

The sorption equilibria in natural zeolite – aqueous solutions systems

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Equilibrium properties of the hydrolysis and ion exchange process have been examined in natural and pre-treated zeolite-clinoptilolite by measuring the concentration of exchangeable Na^+ , K^+ , Ca^{2+} and Mg^{2+} ions with time in the liquid phase. The analysis of the relation of concentrations of ionic species leaving the zeolite and those entering the zeolite structure (H^+ , Zn^{2+}) has found this process to be a non-stoichiometric one. The established non-stoichiometry of the overall mass transfer process through the outer and inner surface of zeolite particles is due to the strength of the bond of exchangeable ions in the structure, as a phenomenon of sorption. The sorption takes place on characteristic locations on the zeolite particle surface, which has been confirmed by SEM images and EDX analysis.

1. INTRODUCTION

Deposits of natural zeolites are a constant object of research due to the complex mineralogical composition and specific structure of zeolites, so that almost daily new processes of application of natural zeolites are discovered and old ones improved, among which the ion exchange takes a prominent position [1]. All natural deposits greatly differ in their mineralogical composition, and minor mineralogical components frequently enhance the application of natural zeolite as raw material in the field of pollution abatement. Namely different physico-chemical effects, as a result of a complex mineralogical composition, almost equally contribute to metal ion uptake from aqueous solutions. The examination of equilibrium properties of the ion exchange process in the natural zeolite sample is important for determination of the stoichiometry and physico-chemical processes on the inner and the outer surfaces of zeolite particles.

2. EXPERIMENTAL SECTION

The natural zeolite-clinoptilolite examined originated from the Croatian deposit, with clinoptilolite content 40-50%. Minor components include illite,

quartz, feldspar, montmorillonite, halite, calcite and ilmenorutile.

A process of hydrolysis and ion exchange of Zn^{2+} ions with natural (PZ) and pre-treated (NaZ) zeolite-clinoptilolite was carried out by means of the batch method, at isothermal and constant hydrodynamic conditions with different contact time of zeolite-aqueous solution. Pre-treatment was performed by equilibration of natural zeolite with the NaCl solution. The hydrolysis and ion exchange process was traced by determination of concentration of exchangeable Na^+ , K^+ , Ca^{2+} and Mg^{2+} ions in the liquid phase for a determined contact time in the zeolite-ion free water system by ion chromatography method. The equilibrium properties of ion exchange were also examined in the zeolite-aqueous solution of the Zn^{2+} ion by determination of concentration in the liquid phase for the contact periods selected by means of atomic absorption spectrophotometry. In all experiments Si is measured spectrofotometrically. The zeolite samples chosen were analysed before and after equilibration by means of scanning electron microscopy (SEM) with energy dispersive X-ray analysis (EDX) on the marked point or line on SEM image.

3. RESULTS AND DISCUSSION

The analysis of results obtained during hydrolysis of samples PZ and NaZ indicates an increase in concentration of all ionic species, where is the Na^+ ion concentration higher than that of K^+ , Ca^{2+} and Mg^{2+} (Figs. 1 and 2). This can be attributed to low hydration energy, which gives the Na^+ ion higher mobility within the crystal structure and thereby higher ion exchange capacity [2]. In the exchange interval examined there are oscillations of certain concentrations, which is due to the batch method conducted process.

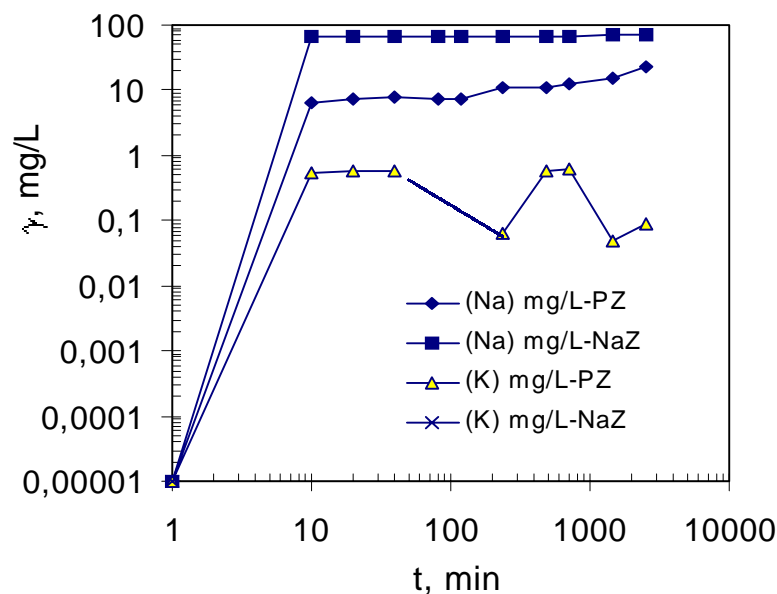


Fig. 1. Increase of concentration of Na^+ and K^+ ions during hydrolysis.

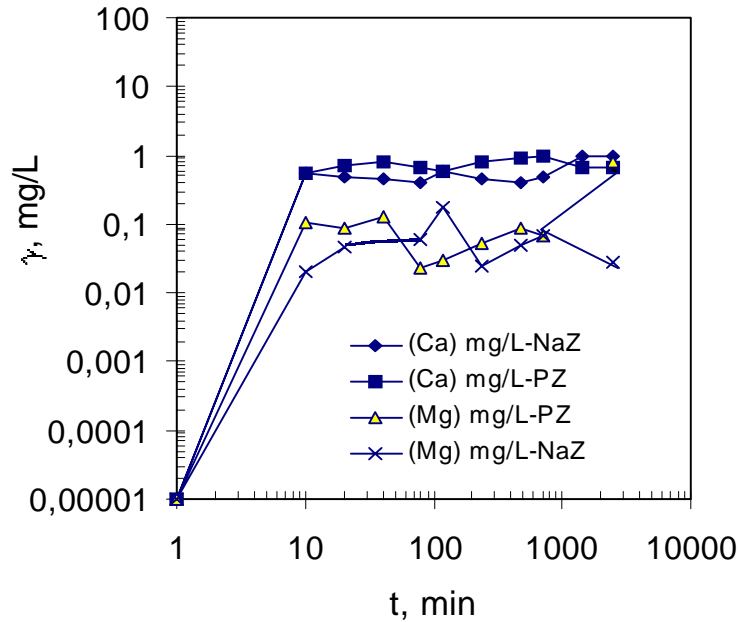


Fig. 2. Increase of concentration of Ca^{2+} and Mg^{2+} ions during hydrolysis.

Exchangeable ions do not achieve equilibrium concentrations, which agrees with the experimentally measured increase of electrical conductivity, although the equilibrium concentration of H^+ ions (constant pH value) is achieved [3]. A tendency of continuous increase in exchangeable Na^+ , K^+ , Ca^{2+} and Mg^{2+} ion concentration has also been recognized during ion exchange process in the NaZ-Zn^{2+} ion solution system, although a constant Zn^{2+} concentration is reached during 500 min. (Fig. 3).

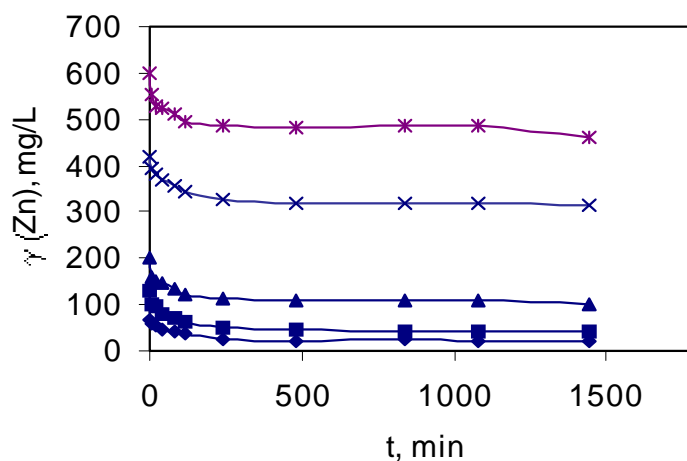


Fig. 3. The amount of Zn^{2+} bound vs. time for different initial concentrations.

This can be contributed to their constant entering solution at different rates, depending on their content in the zeolite structure and on the hydration energy of particular ions [4]. The result of the above mentioned is the non-stoichiometric relation of quantity of exchangeable Na^+ , K^+ , Ca^{2+} and Mg^{2+} ions leaving the zeolite structure and the quantity of the H^+ or Zn^{2+} ion entering the structure during the hydrolysis or ion exchange. This concentration relation has been calculated by establishing a mass balance.

At longer zeolite-aqueous solution contact periods sorption and de-sorption processes take place on the surface, and zeolite particles dissolve partially with simultaneous precipitation of the amorphous silicate component [5,6]. This is confirmed by a continuous slight increase of the concentration of Si in the solution during hydrolysis and ion exchange, as shown in Fig. 4. The phenomenon observed may be considered to be a property of natural zeolite in aqueous solutions.

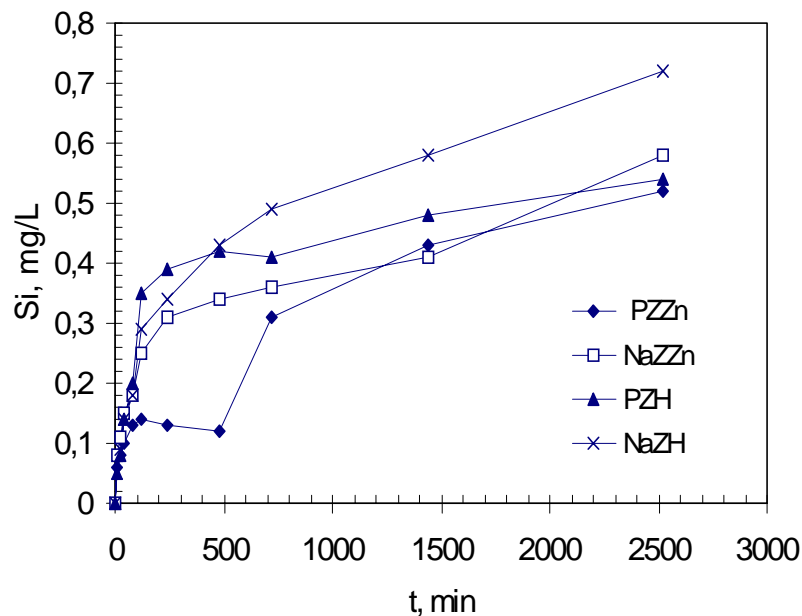


Fig. 4. Increase of concentration of Si during hydrolysis and ion exchange.

The phenomenon of ion exchange and sorption of ionic species from the solution on the surface of the zeolite particle has been proved by SEM micrography of particle

surfaces after pre-treatment and equilibration with zinc ions solution. The SEM image in Fig 5. shows the surface of the grain of zeolite sample with semiquantitative EDX analysis at different points.

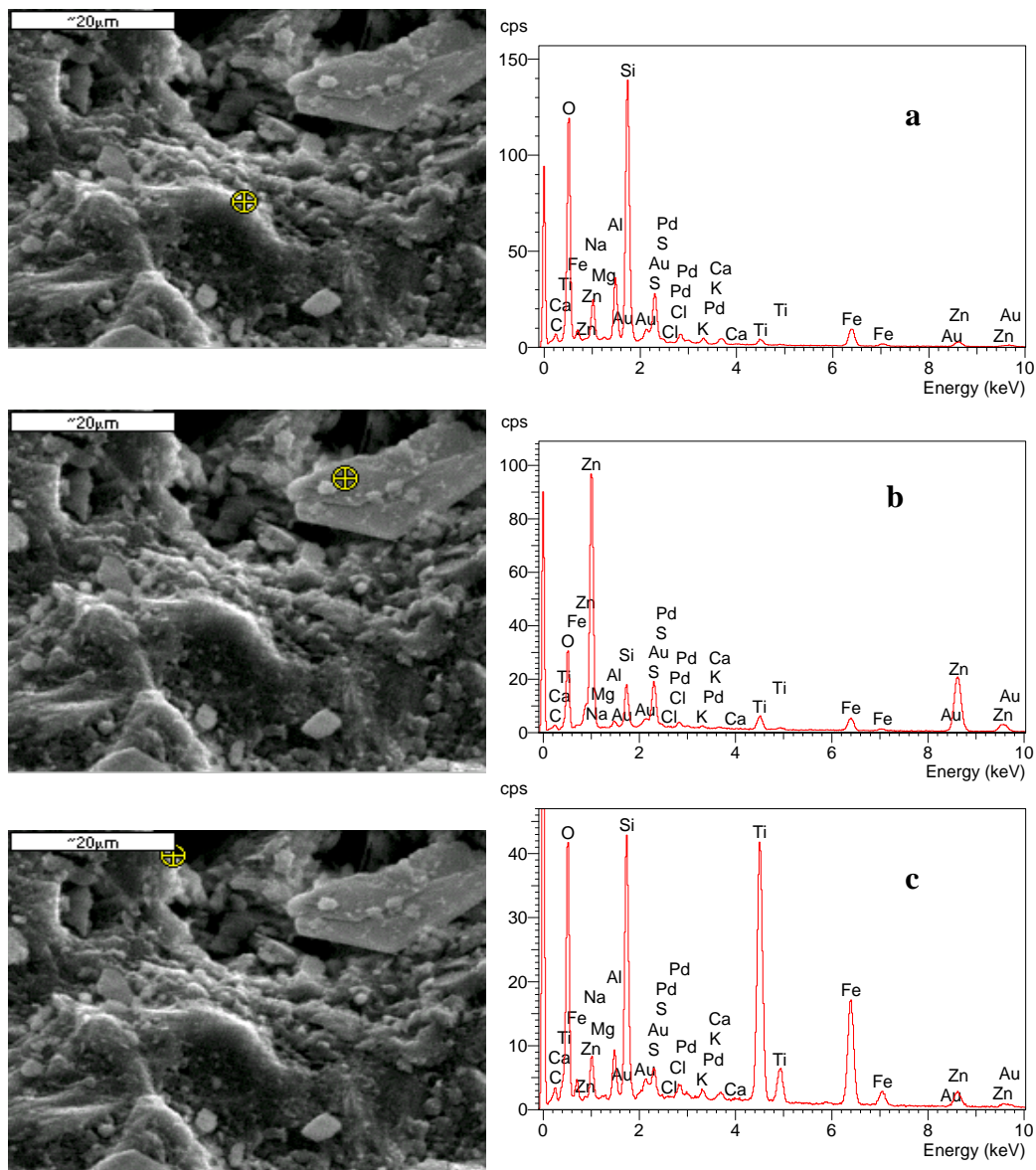


Fig. 5. SEM photomicrograph and EDX analysis at the marked point on the image.

The elementary analysis of the location marked on the image in Fig. 5a has identified Al, Si, O and Zn elements, corresponding to the zinc species bound on the aluminosilicate component. Based on relation of concentration of elements O, Si and Zn, and small concentration of exchangeable cations it can be assumed that zinc is bound by ion exchange. Compared to Fig. 5b zinc is identified in four times higher concentration which can be attributed to sorption process of zinc ionic species on defined points of zeolite particle surface [7,8]. Beside aluminosilicate component (identified Si, Al and O) on Fig. 5c Ti and Fe have been identified corresponding to minor mineralogical component ilmenorutile, and quantity of zinc exchanged is more lesser than in Fig. 5a.

4. CONCLUSIONS

The non-stoichiometric relation of quantity of exchangeable Na^+ , K^+ , Ca^{2+} and Mg^{2+} ions leaving the zeolite structure and the quantity of the H^+ or Zn^{2+} ion entering the structure during the hydrolysis or ion exchange is established by a mass balance. Exchangeable ions in the zeolite enter the solution at different rates, depending on the strength of the bond in the structure and on the number of water molecules coordinated about a single exchangeable cation. Zn^{2+} ions do not reach all free exchangeable positions because of their large hydration radius, i.e. the large number of coordinated water molecules, which agrees with the experimentally determined non-stoichiometric relations between ions bound on the zeolite and the concentration of exchangeable cations entering the solution. The continuous increase in the Si concentration in the solution indicates dissolution of the silicate component in the surface layers of the zeolite particle.

The phenomenon of sorption of ionic species from the solution on the active points on surface of the zeolite particle has been confirmed by SEM micrography of particle surfaces with semiquantitative EDX analysis. The ion exchange and sorption process take place simultaneously, which significantly contribute metal ion uptake from water solutions.

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