Time evolution of a natural clinoptilolite in aqueous medium: conductivity and pH experiments

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Abstract

The chemical behavior in an aqueous medium of a natural zeolitic material, NZ (mainly consisting in crystals of the zeolites clinoptilolite/heulandite) has been studied through electrochemical techniques, complemented by atomic absorption spectrometry. The time dependence of the conductivity of the aqueous medium in the presence of NZ, showed a steep increase at the beginning followed by a slower increase for longer times until saturation of the system is reached. The release of the ions present in the zeolitic material at different times, was followed by means of atomic adsorption spectroscopy, which indicated that the sodium ion is the main responsible for the conductivity response. The interaction of NZ with the aqueous medium revealed a pH increase in the weakly acid region and a decrease in the basic region. The correlation between conductometric and pH-metric studies suggests that an ion-exchange mechanism takes place within the very first minutes of the interaction of NZ with the aqueous medium, followed by the temperature-dependent dissolution of minority phases up to several days. Finally, a comparative study between NZ and a modified form of this zeolite with sodium carbonate (NZ1), showed a faster pH increase with time for NZ1. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Clinoptilolite is a zeolite of the heulandite group being the most abundant in nature. This zeolite contains three channels, limited by a system of tetrahedral rings: two channels of eight and ten tetrahedra parallel to *c* axis of the structure, and a third channel formed by eight member rings and connected to the other two channels [1]. These channels are occupied by water molecules and compensating cations, which neutralize the anionic charge of the framework. It is well established that the multiple uses of these materials are based on their physicochemical properties, which explain their wide range of applications in numerous agricultural and industrial areas. In particular, new materials with a great variety of physical–chemical properties resulting from modifications of natural clinoptilolite have been intensively studied in the last years [2–6].

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The chemical behavior and stability of natural zeolites like clinoptilolite, heulandite and mordenite in different aqueous media, has been reported in the literature due to their technological importance [7–9]. Special attention has been given to the chemical stability of these materials in aqueous solutions at different pH values, particularly in strongly acid or basic media. However, due to the interaction of these materials with the H^+ or the OH^- ions present in the solutions, unwanted physicochemical phenomena have been reported, (i.e. hydrolysis of the solids, degradation, dissolution and phase transformations), which depend on the structural characteristics and the chemical composition of the zeolitic material [7–9]. It is also known that Bronsted and Lewis acid/basic sites, present in the structure of these materials, play an important role in such behavior. From the practical point of view, acid–base properties of zeolites are very convenient for catalysis applications [10,11].

In addition to the structural stability of a zeolite, a second basic chemical property for its use as a controlled release matrix in the human body is its ability to host useful pharmaceutical species, and to release them with a kinetics that suits the specific medical application. The latter is indeed a complex ability that strongly depends on the specific zeolitic material and drug under consideration. Purified natural clinoptilolite (NZ) from Tasajeras deposit (Cuba) has demonstrated good stability in its transit through the gastrointestinal tract, and to be harmless to the human body [4,6,12,13]. Based on such properties, it has been used as raw material for different pharmaceutical forms for the treatment of several pathologies in animals and humans [12,13]. However, the details of the chemical kinetics of this zeolitic material in aqueous medium has not been completely explored.

The aim of the present work is to carry out a preliminary study of the chemical behavior of NZ in aqueous medium, at different temperatures, based on the conductivity evolution of the medium with time. The results are analyzed in the light of a parallel study, through atomic absorption spectroscopy, of the release of ions present in NZ into the aqueous medium. We will also see that the application of these techniques and their combi-

nation with kinetic studies of pH can yield information about the interaction between the zeolite and the aqueous medium, as well as the possible mechanisms that could take place. In order to evaluate the neutralizing/basic capacity of NZ we made a comparative pH study with a modified form of this zeolite, which has shown basic properties [4]. A practical motivation of this study is the potential use of NZ as a matrix for drug release [14] or even for the release of ions with pharmaceutical interest such as Zn^{2+}, whose microbicide effectiveness has been thoroughly tested in humans [15]. We note that conductivity measurements, commonly used to study the controlled release of drugs from standard pharmaceutical matrices [16, 17], have never been employed for the study of natural zeolitic materials in aqueous media, to the best of our knowledge. Therefore, we are also testing the ability of this technique for the study and characterization of zeolitic materials.

2. Experimental

The NZ used in this study was obtained by means of a method reported elsewhere [4,12], designed to enrich the content of zeolite by means of the removal the nonzeolitic mineral phases contained in the rock. The final product does not cause any biological damage to humans as have been proved by previous pharmacological and clinical studies [12,13]. NZ is a powder of 37–90 μm particle size consisting in a mixture of about 70% clinoptilolite-heulandite and mordenite, and 30% of other phases. The purified natural clinoptilolite, NZ, used in this work has the oxide-form chemical composition shown in Table 1 (in wt.%, with the balance as H_2O) [4].

In both conductivity and pH measurements, 200 mg of zeolite powders were added at $t = 0$ from the top of a glass measuring cell containing 100 ml of doubly-distilled water, which was then

Table 1
Oxide-form chemical composition of the purified natural clinoptilolite NZ in wt.% (with the balance as H_2O)

	SiO_2	Al_2O_3	CaO	Na_2O	K_2O	MgO	Fe_2O_3
NZ	66.5	11.3	4.3	2.0	0.6	0.5	1.1

closed to avoid evaporation. The initial pH and conductivity of the water were in the range 5.1–5.5 and 2.0–2.4 μS/cm, respectively. The sensors were always introduced through a lateral inlet keeping the cell sealed, also to avoid evaporation. Agitation at 300 rpm was applied during all the measuring time using a magnetic stirrer. Conductivity measurements were performed at 32°C, 37°C and 42°C, and pH measurements took place only at 37°C. The temperature was guaranteed using a thermostat within ±0.1°C. In each experiment, the conductivity and pH variations with time were monitored until saturation of the system was reached.

The experiments concerning the time dependence of the conductivity were performed by means of a Shanghai Rex Instruments conductivity-meter, model DDS-11A using a platinized platinum electrode with an error of ±0.1 μS/cm. The resulting NZ-water system, at different times, was centrifuged and the liquids were further analyzed by means of atomic absorption spectroscopy in order to determine the Na, K, Ca, Mg, and Fe contents. A PYE UNICAM SP9 atomic absorption spectrophotometer was employed. pH measurements were performed by means of a Crison GLP21 pH-meter with combined glass electrode and a resolution of ±0.1 pH units. In this case, the studied samples were NZ and NZ1. NZ1 was obtained by a hydrothermal treatment of NZ with sodium carbonate, followed by centrifugation and drying, and the resulting product was then submitted to a washing process of 15 min in distilled water. Previous studies carried out on NZ1 showed that this product can be employed as gastric antacid due to its pH regulating capacity [4].

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

3. Results and discussion

Fig. 1 displays the time evolution of the conductivity in the aqueous medium for three different temperatures after addition of NZ. In all the cases,
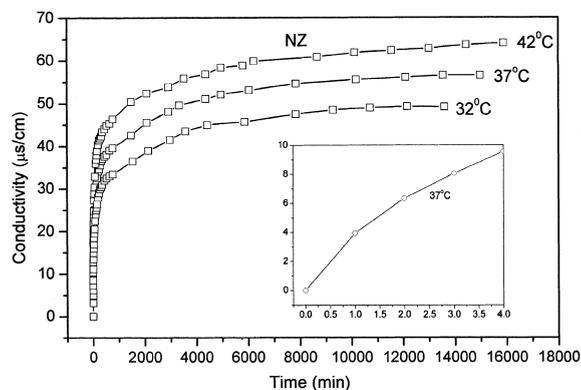
Fig. 1. Time evolution of the conductivity of the aqueous medium after the addition of 200 mg of NZ at different temperatures.

a steep increase of the conductivity takes place in approximately the first 500 min of the process, while a slower increase occurs afterwards, reaching a plateau after 10 000 min in all cases. Both the values of the conductivity at the plateaus and the conductivity increase rate are temperature dependent as it can be observed in the three curves from Fig. 1 (the inset of this figure will be discussed below). Fig. 2 shows the time evolution of different ions in solution as measured through atomic absorption spectrometry. If we also consider the respective mobilities, it is clear that sodium and iron species dominate the conductivity increase. In the case of sodium, not only its concentration, but the
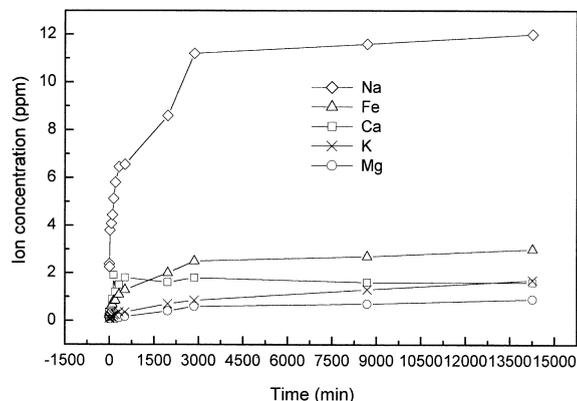
Fig. 2. Time evolution of the ion concentration in the aqueous medium after the addition of 200 mg of NZ at 37°C, as measured by atomic absorption spectroscopy.

similarity between its time dependence and the graphs presented in Fig. 1 suggest that it is primarily responsible for the time dependence of the conductivity. We will discuss below the possible mechanisms responsible for this behavior.

The experimental results of the pH measurements concerning the interaction between the NZ zeolitic material and the aqueous medium are shown in Fig. 3. In both cases, a quick pH increase is observed after the zeolite was added. However, a plateau was observed at 60–100 min after the contact (see inset). After that, a decrease of the pH values towards the neutral pH area was observed, followed by its stabilization at around 6000 min. These results are a clear indication that clinoptilolite tends to neutralize the aqueous medium acting either as proton acceptor or as a proton donor, which makes evident its amphoteric character. This phenomena has been reported by other authors for the case of zeolites with lower Si/Al ratio [7]. The amphoteric character shown by NZ suggests potential pharmaceutical applications. For example, if an appropriate dosage of NZ is able to increase the stomach pH, and to decrease the intestine pH as it goes through the gastro-intestinal tract, it may modify the absorption of certain drugs at both organs. We also show in Fig. 3 the influence of the solid–liquid ratio on the pH, which turns out to be relevant from the pharmaceutical point of view [4]. It can be proved that the pH variation depends on the amount of added

Fig. 4. Time evolution of the pH of the aqueous medium after the addition of 200 mg of NZ and NZ1 at 37°C.

sample since its stabilization was achieved faster for NZ 200 mg than for 400 mg of the same.

Fig. 4 shows the results of the pH measurements vs time for samples NZ and NZ1 up to 100 min. As expected from our previous work on Na_2CO_3–clinoptilolite [4], a larger pH increase with time is observed for NZ1. It is important to note that after 20 min of mixing and stirring with the added amount of the different zeolitic materials, no significant changes in pH values are observed.

The comparison between conductivity and pH-metry results can give some insight into the mechanisms involved in the processes under study. We have chosen for such comparison the experiments performed on a 200 mg sample of NZ at 37°C. Fig. 5 shows a 10^{-pH} vs time graph which describes how the concentration of H^+ ions decrease in solution, i.e., the time evolution of their incorporation into the zeolitic material. The inset displays a zoom of the same graph in time, and suggests that the capture of H^+ by NZ is almost finished around 2 min. An estimation of the number of protons incorporated to the zeolite until that time is 10^{-6} mol. If we accept the approximation discussed above that the Na^+ ions are the leading species responsible for the conductivity increase, Fig. 1 roughly displays the proportion of those ions leaving the zeolitic material as time goes by. The inset in the Fig. 1 corresponds exactly to the same time window plotted in the inset of Fig. 5 for 200 mg of NZ at 37°C, so we can directly

Fig. 3. Time evolution of the pH of the aqueous medium after the addition of (a) 200 and (b) 400 mg of NZ at 37°C.
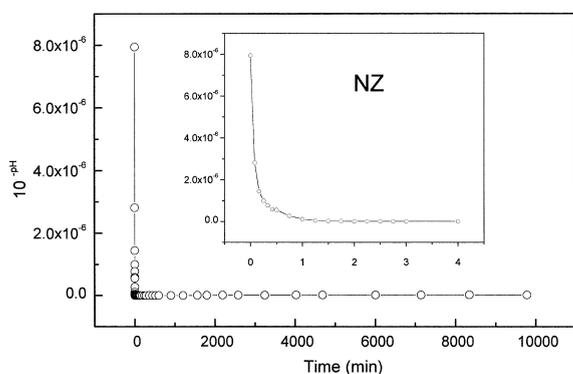
Fig. 5. Time evolution of the H⁺ concentration in solution after the addition of 200 mg of NZ at 37°C.

compare the time dependence of the H^+ incorporation to the material with the time dependence of the Na^+ removal. It is clear that the time evolution of H^+ incorporation into NZ does not visibly affect the Na^+ release. A estimation from the atomic absorption spectrometry measurements indicates that, at $t = 2$ min, 10^{-5} mol of Na^+ have abandoned the zeolitic material, i.e. approximately 10 times more than the amount of H^+ incorporated within the same lapse. Two mechanisms can be responsible for incorporation of the proton into the zeolite. First, the ion exchange with Na^+. Second, the binding of H^+ to the Lewis basic sites linked to framework oxygen atoms of the clinoptilolite. The latter possibility (suggested in Ref. [7]), seems less important in our material, since our zeolite has not received any previous treatment for the activation of such sites, and since our Si/Al ratio is smaller than that of the zeolites studied in Ref. [7]. Assuming ion exchange as the main mechanism for H^+ incorporation into the zeolite, a different phenomenon must be responsible for the continued removal of Na^+ ions *after* 2 min, since no further protons are available for ion exchange. One possibility is to assume that the main source of sodium ions is not the zeolitic phase itself, but other phases which slowly dissolve as time goes by. This explains why the time evolution of the conductivity in the first minutes is practically independent from the features of the H^+ incorporation to NZ within the same time window: only 10% of the Na^+ ions are involved in the exchange process

of H^+, while 90% of the sodium ions contribute to conductivity through a dissolution process of secondary phases. On the other hand, the amount of Na^+ ions released in about 15 000 min represents only one third of the initial sodium content in NZ (see Table 1). This suggests that two thirds of the sodium content did not participate in the ion exchange process for lack of counter-ions (or remain in very stable secondary phases in aqueous medium (near neutral pH) such as feldspars [18]). Also, as is usual in sedimentary deposits [19–21] we expect the presence of small amounts of carbonates, hydroxides and volcanic glass, which may slowly dissolve. Finally, the temperature dependence of the conductivity in the relatively narrow temperature range of our study (Fig. 1) would not be expected from an ion exchange process in NZ [21,22].

It is interesting to estimate the amount of secondary phases necessary to provide the main ions contribution to the conductivity, for example, Na^+. For an estimation, we will assume that it is basically produced by the dissolution of sodium carbonate, which is usually found in such kind of tuff [20,23]. A rough estimation of the amount of this compound necessary to release all the Na^+ ions as measured by atomic absorption spectrometry at 15 000 min is 3 mg. This corresponds to less than 2% of the zeolitic material used in the experiment, which partially justifies why the probable secondary phases responsible for the release of Na^+ are not reported in the phase analysis of NZ [21,24,25]. Barrer et al., for example, managed to detect the presence of salts in a natural clinoptilolite only by comparison with the chemical analysis results from a Na form of this zeolite, after being unable to identify such salts by X-ray diffraction analysis [19].

The pH increase observed in Fig. 3 could be attributed not only to the incorporation of protons to NZ (presumably by ion exchange, as derived from our previous discussion), but also to the presence of OH^- in solution resulting from the hydrolysis of some species present in NZ, such as hydroxides and carbonates, which affects its acid-basic equilibrium. The latter supports the fact that an increase of the pH depends on the amount of added sample.

A final comment regarding the observed decrease of pH for large times is needed. In our case the time decay of the pH in the basic pH-area could be the result of the removal of protons from the surface OH-groups with acid properties (Bronsted acid sites) which were generated during the "washing" process, and also due the effect of the divalent and trivalent cations on the water molecules producing OH-groups, as already discussed in the literature [10,26]. It is worth noting that the existence of two different mechanics related with the pH increase and subsequent decrease is given by the system history. A similar observation has been reported in Ref. [7] starting with aqueous solutions at different initial pH values.

In a previous work, we studied the physical–chemical properties and antacid possibilities of NZ and NZ1 [4,27]. Besides the compositional stability of our zeolitic, we proved the presence of crystalline sodium carbonate in NZ1, as well as exchanged Na^+ ions. The neutralizing capacity was highly improved from NZ to NZ1 and a neutralizing mechanism was suggested, as well as the possible sodium carbonate occlusion in the clinoptilolite channels was also stated. We suggest that the pH increase of the medium observed for the sample NZ1 in Fig. 4 is due not only to the neutralizing action of the carbonate and the substitution of the H^+ ions by the hydrolyzed Na^+ cations of the zeolitic material, which has been experimentally demonstrated [4], but also to the formation of basic sites as result of the hydrothermal transformation with sodium carbonate. This statement is based on the observation that additional basicity in zeolites can be associated with salt occlusion [11], and on the results of a recent computational study of the sites responsible for the basic properties in clinoptilolite with occluded sodium carbonate. A deeper and more detailed analysis about the latter will be reported elsewhere [28].

4. Conclusion

We have studied the temporal evolution of the natural zeolite NZ (and, to a lesser extent, of a sodium carbonate-NZ composite) in aqueous medium through conductometric and pH-metric techniques, complemented by atomic absorption spectrometry. We conclude that these simple electrochemical tools are able to reveal in a fast and inexpensive fashion some details of the various phenomena taking place in the system as time goes by. The increase of conductivity in solution seems to be basically associated to the release of sodium and iron species from secondary phases, which, after a steep increase in the first 500 min, lasts for several days. The very steep increase of the pH for NZ is mainly associated to an ion exchange process, which incorporates protons into the zeolite within the first minutes of the process, and by the hydrolysis of species present in NZ. After several hundred minutes, though, the zeolitic materials show a clear amphoteric behavior. In the case of NZ1, the steep increase of the pH is explained by the exchange process mentioned above, complemented by the neutralizing action of the sodium carbonate. The pH decrease in the basic pH range could be the result of the removal of protons from surface Bronsted acidic sites, and also due the effect of the di- and tri-valent cations on the water molecules. The conductometric and pH-metric studies we have carried out in this work can be regarded as a first step for the use of natural clinoptilolite as a matrix for the slow release of drugs to be applied in animals and, eventually, in humans.

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