeolites are a family of crystalline hydrated aluminosilicates. Their tectosilicate structure forms an open configuration allowing the existence of channels that can be occupied by relatively large ions and water molecules. These ions can be exchanged for others of similar size and charge (Meier & Olson, 1978). The basic structural unit of the zeolite is the tetrahedron in which four oxygen atoms surround a central atom, generally Si $[SiO_4]^{4-}$ and / or Al $[AlO_4]^{5-}$. The arrangement of this crystalline network influences the adsorption capacities of the mineral. On the other hand, the position occupied by the ions in the structure directly influences the effective diameter in relation to the compensation cation (Meier & Olson, 1978). In this work four zeolite samples from different locations in Cuba have been analysed.

Due to the great development of electronic technologies, the use of rare earths elements is increasing worldwide and new methods are constantly being sought for the mining of these elements. Rare earths are a group of chemical elements composed of 17 elements, 15 lanthanides, scandium and yttrium. However, the environmental impact of the exploitation of rare earths is not always taken into account. Unlike the name that these compounds receive as rare earths, they are relatively abundant in the Earth crust. In spite of that, some problems arise in the extraction and exploitation of these minerals. Rare earths do not occur in high concentrations and their extraction is difficult, expensive and polluting due to the disposal techniques of the minerals where they are found, such as monacita, bastnasite or plumboagardite, which contain in their composition lead, nickel and other elements that can be harmful to the environment in high concentrations (Mindat, 2017). The high demand for rare earth elements leads to the search for new tools to treat rare earths minerals and to increase their efficiency of extraction and concentration. Also, it is of high relevance to reduce the risk of contamination of the cations that accompany the rare earths in the minerals, since they are part of the high rates of waste that take place in their extraction. In addition, some of these rare earths are evaluated as critical, framed in two dimensions: the importance of clean energy and the risk of supply. The supply of five rare earth elements, dysprosium, terbium, europium, neodymium and yttrium was found short-term critical. These five elements are used in magnets for wind turbines and electric vehicles. The supply of other elements such as cerium, indium, lanthanum and tellurium was almost critical, in the short and medium term (2015-2025) for the importance of clean energy and the risk of supply (U.S. DOE, 2011).

Natural zeolites could have some relevance for this sector, due to the high cation exchange capacity of some of them as clinoptilolite. In addition, natural zeolites have been used for the retention of heavy metals in solution due to their efficiency and low price (Fenglian & Wang, 2011). The use of zeolites for the concentration of rare earths and associated environmental worrying cations benefits from their cation exchange capacity. But not only for that reason, but also for the shape and size of the channels and cavities of the zeolitic minerals, and the dimensions of rare earth cations and their associated elements that are to be retained or expelled in the channels and cavities of the zeolites (García-Martínez & Pérez-Pariente, 2002). The main objective of this paper is the evaluation of the exchange capacity of four natural zeolites coming from Cuba for the separation of some rare earths and the cations that accompany them.

2. MATERIALS

The geological context associated with the formation of these minerals may be as Iturralde-Vinent (1996a) presented in his work, related to the arches of Cretaceous and Paleocene-Eocene islands. Two fundamental lithological varieties predominate: sedimentary and volcanic rocks. The samples of zeolitized tuff that were used come from the Eastern part of Cuba, that is, the deposits known as Palmarito de Cauto (Sample ZPZ-01), in the province of Santiago de Cuba; Caymans (sample ZYC-02), Loma Blanca (sample ZEOBLANCA-03) and Purnio (sample ZEOPUR-04). These last three samples were taken in the province of Holguín.

In the sample ZPZ-01, the zeolitic mineralization is associated with highly altered crystalloblockic tuffs, which are overlaid by calcareous tuffites, tufa limestones and limestones, and inlaid by polyglycolitic conglomerates. The mineralized horizons have varying potencies between ten and fifteen centimeters (Coutin, Aleksiev & Brito, 1975).

The sample ZYC-02 is composed entirely of heulandite calcium, slightly potassium, with an abundance that reaches 85%. The minority phase is represented by mordenite, whose abundance does not surpass 15 %; as well as by quartz (chalcedony), montmorillonite (13 and 14%) and volcanic glass (Orozco, 1996; Frazao-Ndumba et al., 2007).

The ZEOBLANCA-03 sample consists of a strongly zeolitized tuff, where heulandite-mordenite contents range from 85 to 90 percent (Coutin, Aleksiev & Brito, 1975; Földessy, 1988; Costafreda, 2008). The important manifestations of zeolites studied in this deposit are linked to the Loma Blanca Formation, of Lower-Upper Cretaceous (Aptian-Campanian) age. The zeolitized tuffs form layers up to fifteen meters thick, where they alternate with different lithophytes of tuffs (vitroclastic, lithoclastic and crystalloclastic). Zeolite mineralization is part of a stratigraphic position where the chemistry tends to be more acidic, with a predominance of rhodactic tuffs (Pentelényi & Garcés, 1988).

Finally, the sample ZEOPUR-04, was extracted from the eastern flank of the feldspar deposit known by the name of Purnio, south of the Loma Blanca deposit, where a zeolitized horizon develops. The predominant zeolite variety is the mordenite, practically monomineral, accompanied by a quartz phase. All the lithological formations of this deposit are embedded within the already described Loma Blanca Formation (Pentelényi & Garcés, 1988)

3. METODOLOGY

The chemical characterization, using inductively coupled plasma-optical emission spectrometry (ICP-OES) allowed to determine the elements that compose the zeolite samples. The mineralogical characterization by X-ray diffraction (XRD) technique has been used to establish the mineral family. The morphological characterization of the samples was carried out by scanning electron microscopy (SEM). The application of the Cuban standard 626 (NC-626: 2008) allowed to determine the total cation exchange capacity (CEC) for each of the samples. The silicon has been determined by gravimetric analysis.

3.1. Chemical and mineralogical characterization of natural zeolite samples

The four natural zeolite samples were crushed using a metal mortar and later an agate mortar and subsequent sieving, obtaining representative samples of 2 mm, 1 mm, 0.125 µm and less than 0.125 µm.

To determine the chemical composition of major and trace elements of the samples, the ICP-OES equipment Varian Vista-MPX was used. The zeolite samples were prepared by acid digestion until complete dissolution (UNE 77322-2003). From the data obtained and the amount of silicon determined by gravimetric analysis (UNE-EN 196-2-2014) it was possible to calculate the Si/Al ratio for each of the samples.

The qualitative mineralogical composition was determined by XRD using the crystalline powder method (PTE-RX-004) in an Analytical XPERT PRO MPD equipment, with copper anode tube (45 kV, 40 mA), graphite monochromator and automatic slit. The qualitative interpretation of the diffractograms was carried out with the help of the software HighScore 3.0.4 (PANalytical) and the databases PDF-2 (ICDD) and COD January 2012. Samples of size less than 0.125 µm were analyzed before and after heating in an oven at 500°C for 8 hours to distinguish the families of clinoptilolite (stable at 500°C) and heulandite (unstable at 500°C) (Mumpton, 1960).

SEM photographs for the visual analysis of crystalline morphologies were performed using a scanning electronic microscope Hitachi S-570. In order to evaluate the CEC, the test described in Cuban standard 626 (NC 626: 2008) was carried out for triplicate using the volumetric method of exchange with ammonium chloride.

3.2. Calibration curves for the selected cations

For the atomic absorption analysis (AAS) in the Analytikjena-Contra AA700 equipment, a series of standards were prepared to draw the calibration curves, starting from an initial multielemental standard of 150 ppm of

the 10 chosen elements (La^{3+} , Y^{3+} , Nd^{3+} , Yb^{3+} , Eu^{3+} , Ba^{2+} , Zr^{4+} , Pb^{2+} , Cu^{2+} and Ni^{2+}). The compounds selected for the preparation of the standards are shown in Table 1. They were dissolved in 3 mL of concentrated hydrochloric acid (34-37% PlasmaPURE) and diluted to 100 mL volume, in 0.1 % potassium chloride medium to enhance the ionization of the samples. From this initial standard, those with lower concentrations were prepared. These multielemental standards were prepared to be able to observe the possible interactions that can take place once the different cations in the solution have been mixed.

Table 1 - Compounds used, brand and purity

Compound	Brand	Purity
CeO_2	AnalytiCals	98.0%
La_2O_3	RECTAPUR	99.995%
Y_2O_3	AnalytiCals	99.0%
Nd_2O_3	Merck	-
Yb_2O_3	Merck	-
Eu_2O_3	AnalytiCals	99.0%
$\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$	Panreac	99.0%
ZrO_2	Merck	-
$\text{Pb}(\text{NO}_3)_2$	Panreac	98.0%
$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	R.P. NORMAPUR	99.0%
$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$	L.A.I. Madrid	-

3.3. Test of cation exchange in zeolites

The test was performed for three zeolites (ZPC-01, ZEOBLANCA-03 and ZEOPUR-04) since the sample ZYC-02 did not give the necessary results of good CEC. Three separate exchange tests were performed for each sample, placing 1 g of zeolite in 100 mL of cations solution for 168 hours in a shaking plate, and measuring the ratio C/Co by AAS, C being the actual concentration and Co the initial concentration of each cation. Samples were taken at 24, 48, 72 and 168 hours. This test was done in triplicate, but due to the lack of enough volume for the AAS measurement, the three samples had to be combined, eliminating the possibility of analysis of variance. Both standards and samples were spiked with 10% potassium chloride to obtain a final solution 0.1% in potassium chloride, to improve the ionization of the analytes and to obtain better absorbance results.

4. RESULTS AND DISCUSSION

The results of ICP-AES showed that some of the elements selected for the exchange experiments existed in the initial composition of the samples as compensating cations, such as Y^{3+} , Ba^{2+} , Pb^{2+} , Cu^{2+} and Ni^{2+} . The results of XRD, Si/Al and C/CT ratios can be observed in Table 2.

Table 2 - Results of the characterization of natural zeolite samples.

Sample	Relation Si/Al ⁽¹⁾	DRX - Mineralogy	CEC (meq/100g)
ZPC-01	5.53	Heulandite-Mordenite	105.77
ZYC-02	5.35	Heulandite	89.61
ZEOBLANCA-03	6.01	Heulandite-Mordenite	108.69
ZEOPUR-04	5.60	Heulandite-Mordenite	108.55

(1) Clinoptilolite > 4 Mordenite \geq 5 Heulandite < 4 (Baerlocher, *et al.*, 2001)

The images obtained by SEM showed that the heulandite grew in a way that replaced the volcanic glass while the mordenite grew in porous spaces. In Figure 1 we can observe the acicular habit presented by mordenite.

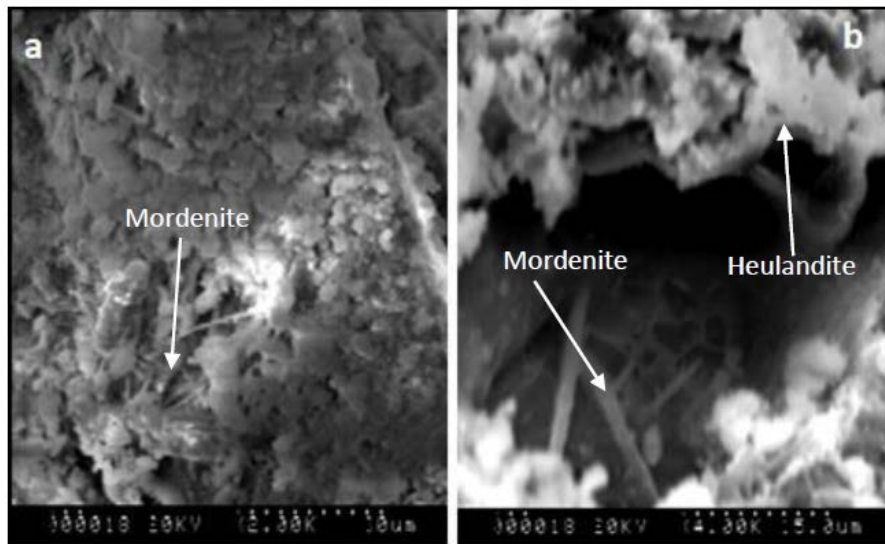


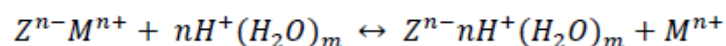
Figure 1 – Photograph by SEM of sample ZEOBLANCA-03. Acicular crystals of mordenite can be observed filling porous spaces and crystals of heulandite replacing the volcanic glass.

Before carrying out the exchange tests, during the calibration of the AAS equipment, it was observed that some of the elements chosen for the experiment did not have a good adjustment of measurements. These elements were Ce^{4+} , La^{3+} , Nd^{3+} y el Zr^{4+} , that were excluded from the exchange tests since they could not be analysed accurately.

From the results obtained in the exchange test, it was possible to obtain graphs where C/Co is related to time. The results that are observed are the concentration of the cations on the sampling at 24, 48, 72 and 168 hours (C) and the concentrations of the cation in the initial solution (Co). C/Co represents the fraction of the M^{n+} cation exchanged by the zeolite. If C/Co is less than 1.0, it indicates that the zeolite has retained this cation, if C/Co is greater than 1.0, the zeolite has leached this cation.

Sample ZPC-01

For the sample ZPC-01, it was observed in the results that there had been no substantial exchanges with the selected elements (Figure 2). For yttrium, it was seen from the graph that there had been leaching by the zeolite, since yttrium was included within its composition. For europium and ytterbium, it was observed that the zeolite did not exchange anything. For barium, there had been leaching by the zeolite, the same had happened for lead, copper and nickel giving a result of C/Co greater than 1.0 at 168 hours. Because these three cations were part of the zeolite composition, but to a lesser extent than barium, these cations were substituted as compensating cations of the negative charge of the zeolite structure by hydrated protons, since the pH of the solutions was very acidic (pH = 1-2) (Ming & Mumpton, 1993).



Sample ZEOBLANCA-03

In the sample ZEOBLANCA-03, it was observed in the results that there had been no substantial exchanges with the selected elements (Figure 2). For yttrium, barium, lead, copper and nickel, it was seen that the zeolite had leached these cations and the final concentration at 168h had increased with respect to the initial one, with the most notable values being yttrium, barium, copper and nickel, since these cations were part of the zeolitic structure.

Sample ZEOPUR-04

In the sample ZEOPUR-04, the results obtained improved slightly those of the previous samples but in general there had been no substantial exchanges with the selected elements (Figure 2). The most remarkable exchange was that of the ytterbium at short times, since the previous ones did not show that capacity. For barium, lead, copper and nickel it was seen that the zeolite had leached these cations and the final concentration at 168h had increased from the initial one.

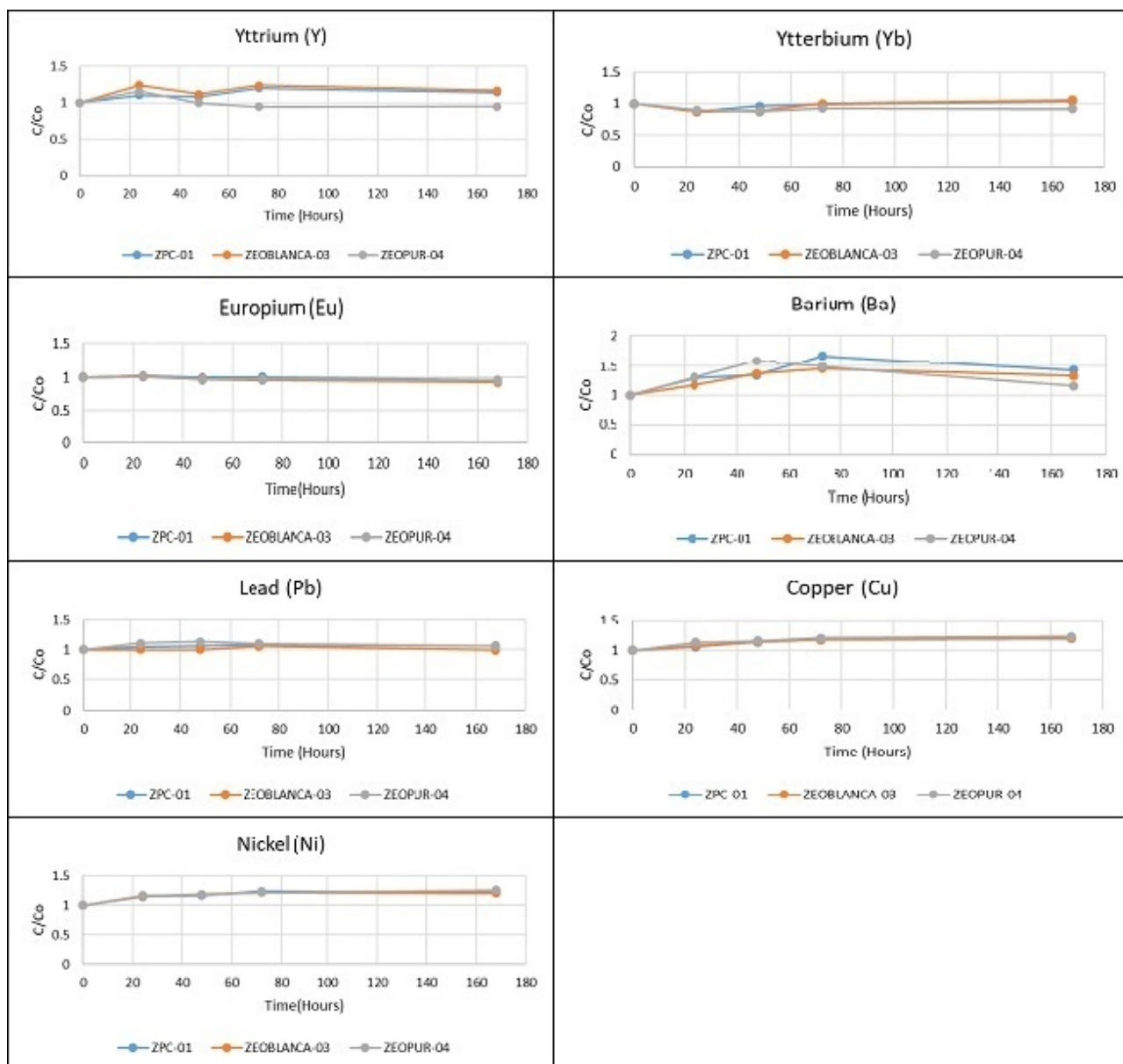


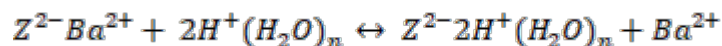
Figure 2- Results of the exchange test where C/C_0 is represented in the y-axis and time in the x-axis. Sampling at 24, 48, 72 and 168 hours.

5. CONCLUSIONS

The Si/Al ratio showed that the zeolites could belong to the mordenite variety since their values exceeded 5, and that they could also belong to the variety clinoptilolite since the Si/Al ratio exceeded 4. However, this last possibility was discarded when analyzed by XRD. From the four samples, one had to be excluded of the exchange experiments, the sample of natural zeolite ZYC-02 due to the results of XRD: the ZYC-02 sample did not keep its crystallinity once subjected to the heat treatment, since most of its mineralogical phases disappeared once calcined, leaving only quartz, calcite and muscovite, so it was concluded that it belonged to the heulandite variety. For the remaining samples, based on the results obtained by XRD, they belonged to the mordenite variety. The mordenite variety was not the most suitable for the exchange between the selected elements since its porous system did not allow a three-dimensional diffusion in its structure for these cations, besides not having large cavities. In the results of ICP-AES, it was possible to observe that there were selected elements that the samples already had in their initial composition, such as: yttrium, barium, copper, lead and nickel, barium being the one with the highest concentration.

No relevant results were found in terms of cation exchange in any of the zeolites analyzed. On the contrary, the zeolites leached Y^{3+} , Ba^{2+} , Cu^{2+} , Ni^{2+} and Pb^{2+} . In addition, it has been observed that the ionic radii have no influence on the exchange with the zeolites, due to the size of the zeolitic channels ($5.9 \times 7.1 \text{ \AA}$ and $2.7 \times 5.7 \text{ \AA}$) since they are much larger than these ionic radii. After 168 h of experiment it can be considered that

the experimental systems have reached the equilibrium. The most significant elements are Ba²⁺ and Y³⁺. Both cations were present in the zeolite as compensating cations of the negative charge of the zeolitic structure. As its concentration in the zeolite was greater or approximate than in the solution, at the end of the experiment the ratio C/Co was greater than 1.0, since they have been exchanged by hydrated protons as shown in this reaction for barium:



It has been observed that the zeolites were totally open systems to the cation exchange, being this exchange governed only by the chemical potential of the different interchangeable cations.

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