

## Effect of acid phosphate media on the stability of clinoptilolite-rich tuff

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**Abstract** The stability of the clinoptilolite-rich tuff from Oaxaca (México) treated with acid phosphate solutions at pH values from 0 to 6 at 70 °C was investigated with base on the dealumination of the zeolitic material and the effective ion exchange capacity property. The aluminum of the natural zeolite was determined by both atomic absorption spectroscopy and near infrared spectroscopy developed in this work. The effective cation exchange capacity (EfCEC) of the clinoptilolite-rich tuff was determined based on the method described by Ming et al. According to the experimental data, the pH of the phosphate solutions influences the stability of the clinoptilolite-rich tuff. The dealumination of the zeolitic material at pH 0 follows a first order kinetic model. It was also found that the EfCEC is the lowest and the material loses crystallinity at the same pH. The presence of phosphorous in the zeolitic material is observed after the treatment with the acid phosphate solutions. Therefore, the treatments of clinoptilolite-rich tuff from Oaxaca with the acid phosphate solutions modify its characteristics depending on the acidity of the aqueous media and consequently its stability varies.

**Keywords** Clinoptilolite · Acid-treatment · Phosphate · Stability

### Introduction

The elimination of heavy metals from phosphoric acid wet-process has been the principal objective of many research works to obtain a high-purity acid for use in the production of fertilizers as well as other chemical products [1, 2].

The purification process of phosphoric acid and phosphate varies depending on the industrial quality requirements, for example the elimination of colorless impurities such as iron and vanadium from phosphoric acid or phosphates for the food industry. Several processes, among them ion exchange, chemical precipitation, ultrafiltration, membrane separation, inverse osmosis, and electrodialysis [3–5], have been used to eliminate impurities from phosphoric and phosphate. However, most of them are expensive and difficult to implement. Natural materials such as zeolites have been considered as alternative adsorbents to remove heavy metals from polluted water [6]. Zeolites are microporous crystalline solids with well-defined structures, which have been used in various fields such absorption, separation, ion exchange, and catalysis. The main reason for the interest in natural zeolitic materials is the increasing demand for inexpensive ion exchange and adsorbent materials by energy production, pollution control, and metal recovery. One of the most investigated zeolites is the clinoptilolite because it is abundant around the world [7–13]. This zeolite could be used as an alternative for the removal of contaminants in phosphoric acid production or in the treatment of wastewaters generated by the phosphate industry.

There are papers about the characteristics and properties of clinoptilolite to remove pollutants from water [14–19],

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however, the removal of pollutants from acid phosphate media or wastewater generated by the phosphate industry by clinoptilolite-rich tuffs is unknown. For this reason, the aim of this paper was to evaluate the stability of the clinoptilolite after its contact with an acid phosphate media (pH values between 0 and 6) at 70 °C, considering the effect of the pH on the zeolitic structure, the kinetics of the zeolitic dealumination after the acid phosphate treatment, as well as the changes on the effective cation exchange capacity (EfCEC) of the clinoptilolite-rich tuff. The characterization of the zeolitic material after the treatment with acid phosphate solutions was also discussed in this work.

## Experimental

### Materials

The natural zeolite used in this work was: clinoptilolite from Etna, Oaxaca, México (NZO) between the parallels 97°13' to W and 17°14' to N. This zeolite was received in rock form. It was crushed and sieved (10 meshes). The average grain size had a diameter of 1.7 mm.

### Acid treatment

The phosphoric acid (PA) used in this work was 85% pure reagent grade. The components of this reagent are reported earlier [20].

An aqueous solution of pH 0 was prepared with this phosphoric acid with a ratio 1:1 ( $PA_{pH\ 0}$ ). The sodium phosphate solutions were prepared based on the phosphate production as follows: 600 mL of phosphoric acid solutions at pH 0 were put into a glass reactor with a heat cover and aliquots of 800, 980, or 1200 mL of 5 M sodium hydroxide solution was slowly added with agitation (150 rpm) and heating at 70 °C to obtain the phosphate solutions at pH 2, 4, and 6, respectively. In this work, these solutions are named as  $PS_{pH\ 2}$ ,  $PS_{pH\ 4}$ , and  $PS_{pH\ 6}$ .

A sample gram of NZO was treated with each phosphate solutions, maintaining a liquid–solid relation of 10, at a temperature of 70 °C with mechanical agitation for 24 h. Then the solid samples were washed with distilled water and dried at 60 °C during 5 h.

### Dealumination

#### *Quantification of aluminum in phosphate solution*

The phosphate solutions obtained at the end of the NZO treatment were analyzed with an atomic absorption

spectrometer for the aluminum quantification. For this purpose an aliquot was taken from the solution, then it was digested with hydrochloric acid and a few drops of nitric acid. Deionized water was added to make 50 mL of the acid solution. The aluminum was determined by atomic absorption using the same Perkin Elmer 3100<sup>®</sup> Spectrometer at a wavelength of 309.3 nm.

In order to compare the amount of aluminum leached from the zeolitic material due to the acid phosphate treatment, the initial amount of aluminum in the zeolitic rock was determined by complete acid digestion using a mixture of fluoric, chloric, and perchloric acids in a ratio of 1:1:1, in a microwave stove with close atmosphere. The aluminum was determined by atomic absorption as was mentioned elsewhere.

#### *Correlation between dealumination of the zeolite and structural bonds of its crystalline network*

A Near-IR Analyzer Antaris Nicolet spectrometer was employed to determine main functional groups of the zeolitic rock, sweeping the wavelength from 14,000 to 4,000  $cm^{-1}$ . The NZO samples after the acid treatment were put inside a 2 mL glass vial and placed in the Antaris carousel.

To distinguish those bands associated with aluminum phases from those associated with silicon,  $\gamma$ -alumina samples were heated from 90 to 500 °C, removing water and taking into account what could be the predominant phase for aluminum by overlapping those spectra with zeolite's spectra.

After the Si and Al phases were identified, sample spectra were fed to the software to follow the dealumination of the acid treated zeolite. A calibration curve of 40 points, 10 repetitions of four different pH treatments, using the first derived spectrum under the main component regression method was used [21].

#### *Dealumination kinetic of natural zeolite*

In order to carry out the kinetic studies of the dealumination of natural zeolite, 0.25, 0.50, 0.75, 1.00, 1.25, and 1.50 g of the zeolitic rock were weighed and treated with a phosphoric acid solution at pH 0, at 70 °C for 3, 9, 18, and 24 h. Later, the aluminum was quantified in the remaining solution.

### Effective cation exchange capacity

The EfCEC was determined based on the method described by Ming et al. [22]. This method consists of the following: 1 g of each zeolitic sample was weighed, including both the reference as well as the previously acid treated materials. Each sample was put in contact with 10 mL of 1 N

sodium acetate at pH 5 buffer solution (room temperature) for 18 h, and then the supernatant fractions were separated by decantation. The solid samples were put in contact twice with 20 mL of 1 N KCl at pH 7 for 18 h at room temperature, and later the supernatant fractions were separated. The solid samples were washed repeatedly with distilled water, until eliminating chlorides completely. Approximately 100 mg of the washed samples were put in contact with 5 mL of 0.2 N CsCl at room temperature. After 6 h, the supernatant fractions were separated. The solid samples were once again put in contact twice with 5 mL of 0.2 N CsCl at room temperature and a sounding was taken for 10 min, after which the remaining solutions were placed in a 100 mL volumetric flask to determine the potassium content that was removed from the ion exchange sites of the zeolite. The potassium was determined by atomic absorption at a wavelength of 766.5 nm. The EfCEC was expressed by the potassium removed in milliequivalents by gram of natural zeolite.

## Characterization

### Scanning electron microscopy

For scanning electron microscopy observations, the samples were mounted directly on the holders and covered with sputtered gold and then observed at 10 and 25 keV in a JEOL JSM-5900 LV electron microscope. The microanalyses were carried out by electron dispersive spectroscopy (EDS) using a DX-4 system coupled to a Phillips XL30 electron microscope.

The microscopic observations were made by placing the previously acid treated zeolitic samples on a carbon strip adhered to an aluminum sample holder and later covered with gold. In order to carry out the corresponding analysis, a PHILLIPS XL30<sup>®</sup> electron microscope was used. The microanalyses were carried out by EDS using a DX-4 system.

### X-ray diffraction

The X-ray diffraction patterns of each sample were obtained using a SIEMENS D500<sup>®</sup> diffractometer, coupled to a X-ray tube with a Cu anode.

## Results and discussion

### Dealumination

#### *Correlation between the loss of aluminum and the structural bonds of the zeolitic crystalline network*

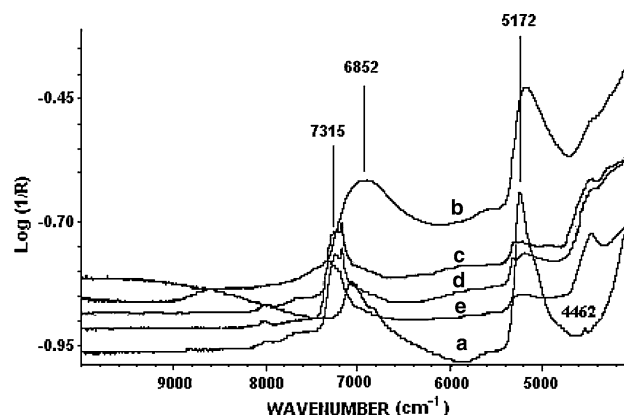
Because clinoptilolite is an aluminum and siliceous oxide combination, in order to identify the correspondence of the

aluminum bands,  $\gamma$ -alumina was used as a comparison material.

Infrared spectrums of  $\gamma$ -alumina before and after heating at 500 °C, identified the main absorption bands and can be observed in Fig. 1. The band found at 5,172  $\text{cm}^{-1}$  is associated with Al–OH because this band practically disappears after heating. A similar result was obtained with the band found at 6,852  $\text{cm}^{-1}$ , however, the bands found at 4,462 and 7,315  $\text{cm}^{-1}$ , which are associated with aluminum oxide (Al–O), were observed after the thermal treatment of the zeolitic material.

In order to make a better association between the NIR bands observed from the zeolitic material with that of the  $\gamma$ -alumina, the samples were put under thermal treatment at different temperatures. When the temperature increases, the before mentioned bands diminish and the bands corresponding to aluminum oxide increase. In the same Fig. 1, the natural zeolite spectrum is observed and it is similar to  $\gamma$ -alumina with the exception of a small band found at 4,462  $\text{cm}^{-1}$ , which is attributed to the Al–O–Si interactions because of the composition of the zeolitic material. We will discuss this association later, because if dealumination of the zeolitic rock occurs due to acid treatments, then one can expect that this band will undergo modifications and as a consequence the aluminum will be present in the acid solution.

Similar results were found for the natural zeolite thermally treated at 500 °C (Fig. 2), with that mentioned before for  $\gamma$ -alumina, where a band is observed at 7,315  $\text{cm}^{-1}$  which is similar to the band observed in the thermally treated  $\gamma$ -alumina samples (Fig. 1). Another peculiarity is that the bands at 5,230 and 7,061  $\text{cm}^{-1}$  of the thermally treated natural zeolite diminish considerably in their area in comparison with the same bands of the non thermally treated zeolitic material. This indicates that these bands can be associated with Si–O–H groups present in the natural zeolite.



**Fig. 1** NIR spectra of NZO (a),  $\gamma$ -alumina (b) and  $\gamma$ -alumina thermally treated at 90 °C (c), 200 °C (d), and 500 °C (e)

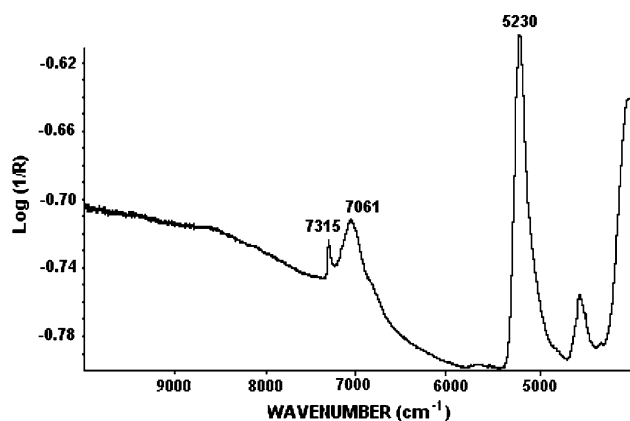


Fig. 2 NIR spectra of NZO thermally treated at 500 °C

The NIR analyses of the ZNO samples treated with phosphate solutions at pH values from 0 to 6 confirm that when the pH value of the phosphate solution diminishes, the band at  $4,462\text{ cm}^{-1}$  diminishes as well (Fig. 3). As was mentioned above, this band belongs to the functional group Al–O–Si, which indicates that the NZO undergoes a dealumination process, with the most significant at a pH value of 0.

Table 1 shows the functional groups associated with the different vibrations based on the analysis of the NIR spectrum of  $\gamma$ -alumina and NZO before and after the acid treatment.

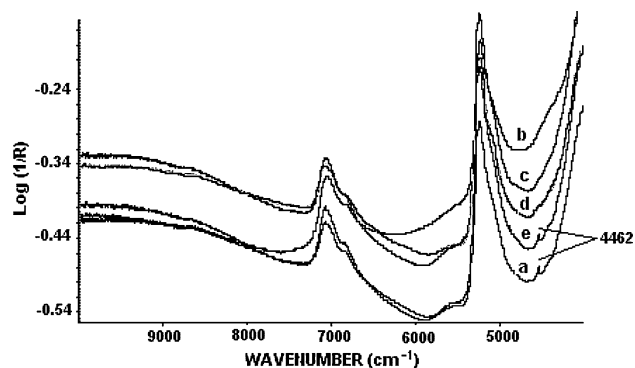


Fig. 3 NIR spectra of NZO (a),  $\text{NZO}_{\text{pH } 0}$  (b),  $\text{NZO}_{\text{pH } 2}$  (c),  $\text{NZO}_{\text{pH } 4}$  (d), and  $\text{NZO}_{\text{pH } 6}$  (e)

Table 1 Functional groups of the NZO identified by NIR

Wavenumber ( $\text{cm}^{-1}$ )	Functional group
4,462	Al–O–Si
5,070	Al–O–H
5,230	Si–O–H
	Si–O–Si
6,820	Al–O–H
7,061	Si–O–H
	Si–O–Si

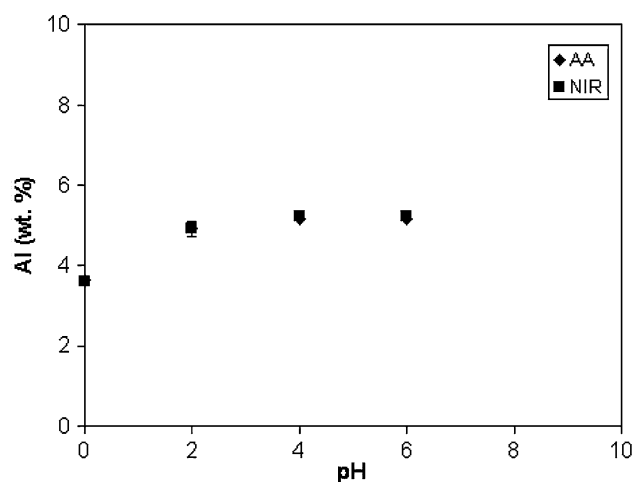


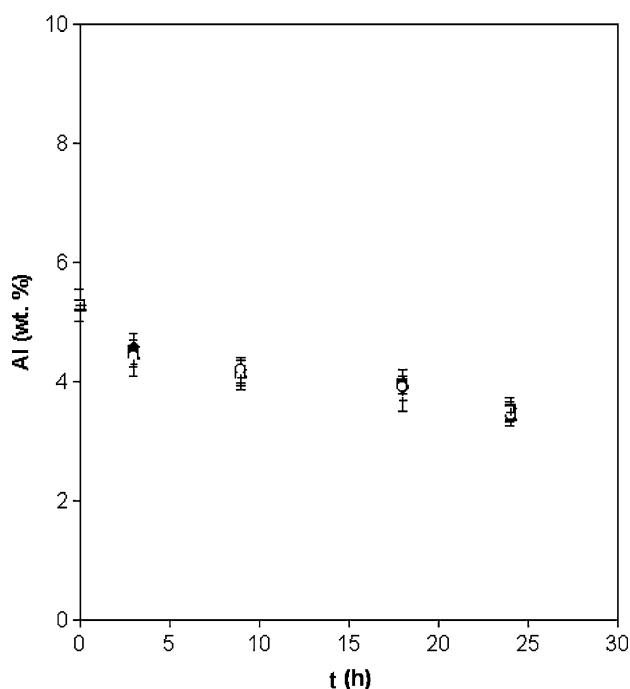
Fig. 4 Aluminum content in the NZO treated with acid phosphate solutions at pH values between 0 and 6, determined by atomic absorption (◆ AA) and near infrared spectroscopy (■ NIR)

A calibration curve for the NIR was constructed from the aluminum concentrations obtained by the atomic absorption analyses, which allowed it to analyze the percentage of aluminum present in the reference zeolitic material as well as in the zeolitic material treated with the different phosphate solutions (pH values from 0 to 6), considering the intensity of the absorption band at  $4,462\text{ cm}^{-1}$  associated with the Al–O–Si vibration. The calibration curve presents a correlation of 0.9968, with an error of 3% that corresponds to the difference between the real values with respect to the calculated values.

Figure 4 shows the comparison between the aluminum concentrations in the NZO after contact with the phosphate solutions at different pH values obtained by near infrared spectroscopy and atomic absorption spectroscopy. These results were validated with the aluminum concentration in the zeolitic material without treatment. The results show the high correlation between the both techniques, NIR and AA ( $>0.99$ ) and the importance to quantify with high confidence level the aluminum content of the zeolites with no digestion of the samples using a spectroscopy technique.

#### Dealumination kinetics of natural zeolite

The aluminum concentration in the NZO is gradually diminished when increasing the contact time with the phosphate solution at a pH value of 0 (Fig. 5), until losing a considerable amount of aluminum. In the untreated zeolitic material, it was found 5.3 wt.% before acid treatment and after the acid phosphate treatment at pH 0 it was found 3.5 wt.% at 24 h of contact time. However, when this zeolitic material is put in contact with phosphate solutions at pH values from 2 to 6, this behavior was not observed and the amount of aluminum remains unaltered in the



**Fig. 5** Dealumination of 0.25 g (◆), 0.50 g (■), 0.75 g (▲), 1.00 g (○) and 1.25 g (+) NZO after contact with acid phosphate solution at pH 0 into a period of 24 h

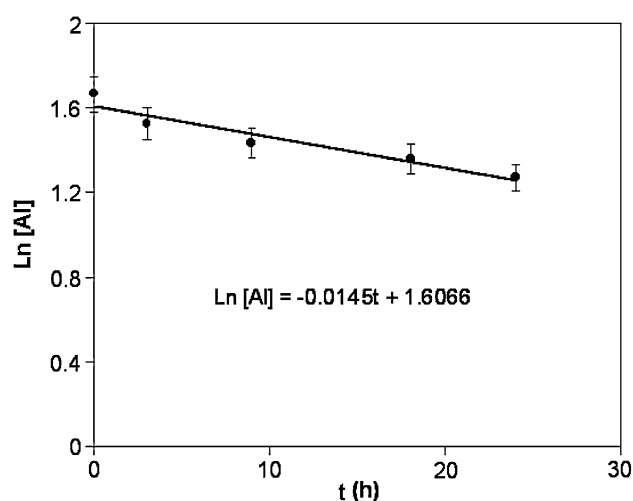
zeolitic material during the acid treatment. Li et al. [23] found that  $\text{Al}^{3+}$  leached from the clinoptilolite under acidic conditions, reaching a concentration of  $13,000 \text{ mg kg}^{-1}$  at pH 1 for 144 h. This represented around 11% of Al in the clinoptilolite structure. In the case of the present work the Al leached from the zeolitic material corresponds to 33.7% at pH 0 for 24 h. This result suggests that the dealumination of the clinoptilolite depends of the nature and precedence of the natural zeolite [20, 24–26].

It is important to mention that in most cases, the initial weight of the zeolitic samples (from 0.25 to 1.25 g) do not influence the dealumination process of the natural zeolite, maintaining a relation mass to volume of 10:1 (Fig. 5).

It was found that the dealumination kinetic behavior of the zeolitic material at pH 0 is described by the first order kinetic model [27] which follows the equation:  $\ln [\text{Al}] = -kt + \ln [\text{Al}]_0$ , where  $[\text{Al}]$  represents the amount of aluminum in the zeolitic material after the contact time  $t$  with the acid phosphate solutions.  $[\text{Al}]_0$  is the initial concentration of aluminum in the zeolitic material before the acid treatment,  $k$  represents in this work the dealumination rate constant and it was equal to  $0.0145 \text{ h}^{-1}$  with a  $r^2 = 0.9258$  (Fig. 6).

#### Effective cation exchange capacity

The EfCEC of the NZO is modified after the treatment with phosphate solution as can be observed in Table 2. The EfCEC is lost after the acid treatment of the zeolitic



**Fig. 6** First order kinetic model to describe the dealumination of NZO treated with acid phosphate solution at pH 0 as a function of time

**Table 2** Effective cation exchange capacities of NZO and NZO treated with acid phosphate solutions

Sample	EfCEC (meq/g)
NZO	1.10
NZO <sub>pH 0</sub>	0.85
NZO <sub>pH 2</sub>	1.01
NZO <sub>pH 4</sub>	1.22
NZO <sub>pH 6</sub>	1.26

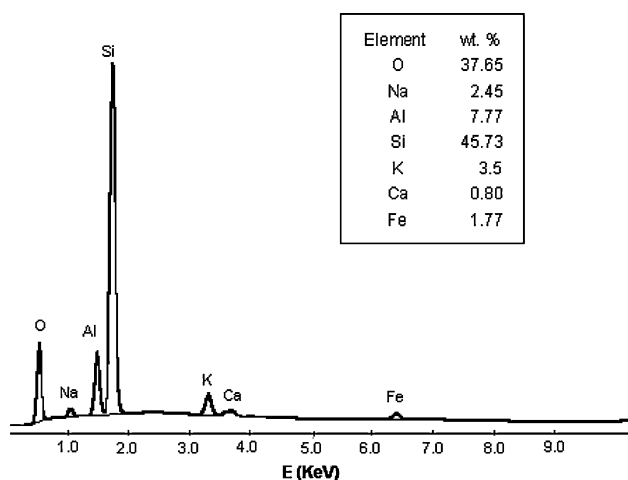
Error of  $\pm 0.05 \text{ meq/g}$

material for solutions with pH values of 0 and 2, equivalent to 22.7 and 8.2%, respectively. This behavior is attributed to the Al leached from the zeolitic structure and consequently a decationation of the zeolitic material is also observed [20, 23]. However, at pH values of 4 and 6 an increase of the EfCEC it was observed corresponding to 10.9 and 14.4%, respectively. This behavior can be explained because at pH values of 4 and 6, the NZO was treated with phosphate sodium acid solutions, favoring the exchange of the  $\text{Na}^+$  ions from the solution for the ions from the zeolitic material, increasing the content of this ion in the zeolitic material and for this reason the EfCEC is improved [28].

#### Characterization

##### Scanning electron microscopy

The energy spectrum obtained from the NZO reveals the presence of O, Si, Al, Na, K, Fe, Ca, and Mg (Fig. 7), as

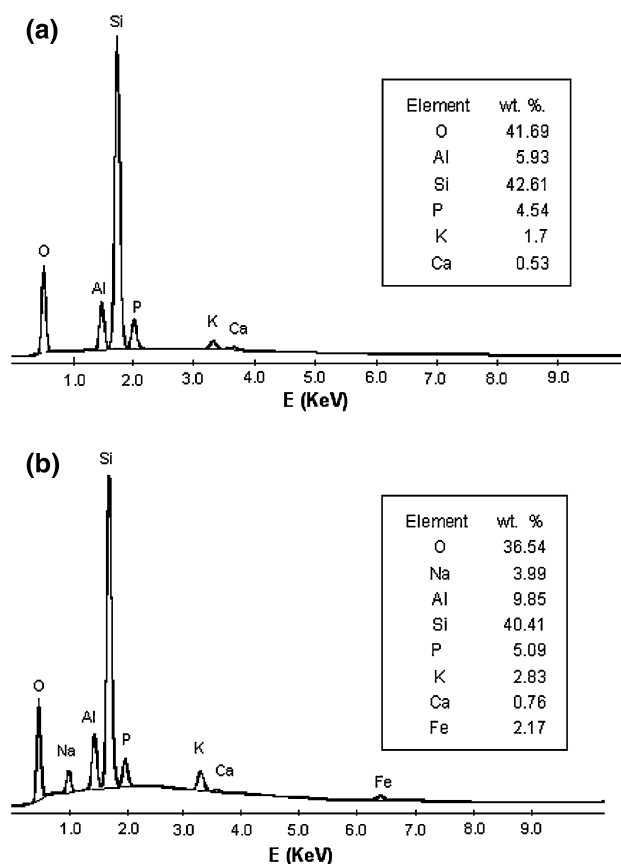


**Fig. 7** EDS analyses of NZO

expected, because the zeolitic material is constituted by crystalline aluminosilicates and other components such as quartz [7, 29]. The NZO samples that were in contact with phosphate solutions at different pH values also contain the previous elements and phosphorus in all the cases. For comparison purposes, EDS analyses obtained for the zeolitic samples after treatment with phosphate solutions at pH 0 and 6 are shown in Fig. 8. This result was not expected, because the zeolitic rock is a cationic and non-anionic exchanger ( $\text{PO}_4^{3-}$ ), however, phosphates could be adsorbed in the surface of the material with the components of zeolitic rock. It is important to mention that the natural zeolite contains aluminum as a structural component and iron as an associated mineral, therefore both could be establish interactions Al–P or Fe–P, in similar way than in other materials according with the pH of the media [30–32].

It is important to mention that sodium and iron were lost from the NZO after its contact with phosphate solution at pH value of 0 because the signals corresponding to the energies of these elements are not observed in the EDS spectrum (1.05 and 6.3 keV for sodium and iron, respectively). In this case the sodium should be considered as an extra framework ion from the zeolite network, however the iron content between 1.7 and 2.2 wt.% (Figs. 7 and 8) is associated as a mineral compound of the zeolitic rock such as ferrite,  $\text{Fe}_2\text{O}_3$  [7, 29].

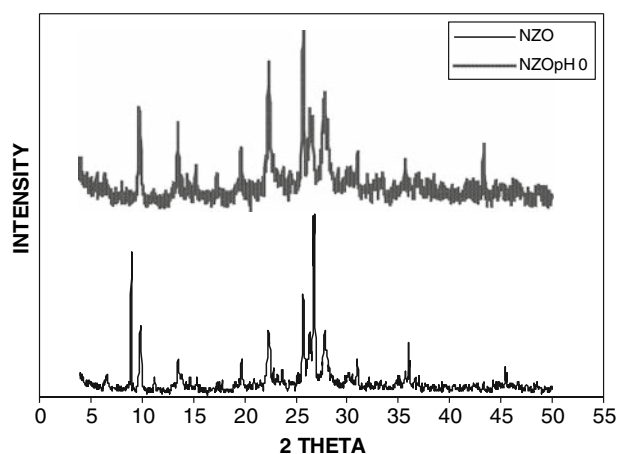
The difference between the aluminum content obtained by EDS analyses (Figs. 7 and 8) and by atomic absorption spectroscopy (Fig. 4) is due to in the first case is considering a semiquantitative technique, this means that it is possible to obtain the surface elemental composition in a very specific area of the sample because is a punctual analyses however the variability of the composition between one area to another could be higher, and in the second case, it is a quantitative technique because in that case is considered the bulk of the sample.



**Fig. 8** EDS analyses of  $\text{NZO}_{\text{pH } 0}$  (a) and  $\text{NZO}_{\text{pH } 6}$  (b)

### X-ray diffraction

Figure 9 shows that the major component of the zeolitic rock from Oaxaca (NZO) is clinoptilolite (JCPDS 25-1349 card) and quartz (JCPDS 33-1161 card) in a minor quantity is found.



**Fig. 9** X-ray diffraction patterns of NZO (—) and  $\text{NZO}_{\text{pH } 0}$  (.....)

The X-ray diffraction patterns of the NZO treated with phosphate solutions at pH values between 2 and 6 are similar to that obtained for the untreated NZO, however, for a pH value of 0 there are differences in relation to the crystallinity of the sample, because there is a change in the basal line of the X-ray diffraction pattern that was not observed in the other cases (Fig. 9). Indeed, when the crystallinity of zeolitic samples was determined before and after treatment with phosphate solution at the different pH values it was found that the NZO put in contact with a phosphate solution at pH value of 0, approximately 9% of its crystallinity it was lost in comparison with the zeolitic sample without treatment. However, the NZO treated with phosphate solutions whose pH values were 2, 4, and 6, no changes in the crystallinity of the zeolitic material were observed.

## Conclusions

The treatment of clinoptilolite-rich tuff from Oaxaca with the phosphate solutions modifies their characteristics depending on the acidity of the aqueous media. At pH 0, the dealumination of the clinoptilolite takes place, it loses crystallinity and its EfCEC diminishes. When the pH is increased to 4 or 6, changes in the crystallinity are not observed and the amount of aluminum is similar to clinoptilolite-rich tuff without treatment, but the EfCEC is slightly increased. The dealumination behavior of the zeolitic material is described by the first order kinetic model.

The clinoptilolite-rich tuff adsorbs phosphates after the treatment of this material with acid phosphate solutions at pH values between 0 and 6.

In this work, a reliable NIR spectroscopic technique was development to quantify the aluminum in the clinoptilolite-rich tuff after the acid phosphate treatments.

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## References

- De Gyves, J., Gonzales, C., Louis, J., Bessiere, J.: Reactivity of the cadmium ion in concentrated phosphoric acid solutions. *Talanta* **36**, 727 (1989)
- Casillas, J.: Fabricación de ácido fosfórico por vía húmeda. Va. Impurezas del ácido fosfórico. Fertilizantes Españoles, S.A., Ingeniería Química, Madrid **23**, 225 (1991)
- Urriaga, A.M., Alonso, A., Ortiz, I., Daoud, J.A., El-Reefy, S.A., Pérez de Ortiz, S., Gallego, T.: Comparison of liquid membrane processes for the removal of cadmium from wet phosphoric acid. *J. Memb. Sci.* **164**, 229 (2000)
- Kislik, V., Eyal, A.: Aqueous hybrid liquid membrane process for metal separation: Part II. Selectivity of metals separation from wet-process phosphoric acid. *J. Memb. Sci.* **169**, 133 (2000)
- Li, X.H., Liu, W.: Study on the application of gore membrane in the production of high purity phosphoric acid, Proceedings of the 4th International Conference, Nanning, Guangxi, China, vol. 656 (2004)
- Vaca, M.B., López, C.R., Gehr, R., Jiménez, C.B., Jiménez, B.E., Álvarez, J.J.: Heavy metal removal with Mexican clinoptilolite: multi-component ionic exchange. *Water Res.* **35**, 373 (2001)
- Tsitsishvili, G.V., Kirov, G.N., Potahnikov, I.B.: *Natural Zeolites*. Ellis Horwood Limited, England (1992)
- Rodríguez-Fuentes y G., Rodríguez-Iznaga, I.: Nápoles, Eliminación de metales tóxicos mediante zeolitas naturales, 5<sup>a</sup>. Conferencia Internacional sobre Zeolitas Naturales (1997)
- Sultan, A., Chughtai, S., Keane, M.A.: The removal of cadmium and lead from aqueous solution by ion exchange with Na–Y zeolite. *Sep. Purif. Technol.* **13**, 57 (1998)
- Langella, A., Pansini, M., Cappelletti, P., De Gennaro, B., De Gennaro, M., Colella, C.:  $\text{NH}_4^+$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  exchange for  $\text{Na}^+$  in a sedimentary clinoptilolite, North Sardinia, Italy. *Microporous Mesoporous Mater.* **37**, 337 (2000)
- Cincotti, A., Lai, N., Orrù, R., Cao, G.: Sardinian natural clinoptilolites for heavy metals and ammonium removal: experimental and modeling. *Chem. Eng. J.* **84**, 275 (2001)
- Vasylechko, V.O., Gryshchouk, G.V., Kuz'ma Yu.B., Zakordonskiy, V.P., Vasylechko, L.O., Lebedynets, L.O., Kalytov's'ka M.B.: Adsorption of cadmium on acid-modified Transcarpathian clinoptilolite. *Microporous Mesoporous Mater.* **60**, 183 (2003)
- Castaldi, P., Santona, L., Cozza, C., Giuliano, V., Abbruzzese, C., Nastro, V., Melis, P.: Thermal and spectroscopic studies of zeolites exchanged with metal cations. *J. Mol. Struct.* **734**, 99 (2005)
- Inglezakis, V.J., Zorpas, A.A., Loizidou, M.D., Grigoropoulou, H.P.: Simultaneous removal of metals  $\text{Cu}^{2+}$ ,  $\text{Fe}^{3+}$  and  $\text{Cr}^{3+}$  with anions  $\text{SO}_4^{2-}$  and  $\text{HPO}_4^{2-}$  using clinoptilolite. *Microporous Mesoporous Mater.* **61**, 167 (2003)
- Erdem, E., Karapinar, N., Donat, R.: The removal of heavy metal cations by natural zeolites. *J. Colloid Interface Sci.* **80**, 309 (2004)
- Petrus, R., Warchol, J.K.: Heavy metal removal by clinoptilolite. An equilibrium study in multi-component systems. *Water Res.* **39**, 819 (2005)
- Athanasiadis, K., Helmrejch, B.: Influence of chemical conditioning on the ion exchange capacity and on kinetic of zinc uptake by clinoptilolite. *Water Res.* **39**, 1527 (2005)
- Cui, H., Li, L.Y., Grace, J.R.: Exploration of remediation of acid rock drainage with clinoptilolite as sorbent in a slurry bubble column for both heavy metal capture and regeneration. *Water Res.* **40**, 3359 (2006)
- Sprynskyy, M., Buszewski, B., Terzyk, A.P., Namieśnik, J.: Study of the selection mechanism of heavy metal ( $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Cd}^{2+}$ ) adsorption on clinoptilolite. *J. Colloid Interface Sci.* **304**, 21 (2006)
- Hernández-Beltrán, N.A., Olguín, M.T.: Elemental composition variability of clinoptilolite-rich tuff after the treatment with acid phosphate solution. *Hydrometallurgy* **89**, 374 (2007)
- Burns Donald, A., Ciurczak, E.W.: *Handbook of Near-Infrared Analysis*. Marcel Dekker, New York (2001)
- Ming, D.W., Allen, E.R., Galindo, C. Jr., Henninger, D.L.M.: Methods for determining cation exchange capacities and compositions of native cations for clinoptilolite, Zeolite'91, Havana, Cuba, Memoirs 3rd. International Conference on the Occurrence, Properties and Utilization of Natural Zeolites vol. 2, p. 31 (1993)
- Li, L.Y., Tazaki, K., Lai, R., Shiraki, K., Asada, R., Watanabe, H., Chen, M.: Treatment of acid rock drainage by clinoptilolite-

- adsorptivity and structural stability for different pH environments. *Appl. Clay Sci.* doi:10.1016/j.clay.2007.04.003
24. Cui, H., Li, L.Y., Grace, J.R.: Exploration of remediation of acid rock drainage with clinoptilolite as sorbent and a slurry bubble column for both heavy metal capture and regeneration. *Water Res.* **40**, 3359 (2006)
  25. Li, L.Y.: Geoenvironmental study-treatment of acid mine drainage using zeolite clinoptilolite. *Emirates J. Eng. Res.* **7**, 39 (2002)
  26. Li, L.Y., Chen, M., Grace, J.R., Tazaki, K., Shiraki, K., Asada, R., Watanabe, H.: Remediation of acid rock drainage by regenerable natural clinoptilolite. *Water Air Soil Pollut.* **180**, 11 (2007)
  27. Mathialagan, T., Viraraghavan, T.: Adsorption of cadmium from aqueous solutions by vermiculite. *Sep. Sci. Technol.* **38**, 57 (2003)
  28. Díaz-Nava, M.C., Olguín, M.T., Solache-Ríos, M., Alarcón-Herrera, M.T., Aguilar-Elguezabal, A.: Characterization and improvement of ion exchange capacities of Mexican clinoptilolite-rich tuffs, *J Inclusion Phenomena Macrocyclic Chem.* **51**, 231 (2005)
  29. Breck, D.: *Zeolite Molecular Sieves*. Wiley Interscience Publisher, USA (1973)
  30. Georgantas, D.A., Grigoropoulou, H.P.: Orthophosphate and metaphosphate ion removal from aqueous solution using alum and aluminum hydroxide. *J. Colloid Interface Sci.* **315**, 70 (2007)
  31. Yang, X., Wang, D., Sun, Z., Tang, H.: Adsorption of phosphate at the aluminum (hydr)oxides–water interface: Role of the surface acid–base properties. *Colloids Surf. A: Physicochem. Eng. Asp.* **297**, 84 (2007)
  32. Peng, J., Wang, B., Song, Y., Yuan, P., Liu, Z.: Adsorption and release of phosphorus in the surface sediment of a wastewater stabilization pond. *Ecol. Eng.* **31**, 92 (2007)