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Zeolitic rocks used as pigment for ceiling paints. Activation of the rock

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ABSTRACT

The performance of a zeolitic rock, mainly clinoptilolite, was evaluated in ceiling paints, due to its adsorption properties. Natural and heated at 350 and at 800 °C materials were tested.
The mineralogical and petrographical composition of the zeolitic rock as well as the chemical composition and thermal behavior were studied.
Ceiling paints, with a PVC of 75% and 11.3% (by volume) of zeolitic rock were formulated. The behavior of the paints was assessed by humidity and ammonium adsorption tests and by adsorption–desorption cycles. A paint formulated without zeolitic rock was used as a blank.
Higher adsorption values were obtained when using heated zeolitic rock in the formulation. The cyclic essays performed showed that the adsorption properties of the paints were half recovered within three hours.

1. Introduction

The unique chemical and physical properties of zeolites make them useful for a wide number of industries and diverse applications (as ion exchangers, dietary supplements in animal husbandry, reforming petroleum catalysis, in puzzolanic cements and concrete, among many others [1–6]).

In spite of having experimented a tremendous diversification of uses in the last half century, the use of zeolites in paints is still poorly developed. They have been incorporated as extender pigments using thermoplastic resins and in inorganic coating on silicate basis obtaining good results [7,8] or they were used with polyuretanic resins avoiding secondary reactions that would occurred in the presence of humidity [9].

The purpose of this research is to incorporate zeolitic rocks in ceiling paints taking advantage of the ability of natural zeolites to adsorb water and gases, to control humidity and odors in closed rooms.

2. Experimental

Zeolitic rocks used in this research were mined from sedimentary deposits located in La Rioja Province (Northwestern Argentina) and they are representative of these deposits in terms of mineralogical composition and chemical and physical properties.

The zeolitic rocks have been classified as chonites (a pyroclastic rock) according to Teruggi [10] with a high content of clinoptilolite (see Table 1). The zeolitic material was added to the ceiling paints in its natural state as well as after heated at 350 °C and at 800 °C for four hours. This treatment activates the zeolite removing the water molecules adsorbed in their cavities and channels [7,11]. The temperatures were selected according to the application and the characteristics of the rock: 350° is the maximum temperature that the rock can be heated without changing the color of the paint, while at 800°, there is no longer structural modifications.

The rock was studied by X-ray powder diffraction (XRD – whole sample) and quantitative analyses were made applying the Rietveld method [12]. Chemical and thermal analyses were also carried out. Physicochemical properties such as total cation exchange capacity, pH of the aqueous extract and density were determined in order to fully characterize the material under study (see Tables 1 and 2). The texture of the zeolitic rocks before and after heated was analyzed by scanning electron microscopy (SEM) in order to observe changes occurred in the macroporosity. The structural stability was also controlled by XRD. Quantitative determinations were performed on selected samples by electron microprobe analyses (EPMA).

The X-ray diffraction patterns (Fig. 2) were obtained in a PhilipsX'pert goniometer using Ni filtered Cu Kα radiation (40 kV, 30 mA) and a proportional counter detector. The samples were mounted in an aluminium sample holder. Step scan data were collected from 0° to 30° 2Θ, with a step width of 0.02 and a counting

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Table 1
Analyses of the natural zeolitic rock

Chemical analyses of major components (% by weight)		Other analyses	
SiO_2	63.22	Clinoptilolite[a]	93.3% (±0.9)[b]
Al_2O_3	12.64	Quartz[a]	2.3% (±1.2)[b]
Na_2O	3.37	Feldspars[a]	4.4% (±0.9)[b]
K_2O	1.45	(Oligoclase and sanidine)	
CaO	2.51	Total cationic exchanged	123.62
MgO	1.03	capacity	Meq/100 g
Fe_2O_3	1.21	pH	~6.0

[a] See text.
[b] The numbers in brackets are the standard deviations produced by the Fullprof. They are obtained by the standard deviation estimated using the factors of the individual scale for each phase, no other error is included.

Table 2
Composition of the paints (% by volume)

Components	Paint A	Paint B	Paint C	Paint D
Water	56.4	56.4	56.4	56.4
Titanium dioxide	6.2	6.2	6.2	6.2
Calcium carbonate (natural)	20.4	10.0	10.0	10.0
Calcium carbonate (precipitated)	1.8	0.9	0.9	0.9
Zeolitic rock	–	11.3	–	–
Zeolitic rock heated at 350 °C	–	–	11.3	–
Zeolitic rock heated at 800 °C	–	–	–	11.3
Resin	9.6	9.6	9.6	9.6
Additives	5.6	5.6	5.6	5.6

δ natural rock = 1.95 g/ml.
δ 350 °C heated rock = 2.05 g/ml.
δ 800 °C heated rock = 2.30 g/ml.

time of 2 s/step. The divergence, receiving and scattering slits were 1°, 0.2° and 1°, and no monochromator was used. The diffractometer control, to scan the samples and the data, was made by a PC using Automatic Philips Diffraction (APD) program. The X-ray diffraction patern was analyzed with the Fullprof program in the profile matching mode [13] to determine the parameters of the unit cell of clinoptilolite using the Rietveld method and to carry out the quantitative analysis of the sample. The absolute error in weight was lower than 3 wt% compared to the results estimated by chemical and thermogravimetric tests [14].

Chemical determinations were made on the whole sample by Instrumental Neutron Activation Analyses (INAA) in Actlabs, Canada, quantificating major elements.

Thermogravimetric and derivative thermogravimetric simultaneous analyses were carried out using a Netzsch STA 409 k equipment, heating a 200 mg sample up to 1000 °C at a constant rate of 10°/min and using a thermocouple of Pt/Rh.

The total cation exchange capacity of the zeolitic natural rock was determined by a method modified from of Ming and Dixon [15]. The pH of the zeolitic rock water suspension was determined after 24 h.

The external surface area of the natural rock was determined using the Brunauer, Emmet and Teller (BET) nitrogen adsorption method. The particle size distribution was obtained with a Micromeritics SedsiGraph analyzer on finely powdered sample.

The density of the rocks was obtained using the standard ASTM G 1475, in order to formulate the paints in volume and to prepare them by weight (Table 2).

The paints were formulated with a PVC (Pigment Volume Concentration) of 75%, value recommended for ceiling paints [16].

The zeolitic rock was grounded and sieved to a size less 0.150 mm and used without any further purification. The pigment mixture was completed with titanium dioxide and calcium carbonate (natural and precipitated).

The film-forming material used in this case was a water-based acrylic resin. The composition of the paints, by volume, is shown in Table 2.

7.0 × 10.0 cm, acrylic panels were used as substrate. The panels had a weight, on average, of 23 g. The painted panels were cured in a dust-free environment held at 25 °C for 15 days prior to testing.

3. Essays on the painted panels

Humidity adsorption, ammonia adsorption and cycles of adsorption–desorption of humidity and ammonia were tested on the painted panels.

The panels were placed in a closed environment with 79.5% of humidity at 20 °C, obtained with an ammonia chloride saturated solution [17]. The panels were weighed before the test in an analytical balance, every hour during the first five hours testing and, every day, during a week.

The ammonia adsorption test was carried out in an environment saturated with the gas. The panels were weighed with an identical procedure used in the humidity adsorption test.

In order to carry out the cyclic essays, the panels were placed in a 79.5% humidity environment during 24 h and then exposed to a 37.1% humidity environment. The panels were weighed at the beginning of the essay and after 3 and 24 h, in each environment.

A similar essay was carried out with ammonia as adsorbat, using an environment saturated with the gas and an environment without the gas.

It should be pointed out that the measurements were repeated several times and, despite the repeatability observed, the reported experimental points are the average of three measurements each.

4. Results and discussion

The results of chemical analyses using the Rietveld method as well as the total cation exchange capacity and pH of the suspension are shown in Table 1. XRD quantitative analysis show that the major component of the rock is clinoptilolite, together with feldspars (oligoclase and sanidine) and small amounts of quartz. Nevertheless, very low intense diffraction peaks detected corresponding to traces of analcime and mordenite (sodium zeolites).

A typical unit cell formula for clinoptilolite given by Gottardi [18] is: $(Na_3K_3)(Al_6Si_{30}O_{72}) \cdot 24H_2O$.

According to the chemical composition of the analyzed rock, the occupation factors used as initial values correspond to the formula $(Na_{2.84}K_{1.76}Mg_{0.2}Ca_{1.24})(Al_{6.16}Si_{29.84}O_{72}) \cdot 21.36H_2O$ proposed by Koyama and Taekuchi [19] with monoclinic space groups C 2/m and unit cell parameters $a = 17.66$ Å, $b = 17.94$ Å, $c = 7.40$ Å, $ß = 116.25°$.

The theoretical Si/Al ratio for clinoptilolite ranges from 4 to 5.25. The quantitative analysis for the natural sample by EPMA shows a Si/Al ratio higher than 4 (Si/Al > 4).

In clinoptilolite, the interchangeable cations are mostly monovalent and their number is higher than the divalent ones [18]. In the studied zeolitic rock chemical analysis show predominant sodium but, it must be taken into account that part of the sodium is also contained in traces of analcime and mordenite (detected by SEM and XRD), and also in the feldspars (oligoclase and sanidine).

When the zeolitic rock is heated at 800 °C the product obtained is colored (7.5YR 8/4) [20], due to the presence of iron in the sample. The zeolitic rock heated at 350 °C has the same color as the natural one, and the paint obtained is white (tristimulus parameters obtained by the CIELab method: $L = 88.9$; $a = 1.0$; $b = 3.4$) while the paint with the rock heated at 800 °C has the tristimulus parameters $L = 86.2$; $a = 4.1$; $b = 7.5$.

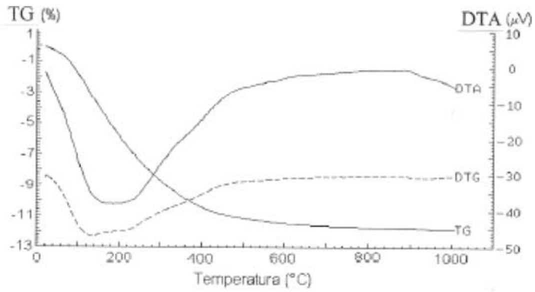

Fig. 1. DTA and TG curves for natural zeolitic rocks used in the paint formulations.

Loss on ignition (LOI) is 13.19%, and it would correspond to 94% of zeolite content if the whole loss is assigned to it. This value is very similar to the zeolitic content obtained by the Rietveld method.

Fig. 1 shows TG and DTA curves corresponding to the zeolitic rock studied. Clinoptilolite belongs to the zeolite group that does not show major structural changes during dehydration processes which exhibits continuous weight-loss curves as a function of temperature. Besides clinoptilolite, synthetic zeolites Y and X, and natural chabazite, mordenite and erionite belong to this type of zeolites which are stable up to temperatures between 700 and 800 °C [11]. As can be seen in the figure, the main structural changes occurred at temperatures below or around 300 °C while the loss of mass is constant at temperatures higher than 700 °C.

The stability of the zeolitic rock was verified through X-ray diffraction of natural and heated samples (Fig. 2). After igniting the sample at 800 °C all the diffractions peaks of clinoptilolite decrease their intensity and a decrease in its crystallinity is also evident. The ignition also concentrates the quartz and the feldspar (sanidine and oligoclase). Enhancing of the reflections can be observed at 20.84 and 26.65 2Θ for quartz and at 27.13 and 27.77 2Θ for sanidine and oligoclase, respectively, showing there have been no transformations of the feldspars (Fig. 2).

SEM analysis were carried out on the natural zeolitic rock and after heated at 350° and 800 °C. In the natural zeolitic rock prismatic clinoptilolite crystals are 40 μm long and 5–30 μm wide. Fibrous crystals of possible mordenite grow on clinoptilolite, as a second generation of zeolite (Fig. 3). Fig. 4 shows the texture of the zeolitic rock heated at 350 °C and Figs. 5 and 6 to the one heated at 800 °C. As it can be seen in Fig. 4, the stability of the zeolite crystals at 350 °C is confirmed. The texture is the same as in the natural zeolitic rock. Yet, an important difference in texture as well as the development of 1–5 μm size porous and the development of

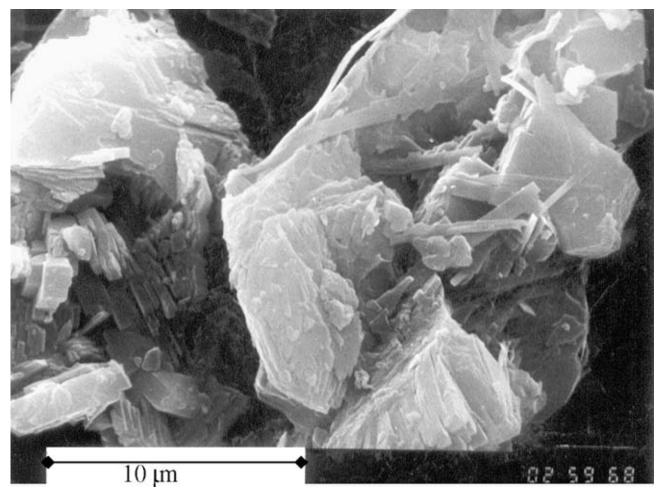

Fig. 3. 5000 ×. Scale: 10 μm. Chip of natural zeolitic rock. Prismatic crystals of clinoptilolite and shreds of possible mordenite.

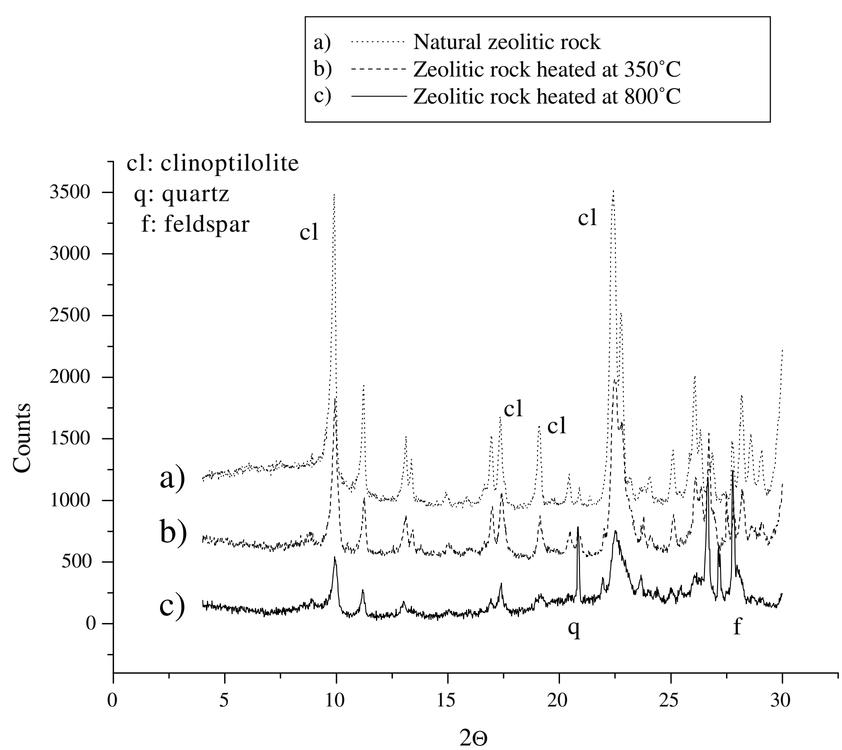

Fig. 2. X-ray diffraction of the natural and heated zeolitic rocks used in the formulation of the paints.

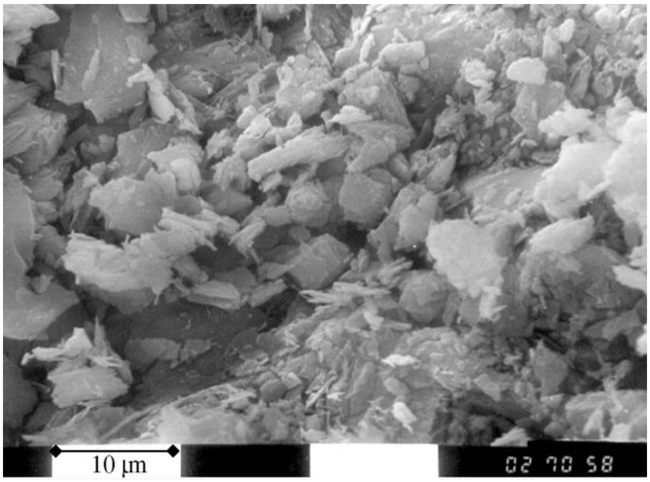

Fig. 4. 2500 × Scale: 10 µm. Chip of zeolitic rock heated at 350 °C.

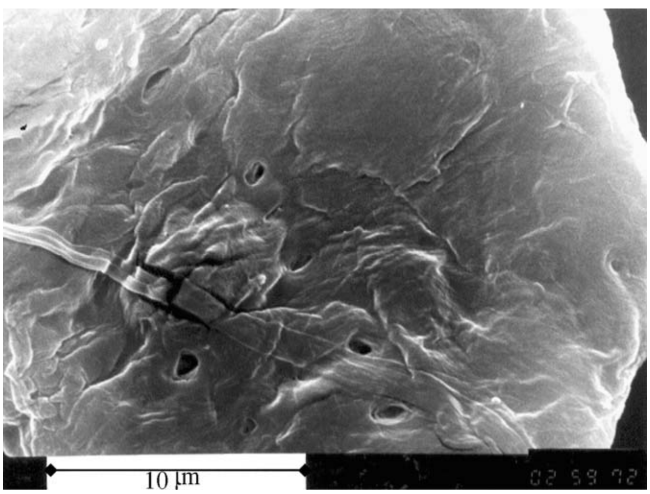

Fig. 5. 5000 × Scale: 10 µm. Suspension in water of the zeolitic rock heated at 800 °C. Destabilization of the structure is attested by porous development.

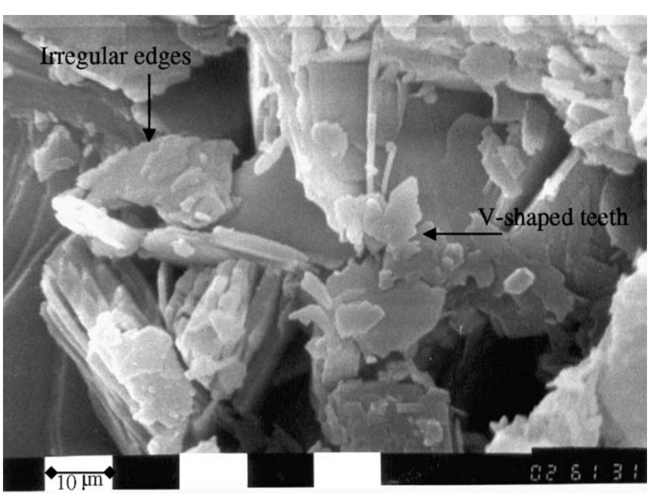

Fig. 6. 12400 × Scale: 1 µm. Chip of zeolitic rock heated at 800 °C. Development of V-shaped teeth and irregular edges on clinoptilolite crystals.

sawyer, V-shaped teeth and irregular edges on the crystals could be seen in Figs. 5 and 6, respectively.

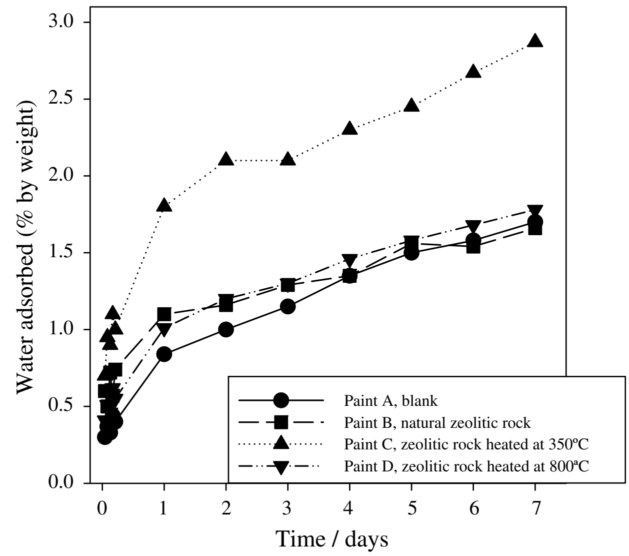

Fig. 7. Water adsorbed (% by weight on dried film) by the paints in an environment with 79.5% of humidity.

The external surface area measured using the BET method was 22 g/m^2, while the particle size distribution showed that the sample has an equivalent spherical diameter of less than 20.0 µm and that 95% has less than 1.0 µm.

Concerning the humidity adsorption test (Fig. 7) carried out in the paints, it can be observed that during the first day of essay there is no difference (% by weight on dried paint) between the adsorption of the paint prepared with heated zeolitic rock at 350 °C (paint C) and the one prepared with natural zeolitic rock (paint B). However, both adsorbed slightly more humidity than the blank (paint A). After 24 h and up to the end of the test, paint C showed a more important capacity of humidity absorption, being D (with zeolitic rock heated at 800 °C) slightly better than the blank.

As regards to the ammonia adsorption test (Fig. 8) during the first hours of essay a better adsorption capacity was observed for paint C, while paint B developed the smallest adsorption capacity taking all the paints into account. The behavior of paint B maybe

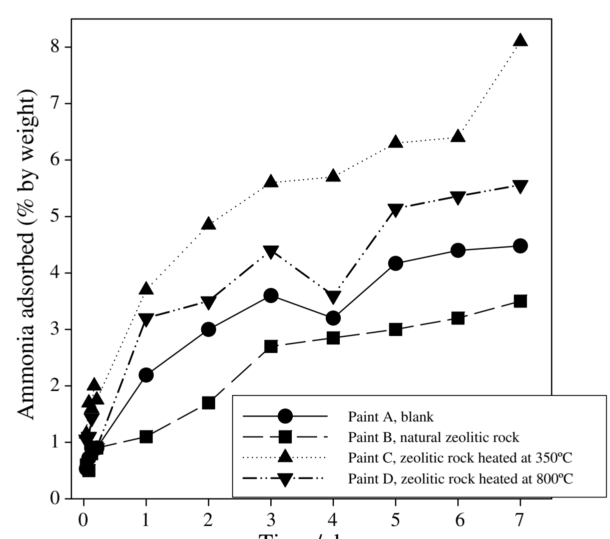

Fig. 8. Ammonia adsorbed (% by weight on dried film) by the paints in an environment saturated by the gas.

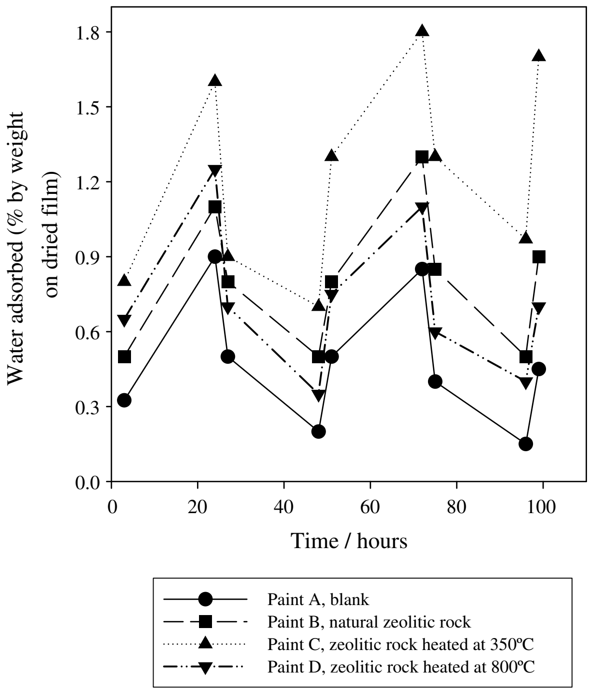

Fig. 9. Humidity adsorption–desorption cycles.

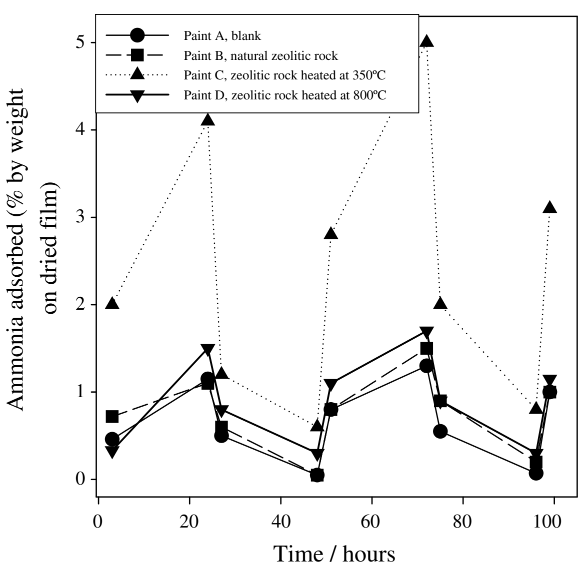

Fig. 10. Ammonia adsoprtion–desoprtion cycles.

due to the very low ammonia adsorption capacity of the natural zeolitic rock, which that was not activated.

The same tendency was kept during the whole essay and the difference in the ammonia adsorption was larger than the ones obtained for the different paints in the humidity adsorption tests.

The recuperation of the adsorption capacity (Figs. 9 and 10) was near 50% after 3 h of the desorption essay. After 24 h, the recuperation was almost complete in all the cases.

The paints prepared with heated zeolitic rock show better adsorption efficiency in all the essays. This fact could be attributed to the activation of the zeolite. However, the zeolitic rock had better performance heated at 350 °C than at 800 °C due to the collapse of the structure in the last case (see Figs. 5 and 6). Moreover, as the rock has a pink color, the paint formulated with it would not be as suitable for ceiling paint as the white paint obtained with the rock heated at 350 °C.

5. Conclusions

- o The addition of zeolitic rock, mainly clinoptilolite, to the formulation of ceiling paints increases their humidity and ammonia adsorption. The paints recover the adsorption capacity within few hours.
- o In order to obtain good performance, it is not necessary to heat the rock to a temperature higher than 350 °C.
- o At 800 °C a structural loss of stabilization is observed with the development of irregular and V-shaped teeth on the zeolite crystals with the consequence of less adsorption capacity.

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References

[1] J. Papp, K. Heinzel, S. Adams, in: D.W. Ming, F.A. Mumpton (Eds.), Natural Zeolites'93, New York, United States, 1995, p. 415.
[2] D.W. Ming, E.R. Allen, in: C. Colella, F.A. Mumpton (Eds.), Natural Zeolites of the Third Millennium, Napoli, Italy, 2000, p. 417.
[3] J. Padin, S.U. Rege, R.T. Yang, L.S. Cheng, Chem. Eng. Sci. 55 (2000) 4525.
[4] T. Armbruster, in: A. Galarnau, F. Di Renzo, F. Faujula, J. Vedrine (Eds.), Zeolites and Mesoporous Materials at the Dawn of the 21st Century, Elsevier Science, Amsterdam, 2001, pp. 13–27.
[5] F.A. Mumpton, in: L.B. Sand, F.A. Mumpton (Eds.), Natural Zeolites: Occurrence, Properties, Oxford, England, 1978, p. 3.
[6] P. Zalba, Ciencia e Investigación, Asociación Argentina para el progreso de la Ciencia 47 (April) (1996) 40.
[7] K. Torii, in: L.B. Sand, F.A. Mumpton (Eds.), Natural Zeolites: Occurrence, Properties and Uses, Oxford, England, 1978, p. 441.
[8] R. Columbié Pineda, G. Rodríguez Fuentes, A. Victorero Rodríguez, J.J. Prieto Valdés, in: G. Rodriguez Fuentes, A.J. González (Eds.), Zeolites '91, Memorias de la 3ra Conferencia Internacional sobre Ocurrencia, Propiedades y Usos de las Zeolitas Naturales, La Habana, Cuba, 1991, p. 219.
[9] J.C. Ferrazzini, Paint Resin 56 (2) (1986) 33.
[10] M.E. Teruggi, in: Diccionario SedimentológicoVolumen I, Rocas clásticas y piroclásticas, Ediciones Científicas Argentinas Librart (ECAL), Buenos Aires, Berlin, 1982, p. 28.
[11] E.M. Flanigen, F.A. Mumpton, in: Mumpton F.A. (Eds.), Mineralogy and Geology of Natural Zeolites, Washington DC, United States, 1981, p. 165 (Chapter 8).
[12] H.M. Rietveld, J. Appl. Crystallogr. 2 (1969) 65.
[13] J. Rodriguez-Carvajal, in: Abstract of the Satellite Meeting on Powder Diffraction of the XV Congress of the IUCr, 1990, p. 127.
[14] R. Bonetto, P. Zalba, M. Conconi, M. Manassero, Revista Geológica de Chile, July (2003) 103–115.
[15] D. Ming, J. Dixon, Clays Clay Miner. 35 (6) (1987) 463.
[16] F.B. Stieg, J. Coat. Tech. 48 (612) (1976) 51.
[17] M. Hodgman (Ed.), Handbook of Chemistry and Physics (1946) 1851–1852.
[18] G. Gottardi, in: L.B. Sand, F.A. Mumpton (Eds.), Natural Zeolites: Occurrence, Properties and Uses, Oxford, England, 1978, p. 31.
[19] K. Koyama, Y. Takeuchi, Z. Kristallogr. 145 (1977) 216.
[20] Munsell Soil Color Charts, Munsell Color Company, Inc., Baltimore, Maryland, United States, 1954.