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REVERSE EQUILIBRIUM STUDY FOR METAL UPTAKE ON CONDITIONED ZEOLITE

The paper presents a fundamental study of the ion-exchange equilibria for aqueous solutions of isomolar salts of metal ions as well as natural and NH_4^+-converted clinoptilolites.

High preference of clinoptilolite to some metal ions was the reason for carrying out comparative regeneration tests using NaCl solutions. Acid-regenerated clinoptilolite saturated with Cu^{2+} ions proved to be more efficient than alkaline-regenerated samples saturated with NH_4^+ ions in removing metal ions. No changes in X-ray diffractograms were detected after treating zeolite with 0.05 N HCl.

Kinetic measurements of ammonium adsorption by domestic and some foreign clinoptilolites were done in order to evaluate the capacity and simultaneously quality of the samples examined.

1. INTRODUCTION

In a series of recent and earlier papers, there are summarized the sorption and ion exchange properties of major natural zeolites, mainly clinoptilolite, with the emphasis on their most exploitable abilities used for industrial purposes [1]–[4].

In many wastewaters, the concentration of heavy metals is low. In high concentrations, these metals are toxic to activated sludge bacteria, hence they may affect seriously the efficiency of biological wastewater treatment process. For this reason the selectivity of clinoptilolite for a number of heavy metals as well as the preference of clinoptilolite to various cations were investigated.

The present paper reports fundamental measurements of the ion exchange equilibria of the ion pairs such as metal cation – NH_4^+ on a clinoptilolite processed. For this reason, available information both on selectivity of the ammonium form of clinoptilolite to

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various metal ions and metal regeneration technique is unsatisfactory. The results obtained in this study have been compared with those obtained by other researchers.

2. MATERIALS AND METHODS

Clinoptilolite from Nižný Hrabovec, East Slovakia, provided by the Research and Development Company for Ceramics and Perlite, Michalovce, was crushed into sieve size fraction (0.2–0.7 mm). Six other samples of clinoptilolite inside the above range of grain size came from Co-ordinating Authority of the Research Project Ceramic Works, Košice, Slovakia. They are as follows:

Clinoptilolite, Castle Creek, Idaho.
Clinoptilolite, Fish Creek Mountains, Nevada.
Clinoptilolite, Mountain Green, Utah.
Clinoptilolite, Sheaville, Oregon.
Clinoptilolite, Buckhorn, New Mexico.
Clinoptilolite, Dzegvi, Federal Republic of Russia.

Clinoptilolite content in Slovakian zeolitic tuff ranges between 35 and 75%. The tuff investigated in this paper consisted of the following components: clinoptilolite (up to 60%), cristobalite (20–25%), feldspars (10–15%) and quartz (about 5%). Mineralogical determination of these constituents was accomplished using PHILIPS diffractometer (radiation CuK_{α}, voltage 40 kV, intensity 20 mA, Ni-filter, diaphragm 1.021).

Thermoanalytical analysis was carried out on an apparatus DuPont 990 using a TGA 951 modulus, at temperature range of 30–1000 °C, heating rate of 10 °C/min and flow rate of N_2 reaching 1 cm^3/s.

The concentration of ammonium in aqueous phase was determined spectrophotometrically at 420 nm by means of Nessler's method. The concentrations of metal cations (Cu, Zn, Pb, Hg, Cd, Co, Ni) were measured by means of atomic absorption spectrophotometer Perkin-Elmer 403 (USA) using flame technique. Other cations commonly occurring in natural waters (Ca, Mg) were analysed according to classic titrimetry.

The equilibrium studies were carried out using isomolar aqueous solution of such divalent metal salts as $Pb(NO_3)_2$, $Cu(NO_3)_2{\cdot}3H_2O$, $Zn(NO_3)_2{\cdot}6H_2O$, $HgCl_2$, $Ca(NO_3)_2{\cdot}4H_2O$, and $Mg(NO_3)_2{\cdot}6H_2O$. Solutions were prepared in distilled water adjusted to pH of 4 with nitric acid.

NH_4^+-converted clinoptilolite was prepared by exposing about 10 g of zeolite with 1 dm^3 of 10% aqueous solution of NH_4Cl being in contact by intensive mixing during 3 days. Thereafter, conditioned samples were thoroughly rinsed with distilled water, oven-dried at 105 °C to a constant weight and then stored in a desiccator.

Static tests in a lab scale were carried out using a horizontal shaking machine as follows:

One gram of zeolite was placed into a 250 cm^3 plastic container to which 100 cm^3 of particular model solution was added. The bottles were shaken for the sure time intervals and thereafter each sample was analyzed quantitatively for any of the above species.

Laboratory equipment necessary for static and dynamic equilibrium tests was provided by special workshop of WRI*.

3. RESULTS AND DISCUSSION

Introductory comparative study of ammonium adsorption and simultaneous quality determination were carried out using Slovakian clinoptilolite and some foreign samples. The domestic clinoptilolite tuff, represented in figure 1 by usual capacity versus time, was compared with American clinoptilolite from Idaho, because the latter was considered as significant zeolite of higher quality. Active mineral content of the sample from Idaho may be considerably high (80–90%). Ion exchange dynamics in such a clinoptilolite may have been supported by almost nonionic nature of exchangeable cations [5]. In figure 1, the plotted curves were mathematically described by regression computation.

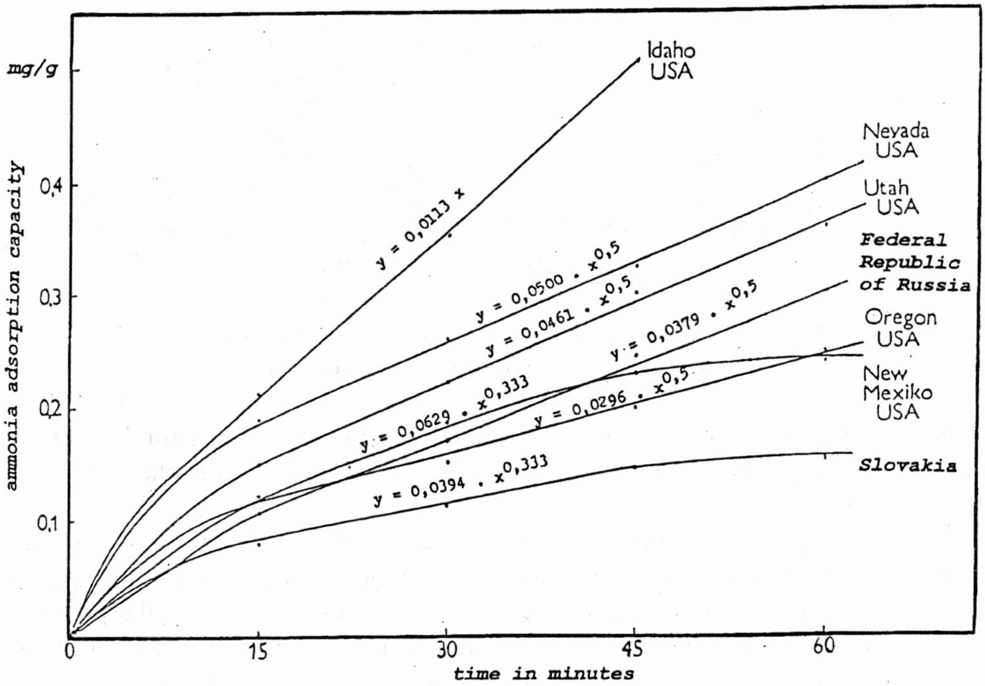

Fig. 1. Ammonia adsorption capacity versus time for the sake of comparing some foreign clinoptilolite samples to domestic one

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*Water Research Institute where the research project was undertaken.

Processed zeolite of clinoptilolite type exhibits selective ion exchange properties for ammonium as well as for certain heavy metals. Some experimental results concerning the ion exchange capacities of clinoptilolite are shown graphically in figures 2 and 3. In order to determine the exchange capacity of clinoptilolite for exchanging each of the chosen cations, static tests were carried out.

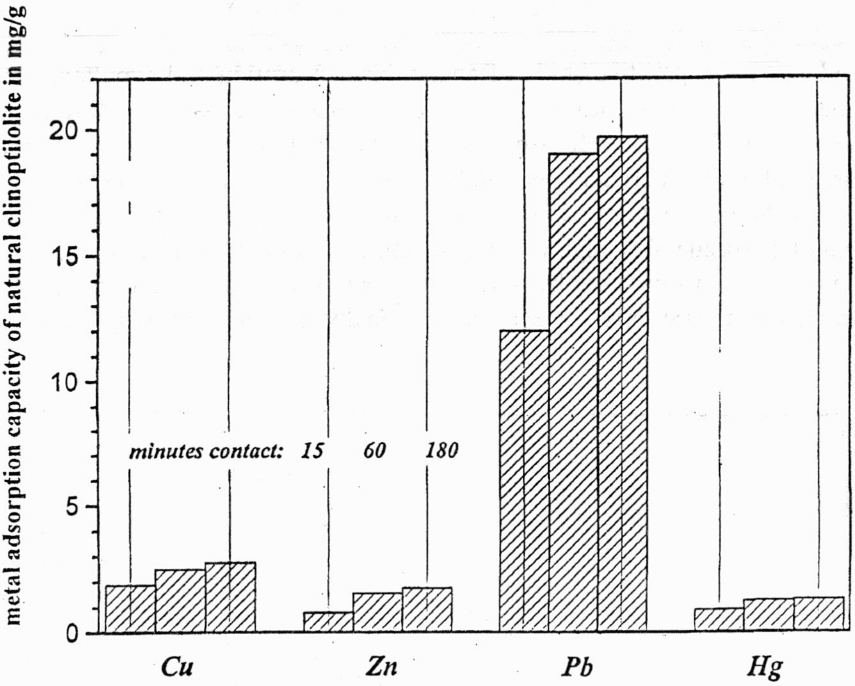

Fig. 2. Increase in the uptake of selected metal cations by clinoptilolite with time in the presence of synthetic water solution

Inspection of figure 2 indicates that the highest metal uptake by natural zeolite was achieved for lead. Significant differences were recorded in relation to the other metals (Hg, Zn, Cu).

Reversible process, in which ammonium ion is exchanged after its passing from the ammonium-converted clinoptilolite to aqueous solution of metal ions (of concentration 10^{-3} mole per liter as in the previous case), corresponds closely with the process of exchange of ions. Nevertheless, affinity of ammonium-converted clinoptilolite for selected metal ions, plotted in figure 3 as kinetic dependence of ammonium elution on time, confirmed adsorption abilities and selectivity of zeolite which can be arranged in the following sequence:

$$\mathrm{Pb} > \mathrm{Cu} > (\mathrm{Zn}) > \mathrm{Hg}.$$

However, if isomolar solutions of metal salts were used, the uptake of metal cations and reciprocal release of ammonium could not be quantified by comparable capacity data. On the basis of the lowest affinity of zeolite for Mg, Ni, Hg and Ca cations we are able to determine the lowest concentration of ammonium which is freed from a sorbed state in zeolite (fig. 3).

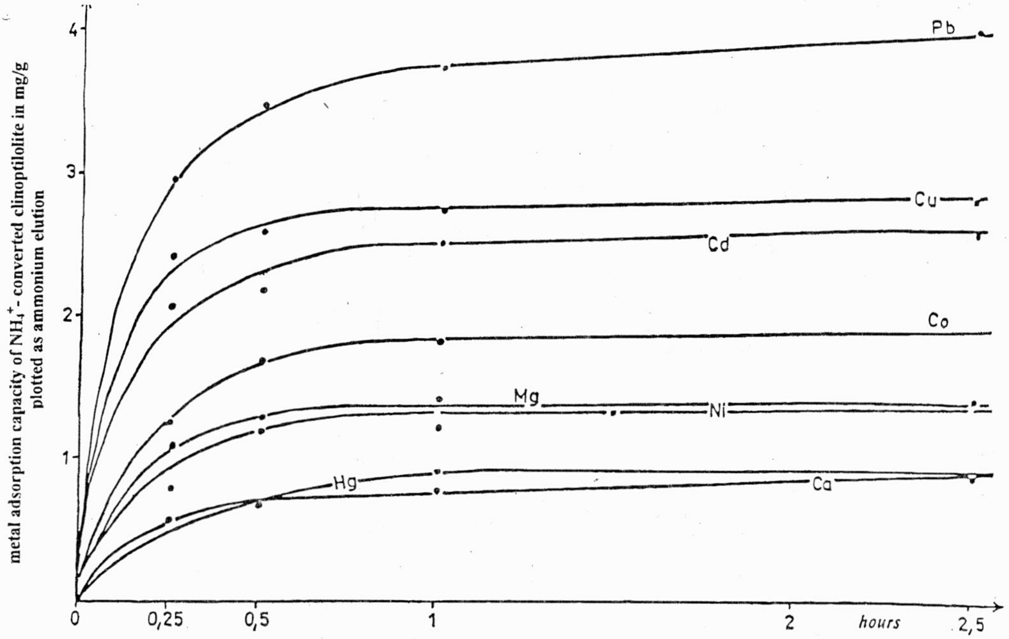

Fig. 3. Ammonium elution from clinoptilolite versus time in the presence of synthetic isomolar metal salt solution

In clinoptilolite, the ratio of silicon to aluminum atoms is approximately equal to 4.3–5.3 which results in weak anionic field within the zeolite. This indicates [1] that the zeolite selectivity is predominantly determined by the free energies of hydration of the competing ions. This statement is in agreement with other papers [5], [6] according to which clinoptilolite shows stronger preference to Pb^{2+} ions (free hydration energy equals −1496 kJ/g) than to Hg^{2+} ions (−2257 kJ/g).

The phenomena observed earlier were investigated in some other way, i.e. exhausted NH_4^+ and Cu^{2+} clinoptilolites were regenerated by means of NaCl solutions of various concentrations. In the case of NH_4^+ clinoptilolite regeneration, highly alkaline brines (2%, 6% and 15%) have been used. The maximum desorption of ammonia by about 10 V/V_0 of NaCl brine is represented by elution curves in figure 4.

Acid-regenerated clinoptilolite samples, saturated with Cu^{2+} ions, were more efficient in removing metal cations, whereas the volume of acid brines necessary for carrying out the regeneration was three times lower than in the above case. The maximum desorption occurred at the bed volume equal to 4 V/V_0. Taking account of the selectivity sequence, it may be stated that clinoptilolite easier ejects metal cations situated at the right positions with respect to ammonium (Cu, Zn, Hg, Ni, Co) than at the left one (Pb) [6]. About 6% solution of NaCl seemed to be satisfactory for regeneration of Cu^{2+} clinoptilolite.

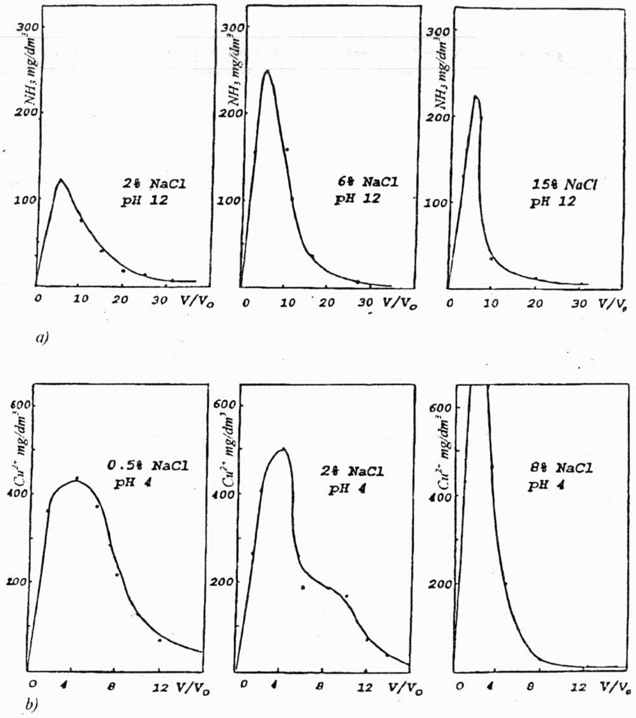

Fig. 4. Regeneration curves of ammonium-exhausted clinoptilolite (a) and Cu^{2+}-exhausted clinoptilolite (b) using NaCl brines

Stationary phase of the Cu^{2+}-regeneration curve is apparently slimmer at 8% solution of NaCl (figure 4b). Opposite, at very low concentrations of NaCl brines, the plot exhibits a diffused phase.

In connection with the acid-regenerated clinoptilolite, some trials of examining the chemical resistance of zeolite in 0.05 N and 2 N hydrochloric acid have been done. Five grams of natural clinoptilolite of the same fraction as above were in contact with 200 cm^3 of diluted HCl during 24 hours. Thereafter the sample was rinsed with water till pH of decantate approached neutral value. X-ray spectra and DTA curves were recorded before and after acid treatment of these samples.

Comparison of both X-ray diffractograms recorded allows us to state that some structure attack and the decrease in peak intensity can be seen in the case of the sample treated with 2N HCl, while no changes appear when clinoptilolite is treated with 0.05N HCl. The spectrum of clinoptilolite activated by means of 0.5N HCl is reflected at characteristic angle of 3.951 Å. This spectrum as characteristic case exhibits lower intensity and is split into two peaks, i.e., 3.934 Å of clinoptilolite reflection and 4.007 Å of anorthite reflection. Anorthite is an accompanying mineral.

Due to thermogravimetric analyses some changes in the sample weights were stated. At the DTA curve endothermic effects at 140 °C were recorded (figure 5b).

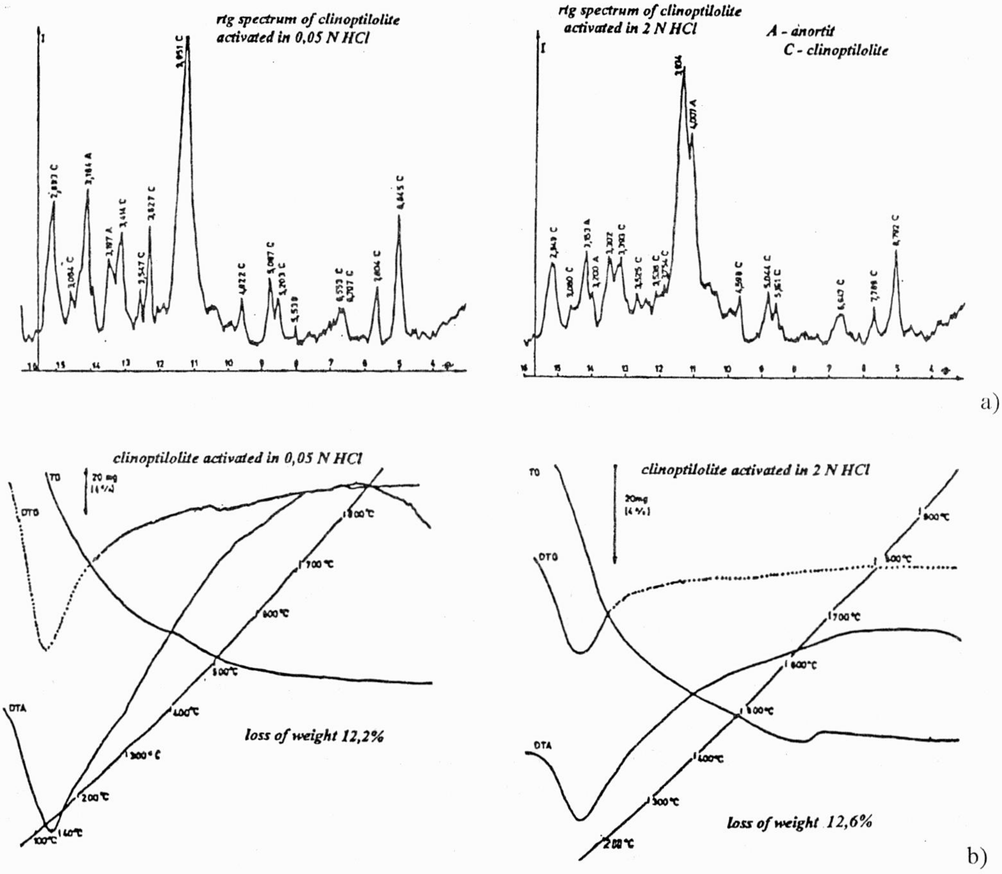

Fig. 5. Diffractograms of natural clinoptilolite conditioned in 0.05N HCl and in 2N HCl (a), and thermogravimetric analyses of the above acid-conditioned samples (b)

4. CONCLUSIONS

Based on the results obtained the following conclusions can be drawn:

1. Clinoptilolite may be a useful ion exchanger for Pb^{2+} and NH_4^+.

2. Samples of clinoptilolite from various deposits of the world were found to have effective ammonium exchange capacities; they are, however, different from those of the domestic clinoptilolite tested.

3. The zeolite examined exhibits resistance to 0.05N HCl which may enable us to apply low acid concentrations (pH = 4) in order to regenerate metal-exhausted clinoptilolite.

4. The rate of ammonium release into isomolar aqueous solutions of salts with metal ions can be arranged according to the following ascending order: Pb > Cu > Cd > Co > Mg > Ni > Hg > Ca.

REFERENCES

[1] SEYFARTH M.C., *The selectivity of clinoptilolite for certain heavy metals*, M.Sc. Thesis, University of Illinois, Urbana, Illinois 61801, USA, 1975.

[2] BLANCHARD G., MAUNAYE M., MARTIN G., *Removal of heavy metals from waters by means of natural zeolites*, Water Research, 1984, 18, 12, p. 1501.

[3] YOSHIDA H., KURATA A., SANGA S., *Removal of heavy metal ions from wastewater using zeolite*, Mizu Shori Gijutsu, 1976, 17, pp. 219–226.

[4] ZAMZOW M.J. et al., *Removal of heavy metals and other cations from wastewater using zeolite*, U.S. Bureau of Mines, Reno, NV, 6th Symposium on Separation Science and Technology for Energy Application, Knoxville TN, 1989.

[5] BRECK D.W., *Zeolite molecular sieves*, J. Wiley and Sons, New York, 1974, p. 771.

[6] SHERMAN J.D., *Ion exchange separations with molecular sieve zeolites*, 83rd National Meeting, Institute of Chem. Engineers, Houston, Texas, March 20–24, 1977.

ODWRÓCONA RÓWNOWAGA W CZASIE ADSORPCJI METALI NA REGENEROWANYM ZEOLICIE

Przedstawiono podstawowe badania na temat równowag wymiany jonowej w wodnych roztworach jonów metali i naturalnie regenerowanych za pomocą NH_4^+ klinoptilolitów.

Duża selektywność klinoptilolitu w stosunku do jonów metali była przyczyną przeprowadzenia porównawczych testów regeneracji z wykorzystaniem roztworów NaCl. Klinoptilolit zregenerowany kwasem i nasycony jonami Cu^{2+} okazał się wydajniejszy w usuwaniu jonów metali niż zregenerowany zasadą i nasycony jonami NH_4^+. W rentgenowskich dyfraktogramach nie wykryto żadnych zmian po potraktowaniu zeolitu 0,05 N HCl.

Pomiarów kinetycznych adsorpcji amoniaku przez klinoptilolity pochodzenia krajowego i zagranicznego dokonano, aby ocenić pojemność i jednocześnie jakość badanych próbek klinoptilolitów.