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THE ION-EXCHANGE PROPERTIES OF NATURAL ZEOLITE MORDENITE

G.A. Mamedova[@]

Nakhchivan Branch of the National Academy of Sciences of Azerbaijan
Institute of Natural Resources, Nakhchivan, AZ 7000 Azerbaijan Republic
[@] *Corresponding author e-mail: chinashka89@yahoo.com*

The cation exchange properties of mordenite (a Nakhchivan natural zeolite) were studied. Ion exchange of the original cations – sodium, potassium and calcium – by magnesium, strontium, cadmium, zinc and nickel cations was carried out. It was found that in the case of Zn cations cation exchange occurs readily at a high speed and the maximum value of the degree of exchange. A low value of the degree of cation exchange is observed for Mg. This is due to the large hydration shell of magnesium, which adversely affects the cation exchange. High values of the exchange rate of Na^+ cations have already been explained at the first exchange of low content of sodium cations and their location mostly in exchange for positions available. The lesser ability to exchange K^+, Na^+ cations than contained in the natural zeolite is due to several reasons. With an increasing number of degrees of ionic exchange value exchangeable cations K^+ vary to a greater degree than the degree of exchange of the cations Na^+. Firstly, the content and size of the K^+ cation are greater than those of the Na^+ cations. Furthermore, a part of the K^+ cations is in exchange for hard cancrinites cells. It has been found that the degree of cation exchange of K^+ (a_K), contained in the original zeolite, with Mg^{2+}, Ni^{2+}, Sr^{2+}, Zn^{2+}, Cd^{2+} cations is considerably lower than the values of the degree of cation exchange of Na^+ (a_{Na}) at the same cations.

Keywords: *natural zeolite, ion-exchange properties, cation, mordenite, degree of exchange, IR-spectrum, stretching vibration.*

Introduction

The ion-exchange capacity of zeolites is one of the key parameters characterizing their sorptive and technological properties. The maximum ion-exchange capacity corresponds to complete replacement of one ion with another in all crystal positions. The ion-exchange properties of zeolites are determined by peculiarities of the chemical affinity of ions with the zeolite crystal structure. In this case, as well as in case of the adsorption of molecules, conformity of the sizes of replacing ions and openings in the zeolitic framework is required. Using ion exchange on zeolites enables to isolate ions, the extraction of which by other methods is often very difficult.

Cation-exchange forms of zeolites are obtained by the introduction of metal ions into the crystal lattice of zeolites by means of ionic exchange [1–5] or impregnation of zeolite with solutions of metal salts [6–9]. Varying the cationic composition of zeolites it is possible to affect significantly their physical and chemical properties including acid resistance and thermal stability.

Information on cation-exchange forms of mordenite in the literature is very limited and concerns mostly conditions of their preparation. At the same time there are no data on the influence of the chemical nature and the content of metal cations M^{2+} and M^{3+} on the physical and chemical characteristics of mordenite [10, 11]. Thermal stability, specific adsorptive and catalytic properties which can be changed by cationic exchange make mordenite a promising mineral for practical application as a component of highly effective heterogeneous catalysts of oil processing and petrochemistry, as well as adsorbents for drying acidic gas media [12].

The purpose of this work is obtaining various cationic forms of a specific zeolite – mordenite – and determining their physical and chemical properties.

Experimental

The sample of natural zeolite from Nakhchivan studied by us is characterized by the following chemical composition, %%: SiO_2 – 65.7, Al_2O_3 – 15. 9, Fe_2O_3 – 1.30, CaO – 5.08, MgO – 0.50%, TiO_2 – 0.05%, MnO – 0.07%, K_2O – 3.80%, Na_2O – 1.10%, P_2O_5 – 0.08%, H_2O – 7.5.

The empirical formula of the mineral was established: $Ca_2Na_2K_{2,8}Al_{8,8}Si_{39,2}O_{96}\cdot 34H_2O$ ·SiO_2/Al_2O_3 molar ratio – the silicate module of natural Nakhchivan zeolite – is equal to 7. It was calculated as follows:

$$M = \frac{SiO_2}{Al_2O_3} = \frac{C_{SiO_2}\cdot M_{Al_2O_3}}{C_{Al_2O_3}\cdot M_{SiO_2}}\ , \qquad (1)$$

where C (Al_2O_3) is the mass fraction of alumina, %;

C (SiO_2) is the mass fraction of silica, %;

M (Al_2O_3) and M (SiO_2) are the molar massed of alumina and silica.

A diffractogram of the natural zeolite is shown in Figure 1.

The most intense absorption band in the IR spectrum of the natural sample is observed at 1058 cm^{-1} and corresponds to the vibration of Si – O – Si bond. The absorption band in the range of 550–560 cm^{-1} corresponds to the vibrations of [SiO_4] tetrahedrons and [AlO_4] framework. The band at 798 cm^{-1} corresponds to the valence vibrations of Al – O, and at 463 cm^{-1}, to the deformation vibrations of Al – O_4. The absorption bands in the range of 3100–3700 cm^{-1} are due to the valence vibrations of zeolite water molecules. The absorption bands in the range of 2100–2500 cm^{-1} are accounted for by the presence of calcium and sodium carbonates.

Cation-substituted forms of the natural zeolite were obtained by repeated ion exchange from 0.1 M solutions of the corresponding nitrates at pH ≈ 6, room temperature and mechanical stirring. The initial mass of zeolite in all the experiments was 10 g. The mass ratio zeolite : salt solution was 1 : 10. When the ion exchange was complete, the zeolites were washed the distilled water until the reaction for the salt anion was negative, and then dried in the air at 100–120°C. The obtained experimental results were processed by the following equation:

$$(\alpha)_i = 1 - \left(M^T\right)_i / \left(M^T\right)_0 , \qquad (2)$$

where α_i is the degree of M^{n+} cation exchange in unit fractions; $(M^T)_0$ is the initial mass of the cation contained in the zeolite used for the exchange; $(M^T)_i$ is the current mass of the cation in the zeolite.

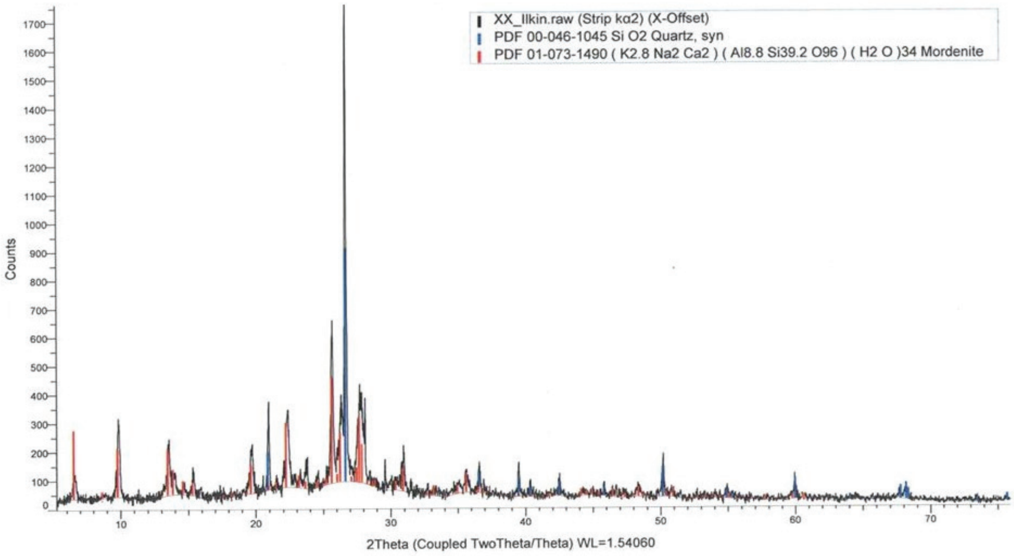

Fig. 1. A diffractogram of the natural zeolite.

After each experiment the crystallinity degree of the samples was calculated with the use of the IR spectra according to the following formula:

$$D = \ln \frac{I_0}{I} = \ln \frac{1}{T} , \qquad (3)$$

where T is transmission; I_0 and I, respectively, are radiation intensities before and after passing the beam through the sample layer of thickness d.

Identification of the zeolite phases was carried out by X-ray phase analysis, IR spectroscopy and electronic microscopy. The phase structure, silicate module and crystallinity degree of the natural zeolite were determined by means of a Bruker 2D PHASER X-ray spectrum analyzer (Cu, K_α, 2θ, 20–80 °). Images of the zeolite phases were obtained with the use of a Hitachi TM-3000 microscope. IR spectra were recorded with the use of a Nicolete IS-10 IR spectrometer in the frequency range of 400–5000 cm^{-1}. Samples of the studied zeolites were prepared in the form of pellets of 1 mm thickness in the air environment with the ratio 1 mg of zeolite / 400 mg KBr mg with the use of a Spectroscopic Creativity Pike Technologies hand press. The recording was carried out in the automatic mode.

Results and Discussion

The cation type determines the exchange rate, that is, it determines the speed of a “guest” cation inclusion into the zeolite cavity and the equilibrium constant of the initial cation exchange for the “guest” cation. Among the latter there are cations undergoing exchange readily and not readily.

Figure 2 presents dependences of the degree of exchange of Na^+ (α_{Na}), K^+ (α_K) and Ca^{2+} (α_{Ca}) cations for Mg^{2+}, Ni^{2+}, Sr^{2+}, Zn^{2+}, Cd^{2+} cations on the treatment duration. It can be seen from Figure 2 that the basic quantity of initial metal cations exchanges within the first 15 min. In order to attain the maximum degree of exchange of the initial cations for Mg^{2+}, Ni^{2+}, Sr^{2+}, Zn^{2+}, Cd^{2+} cations 50 min is sufficient. Further increase in the treatment duration has no noticeable impact on the exchange degree.

The lowest value of exchange degree is observed in case of Mg^{2+} cations, probably because they have a large hydrated film. In case of Zn^{2+} cations the exchange proceeds readily at a high rate, and the exchange degree is maximal.

The values (α_K) of the degree of exchange of K^+ cations contained in the initial zeolite for Mg^{2+}, Ni^{2+}, Sr^{2+}, Zn^{2+} and Cd^{2+} cations are much lower than the values (α_{Na}) of the degree of exchange of Na^+ cations for the same cations. The greatest α_K value is attained in case of the exchange of K^+ cations for Zn^{2+} ions, and the smallest α_K value, in case of the exchange for Mg^{2+} ions. The values (α_K) of the degrees of exchange of K^+ cations for Ni^{2+} and Sr^{2+} are almost the same.

In our opinion, the high values of the degrees of exchange of Na^+ cations in the first minutes of the process are due to the low content of sodium ions in mordenite and their location mainly in positions available for exchange. We think that the lower ability to exchange of K^+ cations than that of Na^+ cations contained in the natural zeolite is a consequence of several reasons. First, the content and sizes of K^+ cations are higher than those of Na^+ cations. Second, a part of K^+ cations is located in cancrinite cells hardly accessible for exchange. While the number of ion exchanges increases, the values of the degrees of exchange of K^+ cations change to a higher degree than those of Na^+ cations.

The maximum values of the degree of exchange of K^+ cations for Mg^{2+}, Ni^{2+}, Sr^{2+}, Zn^{2+} and Cd^{2+} cations form the following series:

$$\alpha_K \rightarrow Mg < \alpha_K \rightarrow Ni > \alpha_K \rightarrow Sr > \alpha_K \rightarrow Zn > \alpha_K \rightarrow Cd$$

The same sequence is observed also in case of sodium and calcium cations.

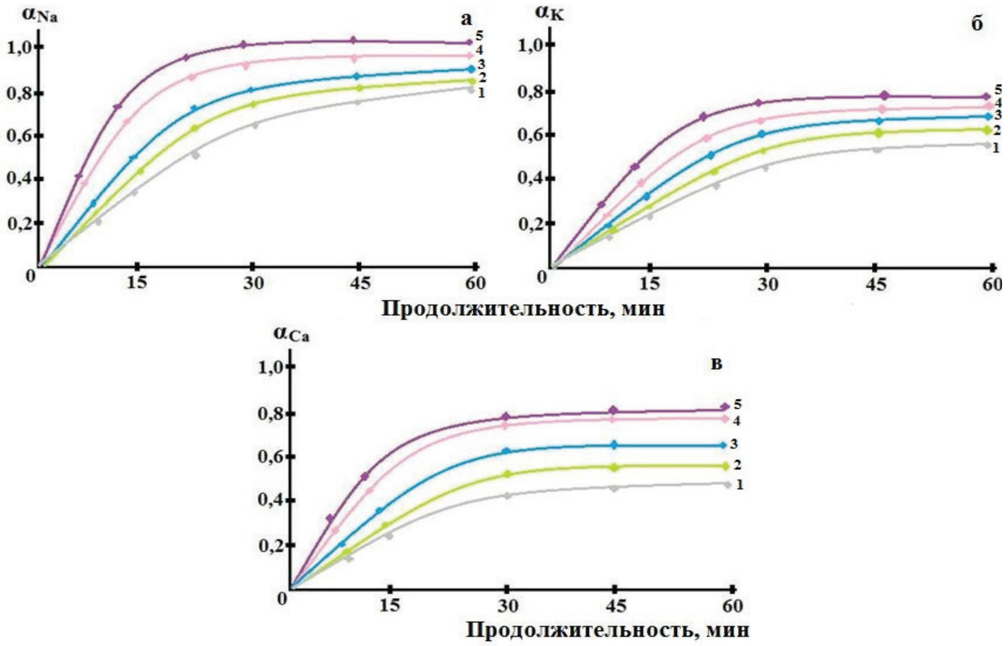

Fig. 2. Dependence of the degree of exchange of initial Na^+ (a), K^+ (b) and Ca^{2+} (c) cations for Mg^{2+}, Ni^{2+}, Sr^{2+}, Zn^{2+} and Cd^{2+} cations on treatment duration. 1 – Mg^{2+}; 2 – Cd^{2+}; 3 – Sr^{2+}; 4 – Ni^{2+}; 5 – Zn^{2+}. [Продолжительность, мин - means During, min]

The obtained results can be explained by the fact that in the chosen conditions the specified cations are present in the solution in the form of aquacomplexes. The sizes and stability of the latter is what generally determines the values of exchange degrees.

It was established due to our researches that the prevalence of calcium and magnesium cations in zeolites mainly affects the character and temperature of dehydration, the thermal stability and the content of zeolite water.

In order to confirm the preservation of zeolite structure upon cation replacement it should be taken into consideration that, when registering the spectrum with the use of KBr pellets (as it is done in most studies), exchange cations are located in large cavities of zeolites in the hydrated state [13].

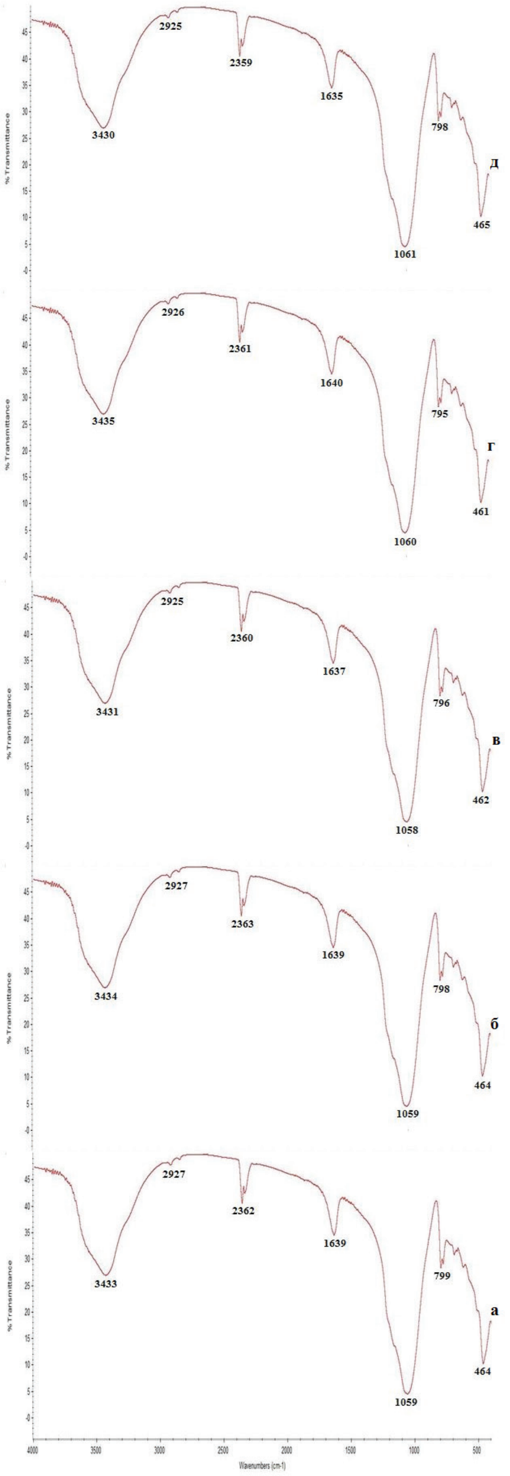

Fig. 3. IR spectra of a cation-substituted zeolite: a – Mg^{2+}, b – Ni^{2+}, c – Sr^{2+}, d – Zn^{2+}, e – Cd^{2+}.

It can be seen from Figure 3 that no considerable changes are observed in the IR spectra of cation-substituted zeolites.

According to the X-ray phase analysis data (Figure 4) the natural zeolite and its cation-substituted forms are characterized by almost identical interplanar distances, but differ from each other in the relative intensities of diffraction lines.

According to the X-ray phase analysis data and to our calculations it was established that the crystallinity degree of each cation varies and fluctuates within the range of 75–80% at the ionic exchange of Nakhchivan natural zeolite.

Thus, we studied for the first time the structure and properties of natural Nakhchivan zeolite – mordenite – and estimated its ion-exchange capacity.

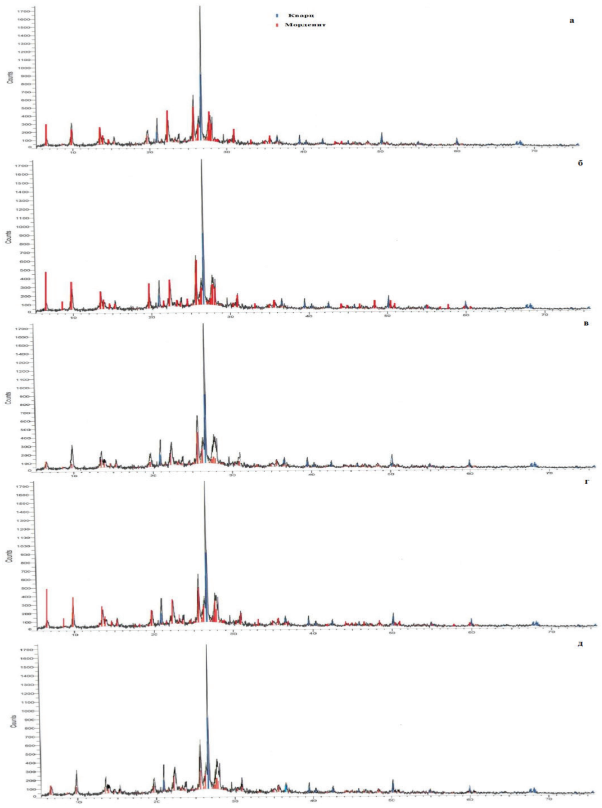

Fig. 4. Diffractograms of cation-substituted zeolite: a – Mg^{2+}, b – Ni^{2+}, c – Sr^{2+}, d – Zn^{2+}, e – Cd^{2+}.

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