

Characterization of Water Absorption and Desorption properties of Natural Zeolites in Ecuador

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ABSTRACT

The feasibility of using natural zeolites from Policia deposit located at Chongon – Colonche mountain range in the ecuadorian coast as dessicant material is evaluated. Samples were collected and mineralogically characterized using X-ray Diffraction, Fourier Transform Infrared spectroscopy. It was found that samples consisted mainly of mordenite and clinoptilolite. A dissicant filter was built using samples reduced to three different sizes: Type I (250-150 μ m), II (150-45 μ m) y III (<45 μ m). The filter was mounted on a wind tunnel and tests to measure difussion velocity of water were performed where the type III samples outperformed the other types. Desorption tests were performed using X-ray Diffraction, Fourier Transform Infrared spectroscopy with the samples subject to heating cycles at 60°C for 24 and 48 hours. Desorption tests showed small losses in the water content with possible changes in the porosity of the samples.

Keywords: *natural zeolites, adsorption, absorption, desorption, diffusion, desiccant material.*

1. INTRODUCTION

Natural zeolites are aluminum silicate compounds with a porous structure forming channels and chambers that are occupied by water molecules and cations (Mumpton 1999). One of the most important properties of form of zeolites is its reversible water absorption capacity, which is present in zeolites structures such as Clinoptilolite, chabazite, and mordenite (Maier-Laxhuber et al. 2002). Natural zeolites are neither dangerous, nor toxic; also the are environmentally friendly, and could control air humidity with the elimination of water vapor (Shigeishi et al. 1979). Furthermore, the material could be reused after regeneration to absorb water vapor. In the regeneration process the material is subject to cycles with temperatures in the order of 50 and 260 ° C and exposure to an air stream (ASHRAE 2009). During the desorption process, hot air is generally used in the heating process which could be obtained from a solar collector, electrical resistance or from escape gases from industrial processes.

Dehumidification technology is essential in several industries, manufacturing processes, transport and conservation of a variety of products, climatization processes (Ruthven 1984). This technology plays a key role in strategies to save energy and increase productivity . In air conditioning applications (ASHRAE 2009), desiccants are used specially when: latent heat is high, energy cost to regenerate the desiccant, and when either thermal and humidity control require air flows to subfreezing points. Further, desiccants could be used to remove contaminants from air streams to improve indoor air quality. Desiccants are also used in drying compressed air and refrigerant circulating in air conditioning and refrigeration systems.

In Ecuador, several studies of natural zeolites have been conducted with the main purpose of characterize their mineralogical properties. The studies have focus their attention to deposits located at cordillera Chongon Colonche in the ecuadorian coast as well as deposits located at Loja province in the Andes mountain range. Additionally, several studies of natural zeolite applications have been performed mostly on agricultural, construction materials, and filtering applications.

In the Policia deposit, the following zeolite structures have been found: clinoptilolite and heulandite with a predominant clinoptilolite phase (Morante Carballo 2004). Both structures have shown good cationic exchange capacity. Zeolites type clinoptilolite have been used as absorbant in cooling and dehumidification tasks(Kanoğlu et al. 2004). In order to further increase our understanding of natural zeolites, this study evaluates natural zeolites extracted from Policia deposit as desiccant with possible applications in absorption and desorption processes. The results obtained will allow us to suggest future research directions in the development of zeolites as dessicant material in dehumidification processes.

2. OBJECTIVES

The main objective of this research work is to evaluate the natural zeolite of Policia deposit as dessicant materials for absorption and desorption of water vapor processes.

As part of the main objective, the following is also achieved: mineralogical characterization of the samples is performed, diffusivity velocity of water vapor as a function of zeolite particle size is determined, as well as the effects of heating temperature in desorption processes in the samples.

3. MATERIALS AND METHODS.

3.1 MATERIALS

Zeolites. Natural zeolites from Policia deposit located at Chongon-Colonche mountain range at Guayas Province in Ecuador were used. The sample rocks obtained from the deposit were crushed, milled and separated following ASTM C136-06 Standard Test Method for Sieve Analysis of Fine and Coarse Aggregates. The material obtained was classified according to its particle size in: Type I (250-150 μm), Type II (150 - 45 μm) and Type III (<45 μm).

3.2 EXPERIMENTAL METHODOLOGY

The following were the experimental tasks performed:

Mineralogical characterization of material. The structure and composition of the collected samples were determined. Specifically, the task consisted on identifying the types of zeolites, hygroscopic and zeolitic water content in other words how water molecules are attached to the zeolite structure, and identification of chemical bonds that are part of the structure of zeolitic material. For this purpose, the following material characterization techniques were used: X-ray Diffraction (XRD), Thermogravimetric Analysis (TGA), Differential Scanning Calorimetry (DSC) and Fourier Transform Infrared Spectroscopy (FT-IR)

Water vapor sorption experiments, experiments were performed to determine difussion velocity of zeolite samples classified by particle size as type I, II and III. Applying Fick's second law, the diffusion coefficient D_{AB} was determined. Before running the experiments, water content present in the zeolite samples was removed by heating the samples at 60 °C in a lab oven for 24 hours. A demountable filter was built with a thickness of 12mm which was mounted in a test bench consisting of an air duct with air velocity equal to 0.4 ± 0.03 m/s, temperature of 27 ± 0.3 °C and humidity of 68 ± 0.2 %. The samples of zeolites were placed inside the filter in a 3

mm subdivision located in the middle of the filter as indicated by Figure 1, this allowed to determine the amount of water absorbed at different spatial location with respect to time.

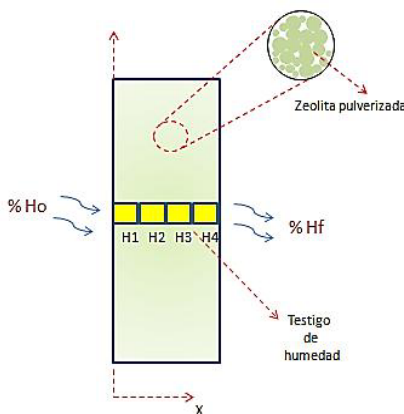


Figure 1: Schematic of Filter Construction.

From the samples in the filter, a portion is extracted to perform a thermal gravimetric analysis (TGA) in order to determine water content of each of the samples. The amount of water absorbed for each sample resulted from the difference of an initial TGA run before running the experiments and final TGA run after running the absorption experiments. Water lost by zeolite samples below 100 °C is considered hygroscopic and is considered a volumetric phenomena; water lost above 100 °C water is attached to the molecular surface of the zeolite structure and is considered zeolitic(Korkuna et al. 2006). To determine diffusion coefficient for each sample, equation 1 was used with data from sorption experiments:

$$\frac{C_A(x, t) - C_{A,B}}{C_{A,i} - C_{A,B}} = erf \left[\frac{x}{2\sqrt{D_{AB}t}} \right] \quad (1)$$

Equation 1 is a solution of Ficks differential equation assuming the case of a semi-infinite solid, in which sub index A is the water vapor and sub index B is zeolite sample.

Water vapor desorption experiments, these experiments allowed us to determine the effect of heating temperature in the desorption process of natural zeolites. In this experiment, the sample with the highest velocity of diffusion was selected. The sample was heated to 60 ° C for 24 and 48 hours simulating a regeneration cycle. After this cycle, the sample was subject to a thermogravimetric analysis to measure the water content of each zeolite sample. Next, Fourier Transform Infrared Spectrometry (FT-IR) was used to determine changes in the bonds of the zeolitic structure.

4. RESULTS

In this section, results of the mineralogical characterization, sorption and desorption experiments are provided.

4.1 MINERALOGICAL CHARACTERIZATION OF SAMPLES

The XRD analysis of the samples indicates the presence of two zeolite structure: clinoptilolite- heulandite and mordenite, alongside other minerals such as quartz and montmorillonite. In order to differentiate between zeolites clinoptilolite- heulandites which have similar crystalline structure, the samples were subject to a thermal

treatment to a temperature of 450 °C for 12 hours as suggested by (Gianneto et al. 2000) where it was determined that sample consisted mostly of clinoptilolite

Figure 2 shows TGA-DSC results where it is possible to observe continuous water loss up to 780 °C. The range between 42 and 100 °C comprises desorption of water not attached to the zeolite structure also called hygroscopic water. Portion in the curve in the range between 100 to 200 °C indicates desorption of water loosely bound to the zeolite structure. At high temperatures, in the range between 200 to 780 °C shows water content strongly bounded to the zeolite. Results show a strong agreement with Knowlton (Knowlton et al. 1981) where there is evidence of slow desorption of clinoptilolite component.

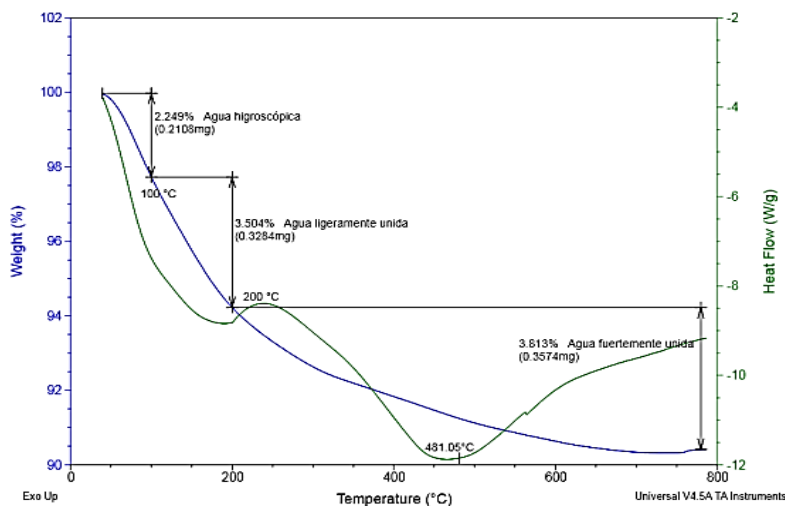


Figure 2: TGA - DSC results of type III sample.

Figure 3 shows Fourier Transform Infrared Spectroscopy in the spectral region between 400 to 4000 cm^{-1} . At a range of wavenumbers of 467 cm^{-1} to 797 cm^{-1} , it is shown several peaks in absorption caused by the deformation of bonds T-O (bonds between aluminum silicates and oxygen) which are independent of the degree of crystallization of the samples. The peak at 1090 cm^{-1} is related to asymmetric stretching vibration T-O of the zeolite structure, which is significant to estimate aluminum content in the crystalline structure as indicated by Perraki (Perraki and Orfanoudaki 2004). The peaks in the region from 1500 to 4000 cm^{-1} are attributed to the presence of zeolitic water and are key in the desorption behavior of the zeolites. A broad band appears at 3429 cm^{-1} which is a feature of hydrogen bonded OH to oxygen ions. The peak at 1641 cm^{-1} is the usual bending vibration of water.

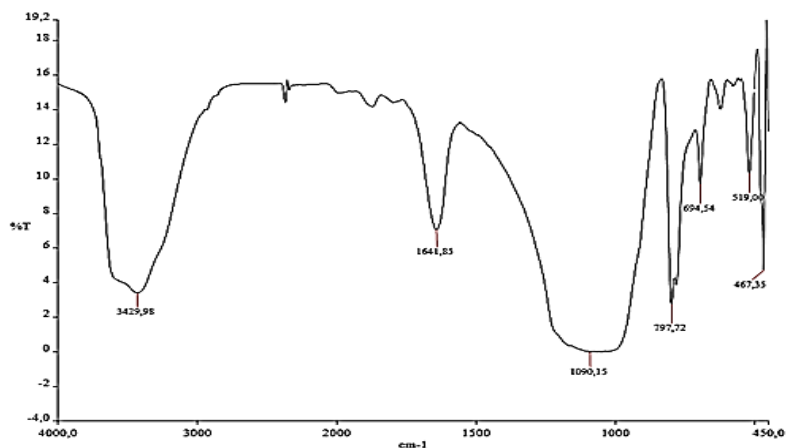


Figure 3. FT-IR results of type III sample.

4.2 SORPTION EXPERIMENTS

Results from sorption of water vapor by the zeolite samples type I, II and III with respect to time are shown in figures 5 to 7. The diffusion coefficient was calculated for each type of zeolite using the semi-infinite model under the following boundary and initial conditions: $C_{A,i} = 0\%$ and $C_{A,s} = 2.3\%$

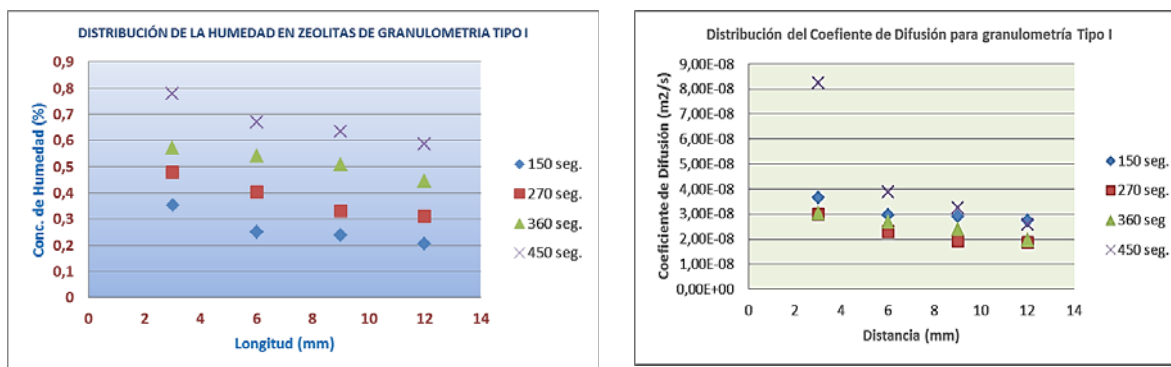


Figure 4: Results of water sorption for type I zeolite samples. a) Percentage of Humidity absorbed, b) Diffusion coefficient

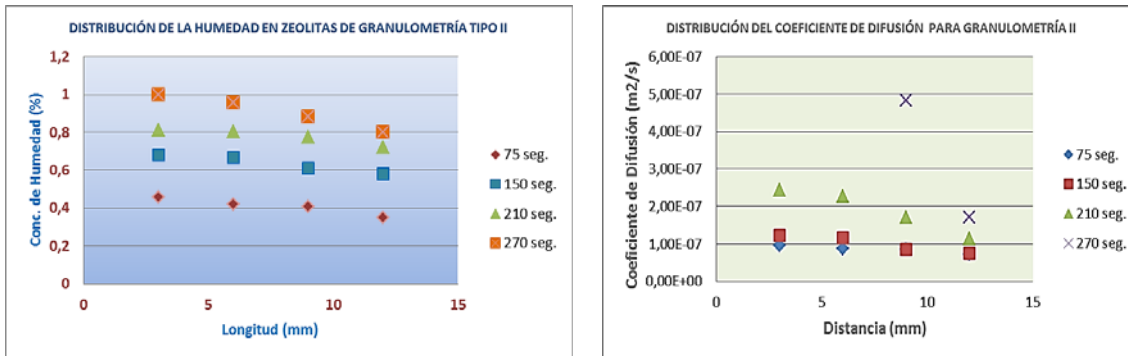


Figure 5: Results of water sorption for type II zeolite samples. a) Percentage of Humidity absorbed, b) Diffusion coefficient

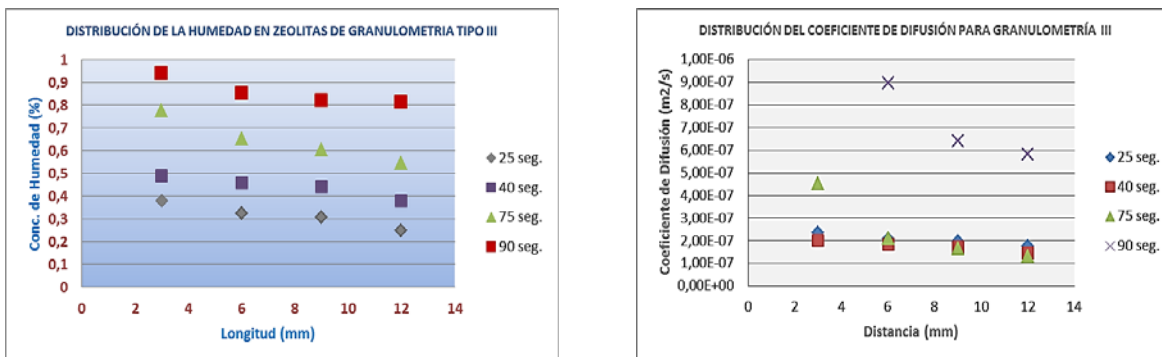


Figure 6: Results of water sorption for type III zeolite samples. a) Percentage of Humidity absorbed, b) Diffusion coefficient

As it is shown in figures, there is a variation of the sorption behavior for each particle size type sample, where Type I (250-150 μ m) showed the slowest sorption velocity. Also, there are atypical values of diffusion coefficient at times near saturation conditions, in the case of type II and type III samples diffusion coefficients in the order of 10^{-5} and 10^{-6} m²/s were found at distances between 3 to 6 mm which are not shown in the figures. At conditions other than saturation, the variation of diffusion coefficient was not significant with respect to position and time. The values obtained in these experiments coincide with configurational diffusion which occurs in microporous zeolites according to Schuring (Schuring 2002) ... Sorption behavior of zeolite samples at saturation point showed an average water content of 2.3% of dry mass of zeolites which is below the amount of water (20 to 40 %) that could be hold per unit mass of commercial desiccant.

4.3 DESORPTION EXPERIMENTS

By using several characterization techniques, it was possible to study the effects of water desorption on zeolite samples. Water content and type in the samples are related possible changes in zeolite structure caused by the heating temperature in the desorption process. Zeolite structures which contain variable quantities of cations and water molecules are highly sensitive to temperature changes. Changes in the structure include modification in the size and geometry of the unit cell of zeolite crystalline structure, and movement of extra-structural cations (Bish and Carey 2001). All of these changes could change the rate of sorption and desorption (Huang et al. 2007).

Figure 7 shows spectrograms obtained using FT-IR technique of a control sample which was subject to no treatment, the other two samples were subject to dehydration at a constant temperature of 60 °C for 24 and 48 hours. It could be seen a small displacement of the frequency 3429 cm⁻¹ related hydrogen bonded OH to oxygen ions. The displacements of frequency were of 7 and 6 cm⁻¹ for dehydration of 24 and 48 hours respectively.

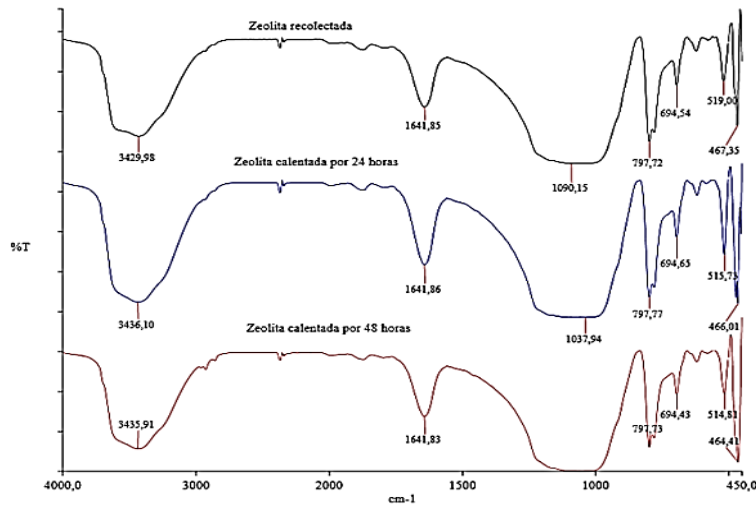


Figure 7: FT-IR results of control sample, 24 hr dehydration sample, 48 hr dehydration sample.

5. CONCLUSIONS

Mineralogical characterization of the material using X-ray diffraction and thermal treatment showed primarily a content of clinoptilolite and mordenite alongside other materials such as quartz and montmorillonite clays. Water content on the zeolite structure in each of its form (hygroscopic, loosely bound and strongly bound) was determined and quantified using thermogravimetric analysis.

Diffusion velocity and water absorption capacity was determined in the sorption experiments for the three types of samples. Results of sorption experiments showed that type III (<45µm) had the largest diffusion coefficient with the following results: Type III (20.389E-08 m²/s) > Type II (11.930E-08 m²/s) > Type I (2.827E-08 m²/s).

Sorption behavior of zeolite samples at saturation point showed an average water content of 10% of dry mass of zeolites which is below the amount of water (20 to 40 %) that could be hold per unit mass of commercial dessicants such as triethylene glycol, PSSASS, silica gel, activated alumna, activated carbon. However, the abundance of the material could make it economically viable.

In desorption experiments, using FT-IR technique a small displacement of 7 and 6 cm^{-1} for dehydration of 24 and 48 hours respectively were found in the peak of 3429 cm^{-1} which is related to hydrogen bonded OH.

It is recommended the use of more precise experimental techniques to characterize diffusion behavior near saturation conditions. It is also suggested to characterized degradation behavior of samples subject to several working cycles as well as a comparison with commercially available materials. It is also recommended to study chemical activation of natural zeolites in order to achieve the improved behavior of synthesized zeolite (molecular sieves).

6. AUTHORIZATION AND DISCLAIMER

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REFERENCES

ASHRAE, 2009. Chapter 32: Sorbents and Desiccants. *2009 ASHRAE HANDBOOK - Fundamentals*. Atlanta, Ga: ASHRAE, pp. 32.1-32.6.

BISH, D.L. and CAREY, J.W., 2001. Thermal behavior of natural zeolites. *Reviews in mineralogy and geochemistry*, **45**(1), pp. 403-452.

HUANG, H., SUMITANI, K., OIKE, T., SUZUKI, K., WATANABE, F., HASATANI, M. and KOBAYASHI, N., 2007. Effect of Microwave Irradiation on Water-vapor Desorption Capacity of Zeolite. *Proceedings of International Symposium of EcoTopia Science*, .

KANOĞLU, M., ÖZDİNÇ ÇARPINLIOĞLU, M. and YILDIRIM, M., 2004. Energy and exergy analyses of an experimental open-cycle desiccant cooling system. *Applied Thermal Engineering*, **24**(5), pp. 919-932.

KNOWLTON, G.D., WHITE, T.R. and MCKAGUE, H.L., 1981. Thermal study of types of water associated with clinoptilolite. *Clays Clay Min*, **29**, pp. 403-411.

KORKUNA, O., LEBODA, R., VRUBLEVS'KA, T., GUN'KO, V. and RYCZKOWSKI, J., 2006. Structural and physicochemical properties of natural zeolites: clinoptilolite and mordenite. *Microporous and mesoporous materials*, **87**(3), pp. 243-254.

MAIER-LAXHUBER, P., SCHMIDT, R. and GRUPP, C., 2002. *Air Ventilated Heating and Cooling Based on Zeolite Technology*, .

MORANTE CARBALLO, F.E., 2004. *Las zeolitas de la costa de Ecuador (Guayaquil): geología, caracterización y aplicaciones*, .

MUMPTON, F.A., 1999. La roca magica: uses of natural zeolites in agriculture and industry. *Proceedings of the National Academy of Sciences*, **96**(7), pp. 3463-3470.

PERRAKI, T. and ORFANOUDAKI, A., 2004. Mineralogical study of zeolites from Pentalofos area, Thrace, Greece. *Applied Clay Science*, **25**(1), pp. 9-16.

RUTHVEN, D.M., 1984. Principles of adsorption and adsorption processes.

SCHURING, D., 2002. *Diffusion in zeolites: towards a microscopic understanding*. Technische Universiteit Eindhoven.

SHIGEISHI, R.A., LANGFORD, C.H. and HOLLEBONE, B.R., 1979. Solar energy storage using chemical potential changes associated with drying of zeolites. *Solar Energy*, **23**(6), pp. 489-495.