

# Natural clinoptilolite as an exchanger of $\text{Ni}^{2+}$ and $\text{NH}_4^+$ ions under hydrothermal conditions and high ammonia concentration

Inocente Rodríguez-Iznaga <sup>a,c,\*</sup>, Ariel Gómez <sup>b</sup>, Gerardo Rodríguez-Fuentes <sup>c</sup>,  
Adelaida Benítez-Aguilar <sup>d</sup>, Juan Serrano-Ballan <sup>a</sup>

<sup>a</sup> Higher Institute Mining-Metallurgical of Moa, Faculty of Metallurgy, Las Coloradas, 83329 Moa, Holguín, Cuba

<sup>b</sup> Structural Analysis Laboratory, Institute of Materials and Reagents (IMRE), University of Havana, Zapata y G sln, La Habana 10400, Cuba

<sup>c</sup> Zeolites Engineering Laboratory, Institute of Materials and Reagents (IMRE), University of Havana, Zapata y G sln, La Habana 10400, Cuba

<sup>d</sup> Center of Research of the Laterite, 84390 Moa, Holguín, Cuba

Received 13 November 2000; received in revised form 22 May 2001; accepted 14 June 2001

## Abstract

Natural clinoptilolite from Caimanes deposit (Moa-Cuba) has been used for the nickel removal from aqueous solution by ion exchange. The  $\text{Ni}^{2+}$  elution, using ammonia-rich solution, has been also studied in form of a nickel removal–elution ion-exchange cyclic process. The stability of clinoptilolite as an exchanger of  $\text{Ni}^{2+}$  and  $\text{NH}_4^+$  cations under hydrothermal conditions and high ammonia concentrations is analyzed. No loss in the clinoptilolite exchange capacity of  $\text{Ni}^{2+}$  and  $\text{NH}_4^+$  ions during the  $\text{Ni}^{2+}$  removal–elution cycles was found. The treatment of the clinoptilolite with  $\text{NH}_4\text{OH}$  concentrated solutions provokes not only the  $\text{Ni}^{2+}$  elution by ion exchange, but also a substantial increase of the  $\text{Ni}^{2+}$  ions removal capacity of the zeolite. This is explained by  $\text{OH}^-$  anions adsorption (or occlusion) on the zeolitic phase particles and the consequent nickel hydroxide precipitation. © 2002 Published by Elsevier Science Inc.

*Keywords:* Ion exchange; Natural zeolite; Clinoptilolite; Removal–elution cycle; Waste treatment

## 1. Introduction

The use of zeolitic materials as ion exchangers for environmental protection and other applica-

tions is stimulated by the good results obtained and also by the non-toxic nature of these materials [1]. In this context, the natural zeolites have particular interest due to their availability and low cost.

One of the most general applications of the natural zeolites, as ion exchanger, is in the removal and recuperation processes of heavy metals from residual liquors. These processes are commonly cyclic and take into account the recovery of the metals and the regeneration of the zeolite to be

\* Corresponding author. Address: Higher Institute Mining-Metallurgical of Moa, Faculty of Metallurgy, Las Coloradas, 83329 Moa, Holguín, Cuba.

E-mail address: inocente@f.oc.uh.cu (I. Rodríguez-Iznaga).

reused [2]. The ion-exchange processes in zeolites are affected by several factors such as: concentration and nature of cations and anions, temperature, pH, and crystal structure of the zeolite. This topic has been the subject of several studies [3–6]. Additionally, the zeolite mineral stability and its structural changes under hydrothermal treatment in various environments, play an important role in its potential applications as an ion exchanger. Consequently, the exchanger should be chemical and physically durable.

Arcoya et al. [7] found that the treatment of the natural clinoptilolite with HCl solution increases both the acidity and the effective diameter of the channels and pores of the zeolite, but it produces an important loss of zeolite phase. Bălbă et al. [8] have studied the hydrothermal action of hydrochloric acid solution and sodium hydroxide solution of different concentrations on the natural clinoptilolite-rich volcanic tuff from Mîrsid-Romania deposit. Their results showed that the treatment with hydrochloric acid solution leads to a partial dealumination of the framework with the subsequent decrease of the ion-exchange capacity of the material. However, the action of sodium hydroxide solution over the natural clinoptilolite-rich volcanic tuff results in an activation process of clinoptilolite (dissolution of an important part of amorphous silica and iron compounds) if the initial molar ratio is  $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3 < 3$  or a re-crystallization process with formation of cubic zeolite-P, if the initial molar ratio is  $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3 > 3$ .

On the other hand, the ion-exchange process may be accompanied by other processes, such as the precipitation of low-solubility phases. Factors such as the characteristics of the zeolite and the accompanying phases, mainly their alkalinity, can influence this precipitation. Many studies are available in the literature on the occurrence of hydrolysis processes and precipitation of low-solubility substances (for example metal hydroxides, carbonates, etc.) during the ion exchange both in zeolites [9–11] and other exchangers [12,13]. The extent of that precipitation depends on the solubility product of the precipitated, the alkalinity of the exchanger and also on the acidity of the salt solution.

The results of all the previous studies strongly suggest that the zeolite should be evaluated at laboratory scale before the design of their industrial application.

The use of natural clinoptilolite from different Cuban deposits for the removal of heavy metals (Ni, Co, Cu, Mn, Fe, etc.) and recovery of nickel from the ammoniacal-carbonate residual liquors of the nickel industry has been the subject of several studies [14,15]. The results showed the potential of the  $\text{NH}_4^+$ -clinoptilolite for the removal of  $\text{Ni}^{2+}$  by ion-exchange processes. In addition to the nickel removal, the recovery of nickel (elution) and the regeneration of the zeolite by treatment with ammonia-rich solutions were considered. During the regeneration an exchange process occurs between the metallic cations, mainly  $\text{Ni}^{2+}$ , retained in the zeolite and the  $\text{NH}_4^+$  ions from the ammonia-rich solution.

In order to increase the effectiveness, efficiency and industrial applicability, the nickel elution and the regeneration of the ammonium zeolite form has been considered by treatment with  $\text{NH}_4\text{OH}$  concentrated solutions [16]. In addition, the use of this ammonia-concentrated solution for  $\text{Ni}^{2+}$  elution and regeneration of the zeolite leads to consider the possibility of adsorption and accumulation of hydroxyl groups on this zeolitic rock. It is well known that, under specific conditions,  $\text{Ni}^{2+}$  and other heavy metal cations react with  $\text{OH}^-$  anions in solution to form low-solubility hydroxides [17]. The aforesaid suggests the possibility that this reaction could take place during the cyclic process of  $\text{Ni}^{2+}$  removal–elution. If this reaction takes place the complexity of the system becomes much higher since the ionic exchange is accompanied by a precipitation process.

The present work is aimed at gaining information on the ion-exchange cyclic process of removal–elution of  $\text{Ni}^{2+}$  using natural clinoptilolite from Caimanes deposit and ammoniacal solution. We have studied, at a laboratory scale, the stability of clinoptilolite as an exchanger of  $\text{Ni}^{2+}$  and  $\text{NH}_4^+$  cations during this process, under hydrothermal conditions and at high ammonia concentrations. The associated nickel precipitation during this cyclic process is also taken into account.

## 2. Experimental

### 2.1. Materials and preparation

The main phase present in the zeolitic rock (raw mineral) from Caimanes deposit, Moa-Cuba, is clinoptilolite. In addition, mordenite, quartz, feldspar and montmorillonite are present. The chemical composition of this mineral in oxide form is 63.2% SiO<sub>2</sub>, 12.32% Al<sub>2</sub>O<sub>3</sub>, 3.92% CaO, 2.62% Fe<sub>2</sub>O<sub>3</sub>, 0.39% FeO, 1.3% MgO, 1.42% K<sub>2</sub>O, 0.93% Na<sub>2</sub>O and 13.9% H<sub>2</sub>O [18].

The zeolite raw mineral was ground and sieved in order to obtain a sample with particle size class >0.25 and <0.5 mm. This sample was purified via washing with distilled water by means of a fluidized bed process [19] in order to remove the non-zeolitic mineral phases. In addition, the denser fraction was discarded. After vacuum filtration and drying, this resulted in a mixture of about 80 wt.% clinoptilolite, 5.5 wt.% quartz and 14.5 wt.% of other phases, including mordenite and montmorillonite. Herein this purified sample is referred to as natural clinoptilolite or purified zeolite (Z).

The ammonium form of clinoptilolite (NH<sub>4</sub><sup>+</sup>-Z) was obtained from the purified zeolite by treatment with 247 g/l NH<sub>4</sub>OH solutions at 25 °C in solid/liquid ratio of 1 g/20 ml. Agitation during 72 h was applied at 120 jolts per minutes using a universal agitator. The NH<sub>4</sub>OH solution was replaced six times. The solid was filtered and washed with distilled water until the pH was neutral, oven-dried at 110 °C, and stored in a dessicator to ensure a constant water content. The total content of exchanged ammonium ions in the NH<sub>4</sub><sup>+</sup>-Z sample was 1.6 ± 0.15 NH<sub>4</sub><sup>+</sup> meq per gram of zeolite (1.6 ± 0.15 meq/g). The concentration of NH<sub>4</sub><sup>+</sup> ions was determined using the Nessler reagent.

### 2.2. Removal of nickel using NH<sub>4</sub><sup>+</sup>-Z

In a suitable container were placed 5 g of NH<sub>4</sub><sup>+</sup>-Z and 100 ml of NiCl<sub>2</sub> solution (containing 2.9 g/l Ni) for 72 h, to remove Ni<sup>2+</sup> ions. The treatment was conducted at 80 °C with agitation of 120 jolts per minutes using a universal agitator. After the treatment the solutions and the solid phase were separated by filtration and the zeolitic phase was

subjected to washing with distilled water. The concentrations of nickel, silicon, aluminum and iron in the liquid phase were determined using atomic absorption spectrometry (AAS).

### 2.3. Elution of nickel using NH<sub>4</sub>OH solutions

The zeolitic phase resulting from the procedure 2.2 (referred as Ni<sup>2+</sup>-Z) was contacted with 100 mL of 247 g/l NH<sub>4</sub>OH solutions for 72 h, to elute Ni<sup>2+</sup> ions. The treatment was conducted at 25 °C with agitation of 120 jolts per minutes using a universal agitator. After the treatment the solutions and the solid phase were separated by filtration. The concentrations of nickel, silicon, aluminum and iron in the liquid phase were determined by AAS. The zeolitic phase was subjected to washing with distilled water.

### 2.4. Nickel removal–elution cycles

Sections 2.2 and 2.3 were repeated 20 times consecutively in form of nickel removal–elution cycles. Fig. 1 shows the flow chart of these cycles.

After each step, the resulting zeolite phase was subjected to washing with distilled water in order to eliminate excess of NiCl<sub>2</sub> or NH<sub>4</sub>OH solution and any possible precipitated particle formed on the zeolite.

The NH<sub>4</sub>OH solutions employed were prepared using ammonia solution 32% extra pure supplied by Merck, while the NiCl<sub>2</sub> used was analytic reagent supplied by Monterrey (NiCl<sub>2</sub> · 6H<sub>2</sub>O 99% pure).

### 2.5. Experimental techniques

Infrared (IR) spectra and X-ray diffraction (XRD) patterns of the zeolitic phase, before and after each treatment, were obtained. IR was conducted in an FTIR PU9600 Pye Unicam Spectrometer, the samples were prepared using the KBr pressed-disk technique, with 1% inclusions of the sample to be analyzed.

The XRD patterns were obtained using a Philips PW 1218 diffractometer with CoK<sub>α</sub> radiation (λ = 1.790260 Å) in the interval 7–55° using a step size of 0.02° and counting time of 15 s.

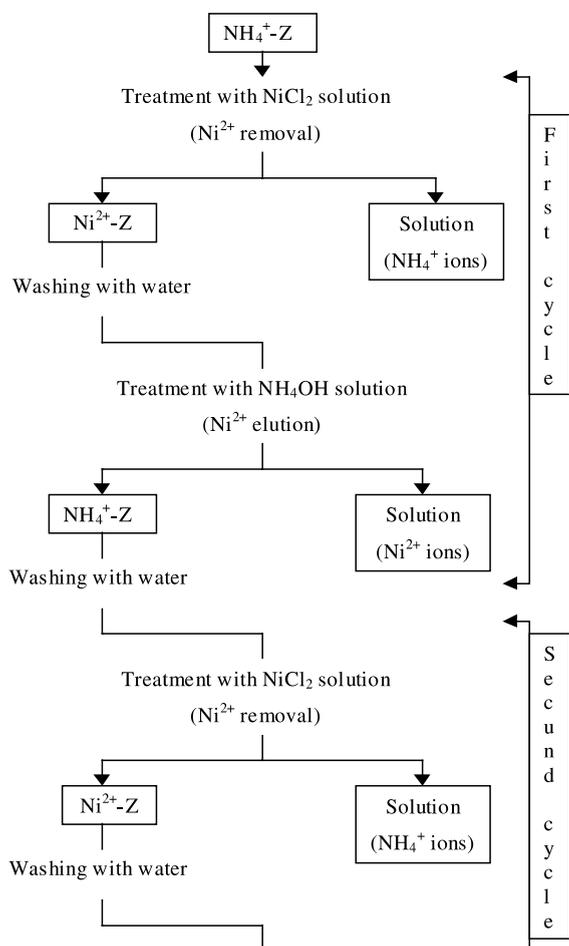


Fig. 1. Flow chart representing the cyclic sequence used for the nickel removal–elution process.

The sensitivity of the method used to determine the Ni, Si, Fe and Al concentrations in solution, by AAS, was 0.059, 0.94, 0.06 and 0.39 mg/l, respectively.

### 3. Results and discussion

#### 3.1. Nickel removal–elution cycles

Figs. 2 and 3 show the results of the elementary analysis of the solutions used in each of the 20 removal–elution cycles. For a better understanding we should keep in mind that each cycle consists of

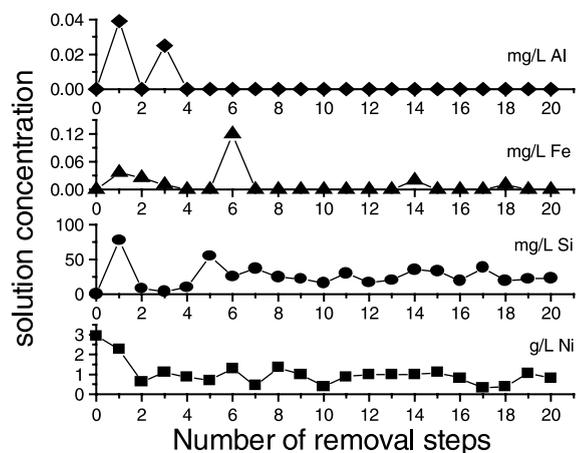


Fig. 2. Concentration of Ni, Si, Fe and Al in the solution resulting after the nickel removal.

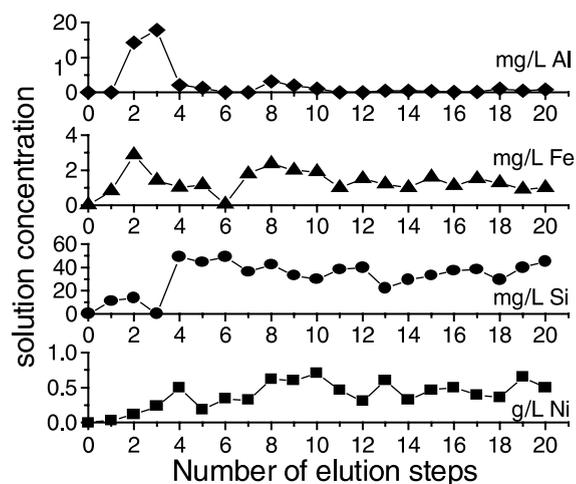
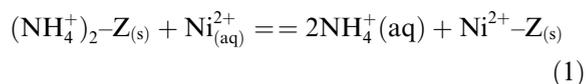


Fig. 3. Concentration of Ni, Si, Fe and Al in the resultant solution after the nickel elution.

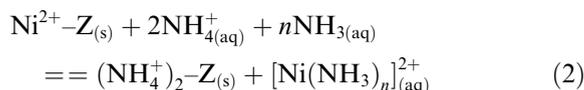
two consecutive steps: first nickel removal and second nickel elution.

In Fig. 2, it is observed that in all removal steps the resulting nickel concentration in solution is smaller than the initial nickel concentration (2.9 g/l). This decrease in nickel concentration can be explained by ion exchange between  $\text{Ni}^{2+}$  and  $\text{NH}_4^+$  ions according to the following reaction:



The subscripts (s) and (aq) denote “in zeolite” and “in the solution”, respectively. As a result from removal step, the  $\text{Ni}^{2+}$  ions are retained in the zeolite and the  $\text{NH}_4^+$  ions enter to the solution.

From Fig. 3, it can be noted the presence of nickel in solution after each elution step. Therefore, the  $\text{Ni}^{2+}$  cations, once retained in the zeolite, were exchanged with  $\text{NH}_4^+$  ions from the ammonia-rich solution, consequently, the nickel content in this solution increased. In addition, the  $\text{Ni}^{2+}$ , once exchanged and into ammonia-rich solution, form an amino-complex of nickel, such as  $[\text{Ni}(\text{NH}_3)_6]^{2+}$  or  $[\text{Ni}(\text{NH}_3)_4]^{2+}$ . The process total can be represented by the following reaction:



The obtained results, with respect to the possibility of removal and elution of nickel, are in accordance to previous studies on the exchange between  $\text{Ni}^{2+}$  and  $\text{NH}_4^+$  ions, performed in non-cyclic form [6,16,20], i.e., a single cycle. However, as a new event, after the first cycle the amount of nickel removed and eluted notably increases Fig. 4 clearly shows this increase. In addition, we can see that there are large differences between the amount of nickel removed and then eluted in each single cycle. For example, in the cycle 10, only 0.5  $\text{Ni}^{2+}$  meq/g were eluted from 1.77  $\text{Ni}^{2+}$  meq/g removed. We can see that in some cases the amount of  $\text{Ni}^{2+}$  meq/g removed is even higher than the milli-

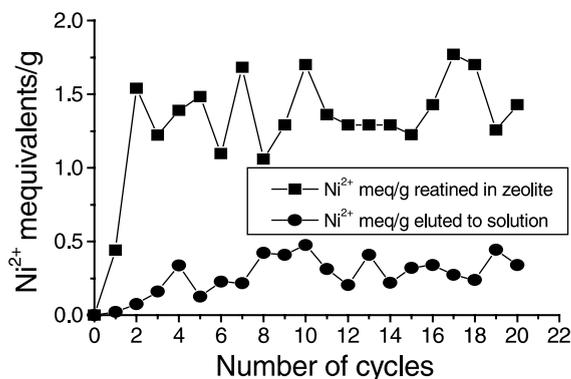


Fig. 4. Milliequivalents of nickel retained and eluted per gram of zeolite in each cycle.

equivalents of  $\text{NH}_4^+$  retained in the starting  $\text{NH}_4^+\text{-Z}$  ( $1.6 \pm 0.15$  meq/g). These differences can be explained considering that, during the removal of nickel, the ion exchange between  $\text{NH}_4^+$  and  $\text{Ni}^{2+}$  ions is accompanied by nickel precipitation in the form of a low-soluble phase. The formation of a fine light green precipitate as a suspension in the  $\text{NiCl}_2$  solution was indeed observed during nickel removal steps, from the second cycle on. The amount of this precipitate was considerable, which allowed us to separate and collect it as a sample for analysis. During the elution steps no precipitation was observed.

The results obtained leads us to consider that there is no significant loss in the clinoptilolite exchange capacity of  $\text{Ni}^{2+}$  and  $\text{NH}_4^+$  ions during the  $\text{Ni}^{2+}$  removal–elution cycles (see Fig. 4).

On the other hand elements such as silicon, aluminum and iron, found in clinoptilolite and other minor phases are observed in solution (see Figs. 2 and 3). With regard to this fact, we can observe that during both the removal and the elution of nickel, the silicon concentration in solution is significant. The iron and aluminum concentrations are only significant in some cycles during the elution, while during the nickel removal their amount is of the order of the sensitivity of the method used for their determination, i.e., 0.06 mg/l for Fe and 0.39 mg/l for Al. The presence of silicon, aluminum and iron in the solutions can be explained by dissolution of the minor phases, companions to the clinoptilolite. This assumption is in accordance with the fact that no detriment was observed in the exchange capacity of  $\text{Ni}^{2+}$  and  $\text{NH}_4^+$  ions in clinoptilolite during the  $\text{Ni}^{2+}$  removal–elution cycles. Kesraoui-Ouki et al. [21] have studied the effects of the treatment of natural clinoptilolite and chabazite with NaCl and NaOH solutions during lead and cadmium removal from effluent wastewater. These authors have observed by SEM that these zeolite crystals had foreign materials—impurities or very fine fragments of the original crystals—on their surface, which were removed during the treatment. They have outlined that the treatment cleans the zeolite surface and enhances the mineral crystallinity, which improved their exchange capacity and the efficiency of removal for Cd and Pb. Also a recent work of our

group has described the dilution of minority phases in solution when Cuban natural clinoptilolite is exposed to long time contact with water [22].

### 3.2. IR spectroscopy

Fig. 5 shows the IR transmittance spectra of the  $\text{NH}_4^+\text{-Z}$  before and after eight and 20 nickel removal–elution cycles, and that of the initial purified zeolite (Z). IR spectra do not show significant change in the bulk solid phase. The clinoptilolite characteristic band at  $615\text{ cm}^{-1}$  does not undergo any notable loss in its intensity even with the severity of the treatment, the only difference observed between the IR spectra lays on the width of the absorption bands. The bands become sharper with every removal–elution cycle. In Fig. 5 it can be seen that bands that are hardly observed in the natural sample are very well defined after the 20th cycle. This fact can be explained by the dissolution of the smaller crystals fraction contained in the sample, such fraction is responsible for the band broadening. The band at  $450\text{ cm}^{-1}$ , characteristic of amorphous silica, does not increase notably, which indicates that the zeolite structure is not affected significantly during the whole cyclic process. On the other hand, the presence of a band at  $1403\text{ cm}^{-1}$  was detected for  $\text{NH}_4^+\text{-Z}$  before and

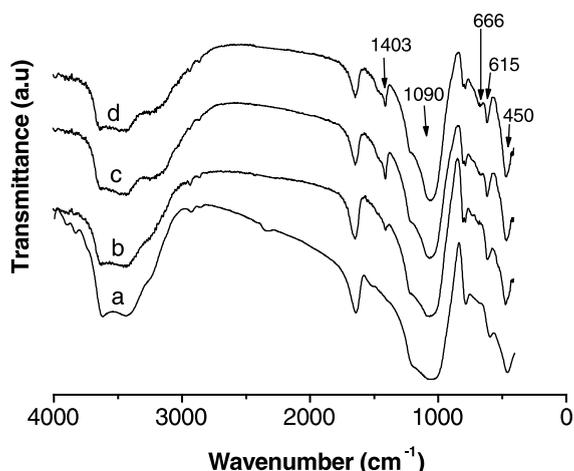


Fig. 5. IR transmittance spectra of the purified zeolite (a),  $\text{NH}_4^+\text{-Z}$  before (b) and after eight (c) and 20 (d) removal–elution cycles.

after eight and 20 removal–elution cycles. This band is close to the vibrations of the  $\text{NH}_4^+$  bending centered at  $1403\text{ cm}^{-1}$  [23], therefore we have assigned the  $1403\text{ cm}^{-1}$  band to  $\text{NH}_4^+$  exchanged in the clinoptilolite. Consequently, the broad band at  $3500\text{ cm}^{-1}$  after eight and 20 cycles was deformed. The  $1403\text{ cm}^{-1}$  band at  $\text{NH}_4^+\text{-Z}$  becomes wider from eight to 20 cycles. This fact might be due to formation of an amino-complex of nickel, such as  $[\text{Ni}(\text{NH}_3)_6]^{2+}$  or  $[\text{Ni}(\text{NH}_3)_4]^{2+}$ , which have a characteristic band over this frequency range [15, 23]. These complex ions remain in the clinoptilolite after the final elution.

Infrared spectroscopy (IR) was also used to identify the light green precipitate, using similar measurement conditions as those employed for the zeolite analysis (see Section 2.5). The IR transmittance spectrum of the precipitate is shown in Fig. 6. The bands observed in the spectra, except those at  $3400$ ,  $1625$  and  $1020\text{ cm}^{-1}$ , coincides with the assigned bands to  $\text{Ni}(\text{OH})_2$  [23]. The  $3650\text{ cm}^{-1}$  band is located over the frequency range of the vibration of the  $\text{OH}^-$  stretching from hydroxyl group,  $3650\text{--}3700\text{ cm}^{-1}$  [23]. This band is typical of metallic hydroxides and indicates the presence of hydroxyl groups. The  $3400$  and  $1625\text{ cm}^{-1}$  bands have been assigned to the free or hydration water [23]. The first one corresponded to a characteristic adsorption band for free water, centered in the  $3200\text{--}3400\text{ cm}^{-1}$  region, and the second does

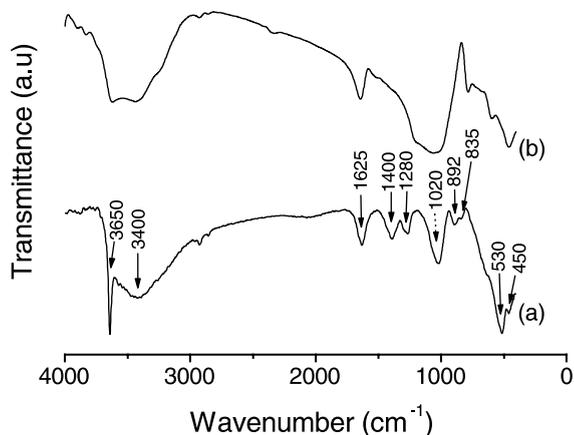


Fig. 6. IR transmittance spectra of the nickel hydroxide precipitated (a) and purified zeolite (b).

to the H–O–H bending motion that appears in the 1600–1650  $\text{cm}^{-1}$  region. We have assigned the 1020  $\text{cm}^{-1}$  band to an impurity of the zeolitic phase. The results obtained by IR suggest that the nickel precipitates in the form of a  $\text{Ni}(\text{OH})_2 \cdot x\text{H}_2\text{O}$ .

### 3.3. X-Ray diffraction analysis

Fig. 7 shows the XRD patterns of the  $\text{NH}_4^+\text{-Z}$  before and after the cyclic process of nickel removal–elution, and that of the initial purified zeolite. No significant change has been observed either in the position of the most intense peaks of the clinoptilolite nor in its crystallinity. We can observe that the main differences between the peaks are in their intensity. The peak corresponding to the (0 2 0) plane of clinoptilolite (see Fig. 7), is the one having the highest intensity variation. These changes in peak intensity are mainly associated with differences in the nature, amount and position of the extra-framework species in clinoptilolite channels. It should be considered not only the  $\text{NH}_4^+$  ions, but also a remained amount of natural cations ( $\text{K}^+$ ,  $\text{Na}^+$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ ) in the clinoptilolite, which is common in ion exchange with natural and synthetic zeolites [9,24,25]. It should be also considered that some  $\text{Ni}^{2+}$  still remains in

the channels of clinoptilolite after the final elution, according to the discussion before about both the differences between the amount of nickel removed and eluted, and the formation of an amino-complex of nickel observed by IR. Petrov [26] in a study of cation exchange in clinoptilolite has reported that the intensity of the (0 2 0) peak is the most likely to vary, since it is strongly related to the extra-framework species, sited in the mirror plane perpendicular to  $b$  axis. Therefore variations in the channel content mainly affects this peak, leaving other peaks almost unaltered. We note that similar behavior was observed when Cuban natural clinoptilolite from Tasajera deposit was treated with sodium carbonate solution [27] and with different solutions of metallic cations [28]. In other studies about ion exchange with other zeolite types it has been observed that the relative intensities of different peaks of the diffraction patterns change with the ion-exchange level, while the positions of the peaks do not change significantly [29]. Comparing the relative intensities of the 0 2 0 peak corresponding to ammonium clinoptilolite before and after the whole treatment it is possible to infer differences in the extra-framework species content. In the four cation sites (M1, M2, M3 and M4) of clinoptilolite both the number of water molecules

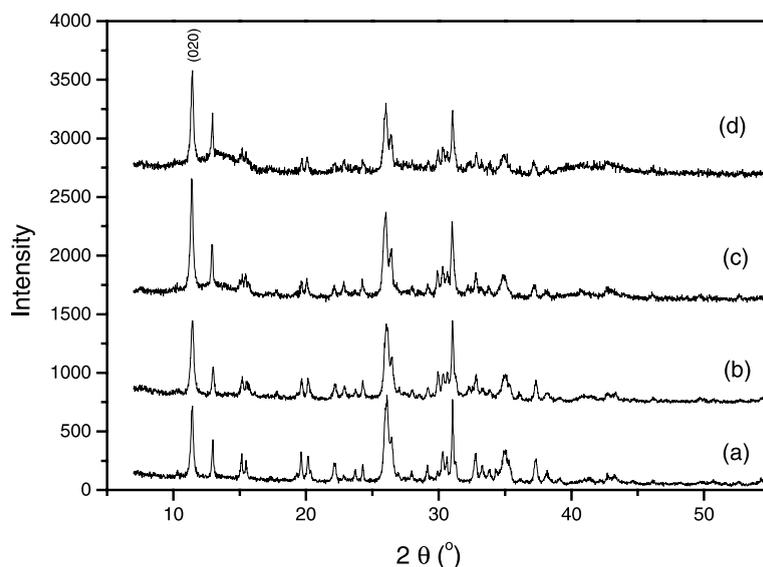


Fig. 7. XRD pattern of the purified zeolite (a),  $\text{NH}_4^+\text{-Z}$  before (b) and after eight (c) and 20 (d) removal–elution cycles.

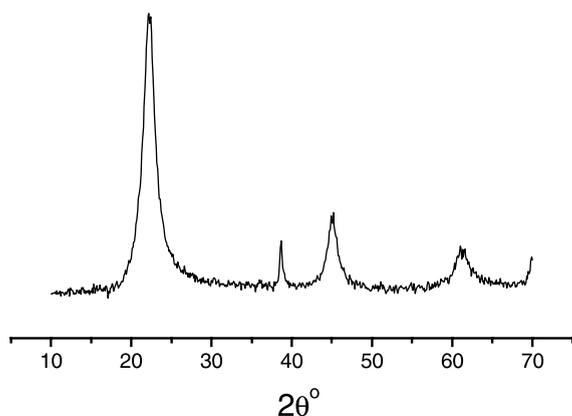
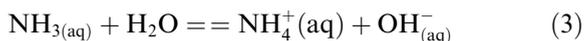


Fig. 8. XRD pattern of the nickel hydroxide precipitated.

and the structural oxygen coordinated by the cations are different.

XRD was also used to identify the precipitated nickel phase; the pattern was recorded from  $10^\circ$  to  $70^\circ$  ( $2\theta$ ) using a step size of  $0.05^\circ$  and counting time of 6 s. Fig. 8 shows the X-ray diffractogram of this precipitate. All peaks observed in this diffractogram correspond to  $\text{Ni}(\text{OH})_2$  (PDF 14-117). The formation of this precipitate can be explained considering two consecutive points. First, during the elution of nickel, besides the ion exchange and the formation of amino complex of nickel (see reaction (2)),  $\text{OH}^-$  anions from ammonia-rich solution used (see reaction (3)) are retained on the zeolitic phase surface. Second, during the removal of nickel, besides the ion exchange of  $\text{Ni}^{2+}$  ions (see reaction (1)), the liberation of the  $\text{OH}^-$  ions retained in the zeolite and their reaction with  $\text{Ni}^{2+}$  ions from  $\text{NiCl}_2$  solution take place, producing the precipitation of nickel hydroxide II according to the reaction (4).



The retention of  $\text{OH}^-$  anions in the zeolite, during the elution steps, can be explained by the occlusion or adsorption of these anions on the zeolitic surface. The  $\text{OH}^-$  ions might be forming part of an electric double layer. According to the electric double layer models, it is formed by two parts: a

immobile monolayer of ions of one sign on the surface of a solid and a mobile or diffuse layer of ions of the opposite sign [17,30]. In our case, as the zeolite surface is negative charged, the immobile monolayer should be formed by  $\text{NH}_4^+$  cations and the diffuse layer by  $\text{OH}^-$  and  $\text{NH}_4^+$  ions. These ions are retained by electrostatic attraction forces. Then, during the removal steps, as the temperature increases ( $80^\circ\text{C}$ ) the thermal vibrations of the ions in the electric double layer rise too. As a result, the electrostatic attraction forces in the electric double layer decreases, which favors the liberation of  $\text{OH}^-$  anions and its concentration into the  $\text{NiCl}_2$  solution increases. The increase of  $\text{OH}^-$  concentration in solution allows the saturation of nickel hydroxide II and its precipitation. This is a necessary condition for the precipitation of this low-solubility hydroxide [17].

The adsorption of hydroxyl groups on the zeolite surface has been reported by other authors [31,32]. Also, it has been reported the occurrence of hydrolysis process and the precipitation of metallic hydroxides, but in a smaller extent, i.e., at traces level [9]. However, in our case, this process is of a great extent and a large amount of nickel hydroxide precipitates. The precipitation reaction of this hydroxide should take place, mainly, on the zeolite surface, i.e., in the solution–zeolite interphase where the  $\text{OH}^-$  ions concentration is higher. A detailed study of the mechanism of  $\text{Ni}(\text{OH})_2$  precipitation will be the subject of future works.

The results obtained by XRD suggest that the hydrothermal treatment and the high ammonia concentrations conducted have not produced significant effect on the structure of the clinoptilolite, but provokes changes in the relative intensity of the diffraction peaks. Additionally, after 20 cycles the presence of an amorphous solid is observed in the XRD patterns, which agrees with the fact, mentioned before, about the dissolution of minor phases, which could then precipitate in the form of amorphous silica. Moreover the peaks of the clinoptilolite phase are sharper; for example the  $020$  peak of the natural clinoptilolite, around  $11.4^\circ$ , has an integral breadth of  $0.34^\circ$ , while the same parameter for the sample after 20 cycles is  $0.29^\circ$ . This indicates that the smallest crystals of this phase are also dissolved contributing, in this

way, to the amorphous background, this fact agrees well with the IR results regarding the enhance of crystallinity.

### 3.4. General discussion

The evidences obtained from XRD and IR analysis lead us to consider that the natural clinoptilolite from Caimanes deposit is stable as an ionic exchanger under hydrothermal conditions and high ammonia concentrations. These results deviate from the reported behavior of some zeolites when exposed to basic environments for prolonged periods of time, i.e., undergo a structural transition. Thus, it has been reported [8,32] that the zeolite-A and clinoptilolite under basic solutions, in NaOH solution, for example, convert to the zeolite-P. In our case, the severity of the treatment is similar. The natural clinoptilolite from Caimanes was exposed to high ammonia concentration (247 g/l de  $\text{NH}_4\text{OH}$ ) in a cyclic form for a prolonged period of time (120 days), but no significant change or detriment on the structure and exchange capacity of the clinoptilolite was detected.

The nickel removal is accompanied by nickel precipitation, which is the fundamental cause of the differences between the amount of nickel removed and eluted. However, it is worth outlining that in recent studies we find that the nickel exchange at low temperatures in this clinoptilolite is not very favored and also it is not complete [16]. In our case, concentrated  $\text{NH}_4\text{OH}$  solutions were used for the nickel elution in order to favor this process, but we should keep in mind that this elution was performed at room temperature. Consequently, we should expect a small amount of nickel still remaining in the clinoptilolite channels after each elution, which should contribute to differences between the amount of nickel removed and eluted. This remaining amount of nickel can be explained by two points. First, the polarizing power of the  $\text{Ni}^{2+}$  ions is higher than that of  $\text{NH}_4^+$  ions. Hence, the interaction power with the framework for these ions is higher for  $\text{Ni}^{2+}$  than for  $\text{NH}_4^+$ , which does not favor the nickel elution. Second, the clinoptilolite has four cation sites (M1, M2, M3 and M4) at which ion exchange can occur [33]. Regarding nickel and ammonium, their lo-

cation has been reported in different sites; the M1 and M3 sites for  $\text{Ni}^{2+}$  and the M2 site for  $\text{NH}_4^+$  [24,25]. The different preference of cation sittings do not favor their mutual ion exchange. A detailed structural analysis using samples with different  $\text{Ni}^{2+}/\text{NH}_4^+$  concentrations is underway.

## 4. Conclusion

We have carried out a detailed study of a nickel removal–elution cyclic process, which is based on the use of natural clinoptilolite from Caimanes deposit, Cuba. We showed that the stability of the material as an exchanger of  $\text{Ni}^{2+}$  and  $\text{NH}_4^+$  cations under hydrothermal conditions and high ammonia concentrations is not affected significantly after 20 nickel removal–elution cycles. The ion exchange between  $\text{Ni}^{2+}$  and  $\text{NH}_4^+$  ions that takes place during the nickel removal is accompanied by nickel precipitation in the form of a low-soluble phase. This precipitation substantially increases the amount of nickel removed, and according to the conducted IR and XRD analysis the nickel precipitates in a hydrated nickel hydroxide form.

The possibility of nickel removal followed by its elution revealed that the process is regenerable.

In practice, these results are important as they constitutes the theoretical-practice basic for the use of ammoniacal solution concentrated to elution and recuperation of  $\text{Ni}^{2+}$  and other cations retained in clinoptilolite. This type of solution or liquor is common at industrial scale, for example in the nickel industry.

## Acknowledgements

The authors appreciate the help of Dr. A.R. Ruiz-Salvador for helpful discussions. Moreover, the authors appreciated the help of the Center of Research of the Laterite (Moa-Cuba). We acknowledge University of Havana for an Alma Mater Research Grant. The Third World Academy of Science (Trieste, Italy) is also thanked for financial support through the Research Grant No. 00-080 RG/CHE/LA.

## References

- [1] J.M. Newsam, in: A.K. Cheetham, P. Day (Eds.), *Solid State Chemistry Compounds*, Oxford, 1992, p. 235.
- [2] S. Noda, in: H. Chon, S.K. Ihm, Y.S. Uh (Eds.), *Studies in surface science and catalysis: progress in zeolite and microporous materials*, Proceedings of the 11th International Zeolite Conference, Seoul, Korea, vol. 105B, 1997, p. 1641.
- [3] E. Torracca, P. Galli, M. Pansini, C. Colella, *Micropor. Mesopor. Mater.* 20 (1998) 119.
- [4] S. Keraoui-Ouki, M. Kavannah, *Waste Manage. Res.* 15 (1997) 383.
- [5] M.T. da Costa, E.F. Sousa-Aguiar, in: D. Cardoso, E.A.U. Gonzalez, S.L. Jahn (Eds.), *2° Curso Iberoamericano Sobre Peneiras Moleculares*, Cyted, Brasil, 1995, p. 397.
- [6] I. Rodríguez-Iznaga, G. Rodríguez-Fuentes, A. Benítez-Aguilar, *Micropor. Mesopor. Mater.* 41 (2000) 129.
- [7] A. Arcoya, J.A. González, N. Travieso, X.L. Seoane, *Clay Miner.* 29 (1994) 123.
- [8] N. Bálbã, G. Mihãilã, C. Luca, P. Onu, in: *Zeolite'97 5th International Conference on the Occurrence, Properties and Utilization of Natural Zeolites*, Italy, 1997, p. 50.
- [9] M.A. Keane, *Micropor. Mater.* 4 (1995) 359.
- [10] R.A. Schoonheydt, L.J. Vandame, P.A. Jacobs, J.B. Uytterhoeven, *J. Catal.* 43 (1976) 292.
- [11] M. Wark, W. Lutz, G. Schultz-Ekloff, A. Dyer, *Zeolites* 13 (1993) 658.
- [12] E.A. Behrens, D.M. Poojary, A. Clearfield, *Chem. Mater.* 8 (1996) 1236.
- [13] E.A. Behrens, A. Clearfield, *Micropor. Mater.* 11 (1997) 65.
- [14] I. Rodríguez-Iznaga, A. Benítez-Aguilar, N. Bruguera, *Revista Minería y Geología* 12 (1) (1995) 25.
- [15] G. Rodríguez-Fuentes, Ph.D. Thesis, CNIC, Cuba, 1987.
- [16] I. Rodríguez-Iznaga, G. Rodríguez-Fuentes, G. Orozco, J. Serrano, J. Breff, A. Benítez-Aguilar, in: G. Rodríguez-Fuentes, S. Ávila Garcia (Eds.), *Catalizadores y Adsorbentes Iberoamericanos para la Remoción de Metales Pesados de Efluentes Industriales*, Cyted, Madrid-España, 2000, p. 219.
- [17] P.W. Atkins, in: *The Elements of Physical Chemistry*, Oxford University Press, Oxford, 1992, p. 191.
- [18] G. Orozco, *Revista Minería y Geología* 13 (3) (1996) 45.
- [19] G. Rodríguez-Fuentes, in: *Proc. Int. Conf. Catalysis, Quimindustria'93*, 1993.
- [20] I. Rodríguez-Iznaga, G. Rodríguez-Fuentes, P.R. Bassano, *Revista Minería y Geología* 14 (2) (1997) 65.
- [21] S. Keraoui-Ouki, C. Cheeseman, R. Perry, *Environ. Sci. Technol.* 27 (6) (1993) 1108.
- [22] A. Rivera, G. Rodríguez-Fuentes, E. Altshuler, *Micropor. Mesopor. Mater.* 40 (2000) 173.
- [23] R. Nyquist, R. Kagel, in: *Infrared Spectra of Inorganic Compounds (3800–45 cm<sup>-1</sup>)*, Academic Press, New York, 1973, p. 74, second printing.
- [24] N. Travieso, G. Labre, J.A. González, A. Arcoya, X. Sedane, in: G. Rodríguez-Fuentes, J. González (Eds.), *3era Conferencia Internacional Sobre Ocurrencia, Propiedades y Usos de las Zeolitas Naturales. Parte I*, Cuba, 1991, p. 150.
- [25] C. De las Pozas, R. Lopez-Cordero, C. Diaz-Aguila, M. Cora, R. Roque-Malherbe, *J. Solid State Chem.* 114 (1995) 108.
- [26] O.E. Petrov, in: D.W. Ming, F.A. Mumpton (Eds.), *Natural Zeolites'93: Occurrence, Properties, Use*, International Committee on natural Zeolites, Brockport, NY, 1995, p. 271.
- [27] A. Rivera, G. Rodríguez-Fuentes, E. Altshuler, *Micropor. Mesopor. Mater.* 24 (1998) 51.
- [28] M. Mir, M.Sc. Thesis, University of Havana, 1996.
- [29] Y. Lee, S.W. Carr, J. Parised, *Chem. Mater.* 10 (1998) 2561.
- [30] A.C. Newman, G. Brown, in: A. Newman (Ed.), *Chemistry of the Clays and Clay Minerals*, Mineralogical society, 1987, p. 1.
- [31] S. Yamamoto, S. Sugiyama, O. Matsuoka, T. Honda, Y. Banno, H. Nosoye, *Micropor. Mater.* 21 (1998) 1.
- [32] D.W. Breck, in: *Zeolite Molecular Sieves*, Wiley, New York, 1974, p. 460.
- [33] K. Koyama, Y. Takeushi, *Zeit. Kryst.* 145 (1977) 216.