

SORPTION OF ^{137}Cs AND ^{60}Co BY CHEMICALLY TREATED CLINOPTILOLITE AND MORDENITE

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Abstract: Influence of a NaOH solution on the exchange ability of clinoptilolite and mordenite with regard to Cs^+ and Co^{2+} have been studied by a radiochemical method. The sorption coefficients were calculated, the total cation exchange capacity and the X-ray structural analysis were measured as well. The experiments were carried out with samples of Slovak clinoptilolite and mordenite.

Key words: clinoptilolite, mordenite, sorption ability of Cs^+ - Co^{2+} .

Introduction

Effect of a NaOH solution on the ion - exchange ability of clinoptilolite towards to Co^{2+} and Cs^+ was described in our previous papers (Hložek et al. 1992; Lukáč et al. 1990, 1992). Clinoptilolites were treated with the NaOH solutions of different concentrations and their sorption abilities towards Cs and Co were investigated. Cs^+ and Co^{2+} are the dominant constituents of nuclear waste waters. It was shown that clinoptilolite is an excellent ion-exchange material for Cs (Ames 1960; Barrer & Munday 1971; Sherry 1968). The applications of this clinoptilolite for the removal of ^{137}Cs from medium and light level radioactive waters were reported in the early seventies (Kato 1974; Dyer et al. 1973). On the other hand, clinoptilolite and mordenite are very poor ion-exchanger for Co (Kožač et al. 1982; Pekár & Timulák 1985). There is a lack of data concerning of the chemical improvement of the ion exchange ability of clinoptilolite (Hložek et al. 1992; Lukáč et al. 1990, 1992) and mordenite except for the study by Goto et al. (1982). In these papers promising results on the improvement of clinoptilolite ion-exchange ability due to the NaOH solution treatment have been reported.

We present here the results on the properties of clinoptilolite and mordenite treated with NaOH solutions of different concentration and the concomitant changes of sorption ability and the surface and structural characteristics of the materials.

Experimental

The experiments were carried out with Slovak clinoptilolite from Nižný Hrabovec and mordenite from Bartošova Lehôtka. The granularity of the materials was within the range of 1.2 - 2.2 mm. The samples were treated with NaOH solutions of the following concentrations: 0.25, 0.5, 1.0, 2.0, 4.0 M; the temperature of treatment was 80 °C and the time of treatment was 4 hours. After decantation the samples were dried at 105 °C. The method of a model radioactive solution (Hložek et al. 1992a) was applied to determine the sorption coefficient of the treated

clinoptilolite and mordenite, natural clinoptilolite and mordenite, and the synthetic ion exchanger Ostion (the copolymer of polyester and divinyl with maximum capacity about 4 mg/g). The method is as follows: to a vessel containing 100 ml of the 0.05 M solution of Co^{2+} labeled with ^{60}Co or the Cs^+ solution labeled with ^{137}Cs the 0.5 g samples of clinoptilolite or mordenite were added. Then the radioactivity of the solutions was measured. After 24 hours the radioactivity was determined again and an additional 0.5 g of the sample was added. These steps were repeated until total of 10 g of sorbent was added.

Also, some surface characteristics of these materials were measured:

- the total specific surface (S_{BET}), the surface of mesopores of diameters 2 - 50 nm (S_{MESO}) and the volume of micropores (V_{MIC}) were measured by the static volume method of N_2 adsorption at the temperature of liquid nitrogen;
- the total ion-exchange capacity (CEC) was determined by the static method;
- the crystal lattice changes of modified clinoptilolite and mordenite were determined by the X-ray structural analysis.

Results and discussion

The chemical treatment of clinoptilolite and mordenite substantially affected their ion-exchange ability which is clearly visible from the sorption coefficient values. Fig. 1 shows the dependence of the model solution radioactivity labeled with ^{60}Co on the amount of added clinoptilolite. Fig. 2 shows a similar dependency of added mordenite. Very similar curves were obtained for the Cs solution labeled by ^{137}Cs . Both figures show the effect of the NaOH treatment on the sorption ability of both materials. It is clear from Fig. 1 that the sorption ability of clinoptilolite treated with 4 M NaOH solution is very close to the sorption ability of synthetic sorbent. From this, curves of the sorption coefficients of clinoptilolite and mordenite for Co as well as Cs were calculated. Fig. 3 shows the clinoptilolite and mordenite sorption coefficients for Co plotted as a function of the molar concentration of NaOH used for the chemical treat-

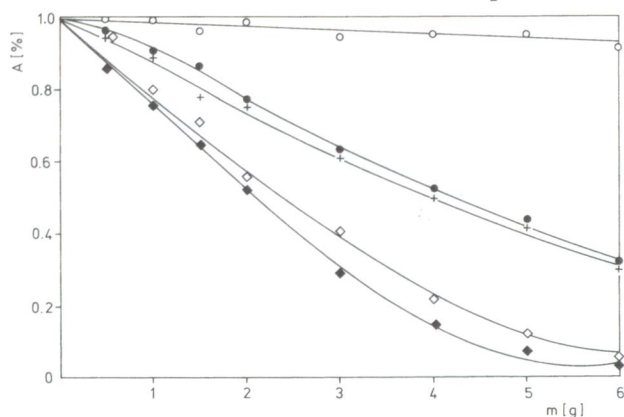


Fig. 1. Decrease of radioactivity of Co^{2+} model solution after adding the absorbent (clinoptilolite).
 o - natural clinoptilolite; ● - clinoptilolite modified by 1M NaOH solution; + - modified by 2M NaOH solution; ◇ - modified by 4M NaOH solution; ◆ - synthetic sorbent Ostion.

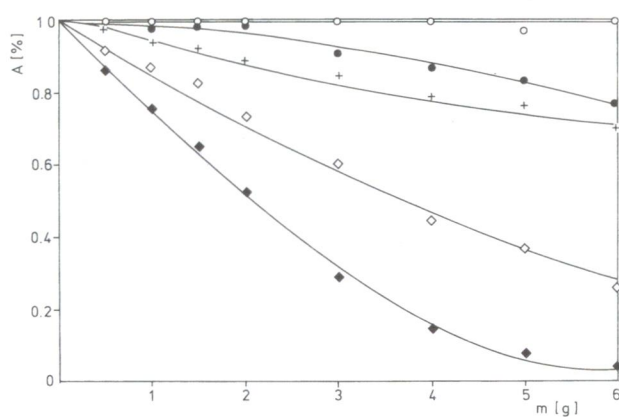


Fig. 2. Decrease of radioactivity of Co^{2+} model solution after adding the absorbent (mordenite).
 o - natural mordenite; ● - mordenite modified by 1M NaOH solution; + - modified by 2M NaOH solution; ◇ - modified by 4M NaOH solution; ◆ - synthetic sorbent Ostion.

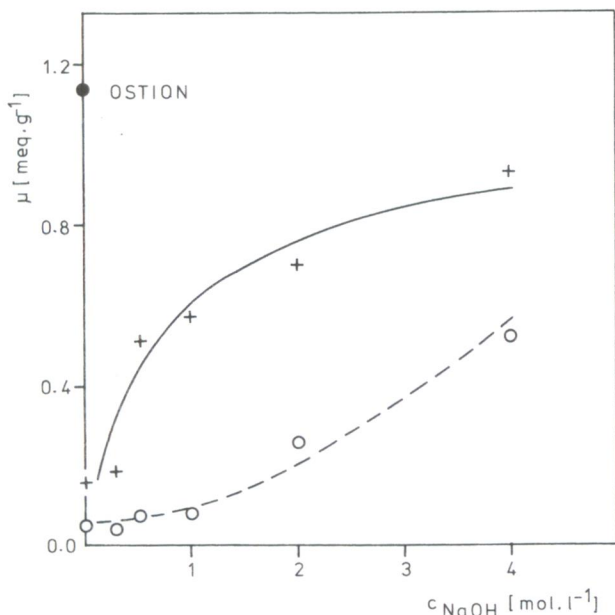


Fig. 3. Dependence of sorption coefficients μ_{Co} of modified clinoptilolite and mordenite on NaOH concentration. Solid line corresponds to μ_{Co} of clinoptilolite, dashed line corresponds to μ_{Co} of mordenite.

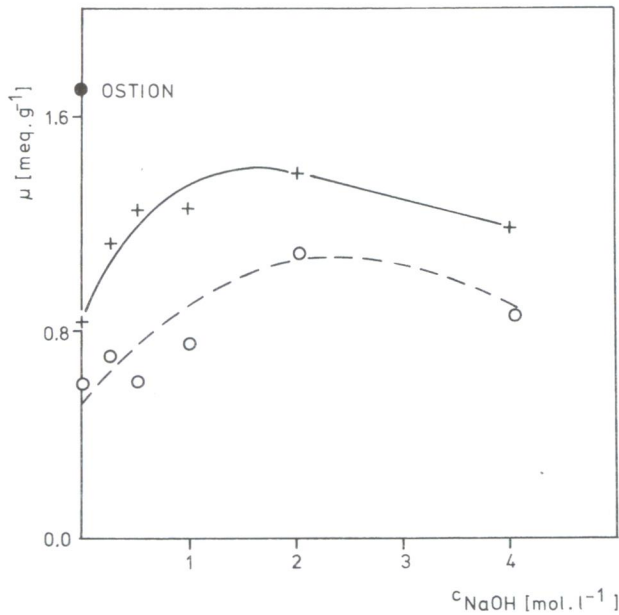


Fig. 4. Dependence of sorption coefficient μ_{Cs} of modified clinoptilolite and mordenite on NaOH concentration. Solid line corresponds to μ_{Cs} of clinoptilolite, dashed line corresponds to μ_{Cs} of mordenite.

ment. Similarly, Fig. 4 presents the changes of clinoptilolite and mordenite sorption coefficient for Cs. The sorption coefficient for Co was found to increase with the NaOH concentration (Fig. 3). On the other hand, the clinoptilolite and mordenite modified with a solution of a lower NaOH concentration (about 0.5 M) demonstrates the highest sorption ability for Cs (Fig. 4). Both figures indicate that the sorption coefficients are higher for clinoptilolite than mordenite. This fact can be accounted for by a higher content of an active component in clinoptilolite as compared with that in mordenite and that component manifests very similar behaviour in both minerals. The treatment of the materials with sodium hydroxide solutions resulted in a steady destruction of their crystalline lattice in the same formation of zeolite Na - P is demonstrated by their X-ray spectra diffraction pattern (Figs. 5, 6). The most profound loss of the crystallinity was observed at the highest concentration of NaOH.

The structure changes of both tuffites due to treatment with NaOH solutions were corroborated also by the variation of surface characteristics such as S_{BET} , S_{MESO} and V_{MIC} . At low concentrations of NaOH the modification of the crystal structure is not very pronounced and the observed variation of the specific surfaces and the micropore volumes are accounted for mainly by the formation of a monocation lattice. Here the exchangeable cations, e.g. K^+ , Ca^{2+} , Mg^{2+} , were replaced with the Na^+ cation. Presumably, the presence of this smaller cation in zeolite channel network affects the surface characteristics of the adsorbents. This assumption is supported by the decrease of volumes of typical zeolitic micropores (0.3 - 1 nm) V_{MIC} . Both materials manifested an increase of the ratio of $S_{\text{MESO}}/S_{\text{BET}}$ with the increase of NaOH concentration (S represents the specific surface of mesopores having their diameters between 2 to 30 nm and it was obtained by using the method of t - straight line). However, the

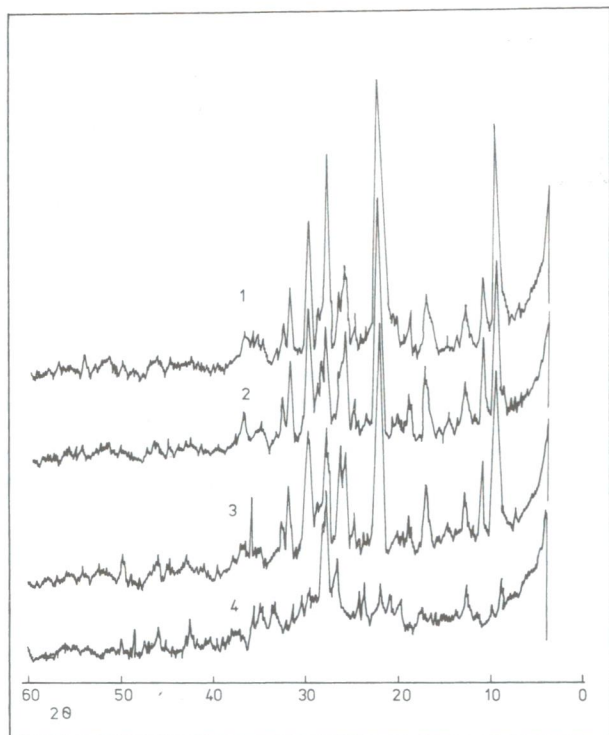


Fig. 5. X-ray diffraction pattern of modified and original clinoptilolite. 1 - original clinoptilolite, 2 - clinoptilolite modified with 1M NaOH solution, 3 - clinoptilolite modified with 2M NaOH solution, 4 - clinoptilolite modified with 4M NaOH solution (Rad. $\text{CuK}\alpha$).

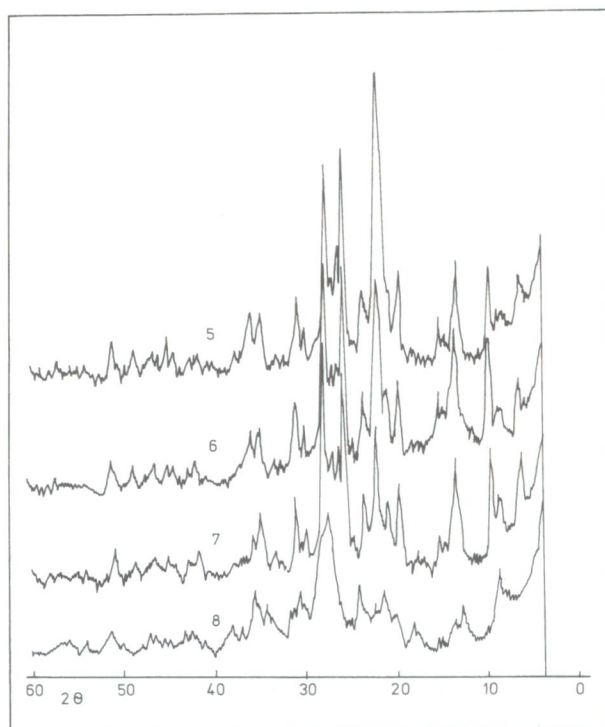


Fig. 6. X-ray diffraction pattern of modified and original mordenite. 1 - original mordenite, 2 - mordenite modified with 1M NaOH solution, 3 - mordenite modified with 2M NaOH solution, 4 - mordenite modified with 4M NaOH solution (Rad. $\text{CuK}\alpha$).

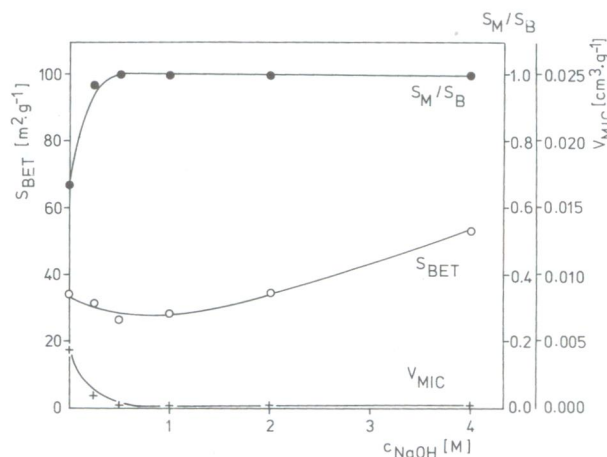


Fig. 7. Dependence of S_{BET} , $S_{\text{MESO}}/S_{\text{BET}}$ and V_{MIC} of modified clinoptilolite on NaOH concentration.

○ - S_{BET} ; ● - $S_{\text{MESO}}/S_{\text{BET}}$; + - V_{MIC} .

shape of plots of S_{BET} and S_{MESO} against the concentration of NaOH is different for each sorbent. In the case of clinoptilolite (Fig. 7) the values of both S and S reach their maximum value of $53 \text{ m}^2 \cdot \text{g}^{-1}$ and $54 \text{ m}^2 \cdot \text{g}^{-1}$ respectively, at the highest concentration of NaOH (4M). For the mordenite (Fig. 8), the value of both parameters decreases steadily with the NaOH concentration. The value of S_{BET} drops from its original $76 \text{ m}^2 \cdot \text{g}^{-1}$ down to $25 \text{ m}^2 \cdot \text{g}^{-1}$ and that of S_{MESO} from $35 \text{ m}^2 \cdot \text{g}^{-1}$ to $19 \text{ m}^2 \cdot \text{g}^{-1}$. One may conclude, therefore, that the overall effects of the treatment on the surface characteristics is similar for both materials, i.e. the $S_{\text{MESO}}/S_{\text{BET}}$ ratio reaches the same value at the highest NaOH concentration.

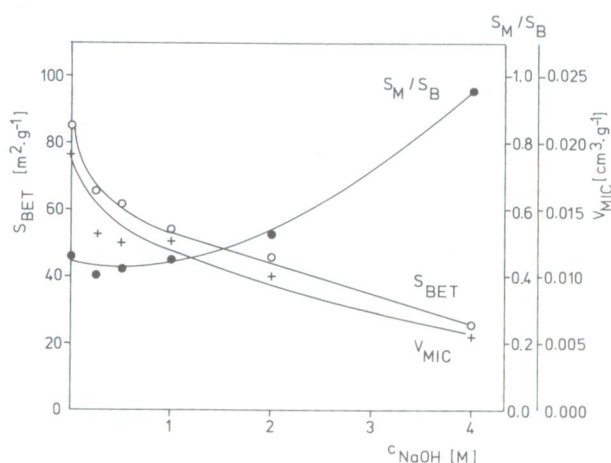


Fig. 8. Dependence of S_{BET} , $S_{\text{MESO}}/S_{\text{BET}}$ and V_{MIC} of modified mordenite on NaOH concentration.

○ - S_{BET} ; ● - $S_{\text{MESO}}/S_{\text{BET}}$; + - V_{MIC} .

However, the treatment affects the specific surfaces of each material in different way. This results probably from a different content of zeolitic phase in each material as well as from different properties of the original materials. Another important characteristic of these materials is the value of Cation Exchange Capacity (CEC) ($\text{meq NH}_4^+/\text{g}$ of adsorbent) i.e. the total amount of exchange cations. Unlike for mordenite where the CEC value increases steadily, with NaOH concentration (Fig. 9), the CEC determined for clinoptilolite shows a minimum at 0.25 - 0.5 concentration of NaOH solution.

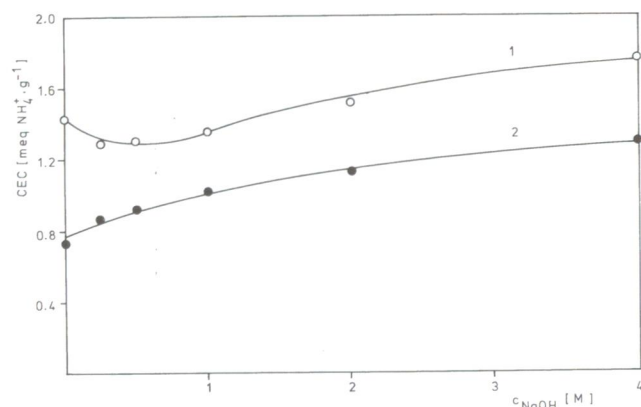


Fig. 9. Plot of CEC of treated clinoptilolite and mordenite vs. modifying NaOH concentration.
1 - clinoptilolite, 2 - mordenite.

Conclusion

We have investigated the chemical and physical properties of clinoptilolite and mordenite treated with NaOH solution. The chemical treatment caused excessive changes in their crystal lattice. These changes probably reflect the changes in the ion-exchange ability and in the above mentioned physical characteristics. The presented results indicate that the changes of physical and chemical properties of the material are affected by some factors depending on the NaOH concentration such as:

- cation modification of clinoptilolite and mordenite to a sodium form by Na^+ cations;
- step by step crystal lattice destruction caused by the treatment with NaOH solution.

Chemical treatment of the materials with a low concentration NaOH solution induces transformation of the polycationic form of clinoptilolite and mordenite to the sodium form. On the con

trary, treatment at the high NaOH concentration show that the dominant effect of NaOH is the transformation of crystal structure into an amorphous one. The above treatment of clinoptilolite and mordenite resulted in absorbents with higher sorption capacity than the original materials.

References

- Ames L. L., 1960: Zeolit extraction of casium from aqueous solution. *Amer. Mineral.*, 45, 689.
- Barrer R. M. & Munday B. M., 1971: Cation exchange reactions of zeolite Na-P. *J. Chem. Soc.*, 2909.
- Dyer A., Phillips G. O. & Townsed R. P., 1973: Synthetic zeolites as models for biological systems. *J. Chem. Soc. Farad. Trans.*, 71, 803.
- Goto Y., Matsuzawa J. & Matsuda S., 1982: Removal of cesium and strontium by natural zeolites and the improved zeolites from aqueous solution and their fixation in zeolites *Dev. Sedimentol.*, 35, 489.
- Hložek P., Lukáč P. & Foldesová M., 1992: Influence of some cations on the sorption ability of modified clinoptilolites. *J. Radioanal. Nucl. Chem., Lett.*, 164, 109.
- Hložek P., Foldesová M. & Lukáč P., 1992: Study of NaOH-treated clinoptilolites and their physical and ion-exchange characteristics with regard to Cs and Co. *J. Radioanal. Nucl. Chem., Lett.*, 165, 175.
- Kato K., Shiba M. & Okamoto J., 1974: Properties of synthetic zeolite. *Hoken Butsuri*, 9, 11.
- Kozač J., Očenáš D., Rusnák D., Hoffman J. 1982: Mineralogy, properties and utilization possibilities of zeolitic tuffites from Nižný Hrabovec (eastern Slovakia). *Miner. slovac*, 14.
- Lukáč P., Foldesová M. & Hložek P., 1990: Study of the sorption ability of zeolite tuffite using the standard solutions with regards of Co and Cs. *J. Radional. Nucl. Chem., Lett.*, 36, 186 (in Slovak).
- Lukáč P., Foldesová M. & Hložek P., 1992: Sorption ability of chemically treated clinoptilolites with regard to cobalt and cesium. *J. Radional. Nucl. Chem., Lett.*, 164, 241.
- Pekár A. & Timulák J., 1985: Applications of zeolite tuffite for cementation of radioactive concentrates. *Jaderná energie*, 31, 128 (in Slovak).
- Sherry H., 1968: Ion-exchange properties of zeolites. III. Rare earth ion-exchange of synthetic fanjasites. *Inorg. Nucl. Chem.*, 31, 2599.