

# CHEMICALLY MODIFIED ZEOLITES: SURFACES AND INTERACTION WITH Cs AND Co

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## Abstract

Inorganic exchangers, including zeolites, have interesting properties such as resistance to decomposition in the presence of ionizing radiation or to high temperatures, what make them applicable for the purification of low and middle polluted radioactive waste waters. The research was focused on model radioactive waste effluents and the investigated metals were cobalt (Co) and cesium (Cs). The performance of natural zeolite of clinoptilolite type and zeolite chemically modified with NaOH solutions was determined by studying their surface and sorption properties using volumetric method and static radioindicator method. The measurements of zeolite's surfaces showed the double increase of the specific surface along with an increase of mesopore's diameter. The reason is the extraction of silicon from zeolite caused by NaOH solution what creates secondary mesoporous structure. The radioactive tracer technique was used to evaluate sorption properties of zeolites and the best sorbent was selected based on  $K_D$ ,  $\mu$ ,  $\Gamma$  and  $S$  values. The sorption abilities of natural and chemically modified zeolites for Cs uptake were comparable. The uptake of Co with natural zeolite was negligible and it increased up to 14 times for modified zeolites depending on the concentration of treated NaOH solution.

**Key words:** Zeolite, Chemically modified zeolite, Surface and sorption properties, Volumetric method, Radioindicator method

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## 1. Introduction

Natural microporous materials - zeolites occur in various geological environments and soil formations. Their crystal structure is characterized by the presence of intracrystal micropores (channels or interlayer void spaces) providing high microporosity. Primary building units are  $(Al, Si)O_4$  tetrahedra. When  $Al^{3+}$  substitutes  $Si^{4+}$  in the central cation position of the tetrahedron, a net-negative charge is generated and this charge is balanced by monovalent and divalent cations. Zeolites have an ability to exchange most of their constituent cations without major change of the structural framework [1-2]. The areas of application for natural zeolites (diameter of cavities less than 2 nm) are well defined. Nowadays, ecological problems initiate studies of new materials, among witch can find altered zeolites with new and unique properties gained by a chemical modification. Chemical modification is utilized as a main tool to increase sorption capacity of natural zeolites. Typically one uses ion exchange, which transforms zeolite into a monocation form, for example modification of Na-zeolite, by hydroxides or salts. In this process Si is extracted from Al-Si framework structure of zeolite and properties like sorption capacity, surface changes, capacity activity etc. can change [3]. The investigation of the interaction between Cs or Co cations and natural or chemically modified zeolites can be subject of special importance for the nuclear industry because these cations are dominant radionuclides in low and middle radioactive waste waters. Natural and chemically modified zeolites can be one of the alternatives for separation of these cations, since they offer high capacity, good selectivity, radiation resistance and compatibility with glass and cement [4].

Within the content of this work, the changes in the surface and in the sorption capacity of natural and chemically modified zeolites were studied by the volumetric method and by the static radio indicator method.

## 2. Material and methods

Natural zeolite of clinoptilolite type from deposit Nižný Hrabovec (NH), Slovakia was used for the experiments [5-6]. The zeolitic material was sieved to obtain grains of size 1.5-2.5 mm. Some samples of the zeolite were put into Na form after pretreatment with 2 or 4 mol/L NaOH solutions (in the subsequent text only NH2M, NH4M). Both natural and chemically modified zeolites were explored using various techniques and results were reported in our previous papers [7-11].

The structure changes caused by NaOH solution were analyzed by the variation of surface characteristics such as  $S_{\text{BET}}$  (specific surface calculated by BET method),  $St$  (specific surface of mesopores+external surface was obtained by using the method of t-plot),  $V_{0,98}$  (volume of pores recounted to the liquid nitrogen) and  $D_p$  (diameter of mesopores). The exact procedure was presented in [12-14].

The sensitive analytical technique for the study of the sorption of natural materials is the usage of radioisotope tracers to label the corresponding cation. The exchange behavior between natural zeolite or zeolitic systems containing  $\text{Na}^+$  and  $\text{Cs}^+$  or  $\text{Co}^{2+}$  cations in solution was studied by the static radioexchange tracer technique [15]. Quantitative information about the replacement of cations can be obtained by an increase of the solution's radioactivity in time. Individual solutions were prepared by dilution of corresponding initial stock solutions labeled with the appropriate radioactive tracer  $^{137}\text{Cs}$  or  $^{60}\text{Co}$ . Then 200 mg of zeolitic materials were individually mixed with 15 mL of labeled solutions for 24 hours. Then the radioactivity of 5 mL of supernatant was measured by gamma-ray spectrometry using NaI(Tl) detector. The radioactivity of loaded zeolites was measured using the same technique. The sorption coefficient  $\mu$ , distribution coefficient  $K_D$ , sorption capacity  $\Gamma$  and percent of sorption values  $S$  were calculated according to known equations for studied zeolitic materials [16].

## 3. Results and discussion

As shown in Fig. 1, at the concentration 2M NaOH the modification of the surface is not very substantial and it is mainly provoked by the formation of a monocation lattice. Here the exchangeable cations, e.g.  $\text{K}^+$ ,  $\text{Ca}^{2+}$  etc. were replaced with  $\text{Na}^+$  cation. Presumably, the presence of this smaller Na cation in the zeolite's framework affects the surface characteristics of zeolite. This assumption statement is supported by an increase of the specific surface, ratio  $S_t/S_{\text{BET}}$ , total volume of pores and diameter of pores depending on the concentration of NaOH. For example, the specific surface  $S_{\text{BET}}$  attains the maximum value 55.7  $\text{m}^2/\text{g}$  at the concentration 4M NaOH. The results suggest that the chemical modification of zeolite causes changes of surfaces, induces the extraction of silicon from the zeolite framework and consecutively the constitution of secondary mesoporous structure. Tab. 1 and Tab. 2 list computed sorption characteristics of explored zeolites obtained by means of sorption of Cs or Co cations from the labeled solutions.

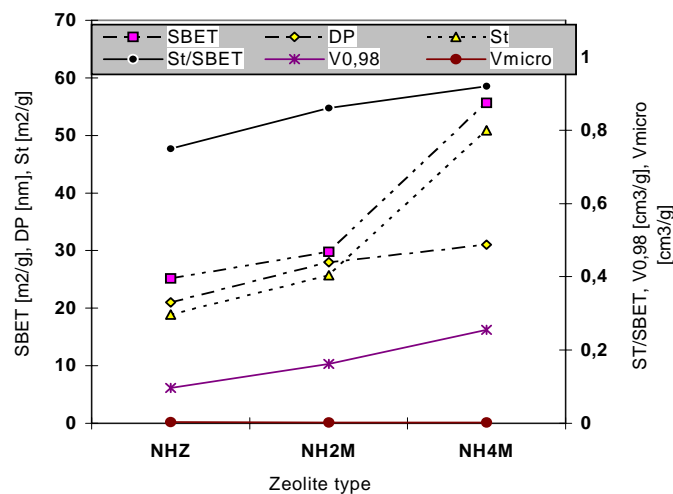


Fig. 1 Surface characteristics of investigated zeolites

Tab. 1 Sorption characteristics for the sorption of Cs from model aqueous solution

zeolite	S	$K_D$	$\mu$	$\Gamma$
	[%]	[ml/g]	[mg/g]	[mmol/g]
NHZ	27.4	64.99	572.5	0.430
NH2M	47.6	112.90	953.0	0.717
NH4M	43.,4	102.94	868.9	0.654

Tab. 2 Sorption characteristics for the sorption of Co from model aqueous solution

zeolite	S	$K_D$	$\mu$	$\Gamma$
	[%]	[ml/g]	[mg/g]	[mmol/g]
NHZ	1.90	2.86	42.0	0.139
NH2M	10.3	17.13	228.0	0.769
NH4M	27.3	56.40	603.0	2.049

The higher cesium uptake was achieved using pretreated zeolites NH2M or NH4M, but it was comparable to the uptake of the natural zeolite. The uptake of Co by natural zeolite was negligible. Thus, we can conclude that in this case the hydration of cobalt cations and the creation of bulky Co-hydrated cations have a significant effect on the sorption. The uptake of Co by NH2M and NH4M was 5.4 and 14 times higher, respectively than the sorption of natural zeolite. It should be mentioned that the chemical interaction of the analyzed zeolites with Co cations strongly depends on the structural properties such as size of channels and framework density, as well as on the chemical composition of zeolite and chemical speciation of Co cation.

In waste solutions there are phenomena which influence ion exchange, such as hydrolysis, dissolved carbon dioxide, competing cations and also process of modification. These factors have usually a negative effect on the performance of an ion exchanger but sometimes, after pretreatment, they create more favorable conditions for metal sorption. Collected data are not complete and cannot be applied to model surface or ion exchange equilibria but they come in useful for the sorption of Co and Cs from waste waters or radioactive waste waters by chemically modified zeolites.

#### 4. Conclusions

Experimentally obtained data lead to the following conclusions:

- chemical modification of the zeolite of clinoptilolite type with NaOH solutions (2 or 4 mol/L) caused changes of zeolite's surface –an increase of the specific surface and the amount of meso and even macropores as a result of the extraction of silicon and consequential creation of the secondary mesoporous structure
- sorption abilities of natural and chemically modified zeolite for Cs uptake were comparable
- uptake of Co by natural zeolite was negligible. The high apparent increase of the sorption ability of Co by chemically modified zeolites is the result of the extraction of Si from zeolite lattice and the creation of secondary mesoporous system after NaOH treatment, allowing the sorption of bulk Co-hydrated cations. This effect depends on the concentration of treating NaOH solution.
- the results reported in this paper support the possibility of removal Cs and especially Co (including radionuclides  $^{137}\text{Cs}$  and  $^{60}\text{Co}$ ) from waste waters by an application of Na-zeolites.

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