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STUDY OF PHYSICAL AND THERMOCHEMICAL PROPERTIES OF MODIFIED ZEOLITES

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Abstract

The treatment of zeolite with a solution of NaOH at different concentrations creates modified forms of natural zeolites.

These modified zeolites exhibit an increased uptake of caesium and a satisfactory uptake of cobalt. The structural changes in the modified zeolites were studied by XRD analysis, which reveals the mineral compositions of the studied materials. The thermodynamic properties of the modified zeolites were studied by means of DTA and thermogravimetry, and the chemical composition too was determined.

Keywords: sorption of Cs and Co, thermochemical properties, zeolite

Introduction

Nuclear power stations produce huge amounts of liquid radioactive wastes. The dominant radionuclides in these wastes are ^{137}Cs, ^{90}Sr and ^{60}Co. One possibility for their immobilization is the use of different ion-exchangers. The inorganic ion-exchanger offer the advantages of high capacity, good selectivity, reproducible stoichiometry, radiation resistance and compatibility with glass and cementation waste forms [1]. One excellent and relatively cheap ion-exchanger is zeolite. The basis of the zeolitic structure is spheres consisting of 24 SiO_4 tetraeders joined together by Si–O–S groups. The cavities and channels in this structure can hold metal cations (mostly alkali metals and alkaline earth metals) or molecules (e.g. H_2O). The structure of a zeolite determines its specific physical and chemical properties, such as ion-exchange ability and absorption, reversible dehydration and hydration. In Slovak Republic, there are rich deposites of zeolitic materials which contain about 70% clinoptilolite [2].

The clinoptilolite content determines the sorption ability of these materials. The chemical and morphological properties of Slovak zeolite [3] are similar to those of the well-known clinoptilolite from the Hector or Castle Creek deposits in the USA. It exhibits an excellent sorption uptake of caesium [1] and, after specific chemical treatment, it has a good uptake of cobalt [5–7]. Recent ex-

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periments show that zeolite treated with NaOH withstands the alkaline environment in concrete [8]. The resulting composite has excellent physical and mechanical properties that would be very suitable for the solidification of nuclear wastes.

Experimental

The zeolitic material used in these experiments was from the Nižny Hrabovec deposit (grain size from 1.2 to 2 mm). The XRD analysis indicated that this material mostly contained clinoptilolite (theoretical formula $Na_{2.3}K_{1.7}Ca_{0.5}Mg_{0.2}Al_{0.2}(Si_{30}Al_6)_{72}\cdot 24H_2O$). The natural zeolite was chemically treated [6–8] by heating in 1 *M*, 4 *M* or 6 *M* solutions of NaOH at 80°C for 4 h. After heating, the samples were washed with distilled water and dried. This treatment yielded variously modified zeolites with different compositions and properties. The uptakes of Co and Cs were controlled by the method of model radioactive solutions: 0.05 g samples of zeolite were added to vessels containing 10 ml 0.05 *M* $CoCl_2\cdot 6H_2O$ solution labelled with ^{60}Co, or 0.05 *M* CsCl solution labelled with ^{137}Cs (the radioactivity of solutions was measured with a well scintillation detector). After 24 h, the radioactivities of the solutions were measured and further 0.05 g zeolite samples were added. These steps were repeated several times. The measurements permitted calculation of the sorption coefficients of Cs and Co.

The changes in the zeolitic material on reaction with NaOH solution were characterized by chemical analysis, XRD analysis (DRON 2,09) and DTA (Q-1500) derivatograph.

Results and discussion

The uptake of a radionuclide was characterized by the sorption coefficient μ, defined according to the formula

$$\mu = -k\frac{cV}{\nu}$$

where k is the slope of the linear part of the isotherm, c is the molar concentration of the solution, V is the volume of solution used, and ν is the valency of the labelled ions.

Table 1 gives the sorption coefficients (Co, Cs) of the treated zeolite. The maximum uptake of caesium by the zeolite treated with 1 *M* NaOH solution and the maximum uptake of cobalt by the zeolite treated with 4 *M* NaOH solution are shown:

Table 1 Sorption coefficients of natural and modified zeolites

Type of zeolite	Sorption coefficient / meq g^{-1}	
	Cs(I)	Co(II)
P*	0.80	0.10
modified with 1 *M* NaOH	1.30	0.28
modified with 4 *M* NaOH	1.02	0.42
modified with 6 *M* NaOH	0.96	0.40

**P* = natural zeolitic material (Nižny Hrabovec)

The chemical compositions of the natural and modified zeolites are to be found in Table 2. This Table shows that the content of SiO_2 is significantly decreased in the zeolites treated with 4 *M* or 6 *M* NaOH solution, whereas the contents of Al_2O_3 and Na_2O and the loss on ignition are increased. These effects are due to the chemical reactions of NaOH, and mainly to the washing-out of the soluble phase.

Table 2 Chemical compositions of natural and modified zeolites / wt. %

Component	Natural zeolite	Zeolite modified with		
		1 *M* NaOH	4 *M* NaOH	6 *M* NaOH
L.O.I.*	11.45	12.32	23.51	29.28
SiO_2	68.25	62.83	43.75	36.30
Al_2O_3	11.66	12.47	14.44	15.43
Fe_2O_3	1.17	1.30	1.76	1.87
CaO	3.62	3.97	5.05	4.29
MgO	1.30	1.77	1.91	1.39
Na_2O	0.70	2.14	7.82	9.54

*L.O.I. = loss on ignition

Figure 1 provides XRD pictures of the treated zeolites in comparison with that of the natural sample, while Fig. 2 presents the XRD patterns of the same material after annealing up to 1000°C.

Table 3 gives the losses in mass of samples evaluated from the DTA curves.

The results show that the treatment with 1 *M* NaOH solution changed the zeolite only very weakly. The XRD analysis revealed that the dominant phase of natural and modified zeolite (with 1 *M* NaOH solution) is clinoptilolite; quartz was also identified [9]. Heating of natural zeolite and that modified with 1 *M* NaOH up to 1000°C was demonstrated by thermal analysis to cause an increase in the mass loss (from 11 to 13%).

Figure 3 presents DTA curves for all these zeolitic samples. The changes are seen to be continuous for zeolite treated with 1 *M* NaOH and for natural zeolite.

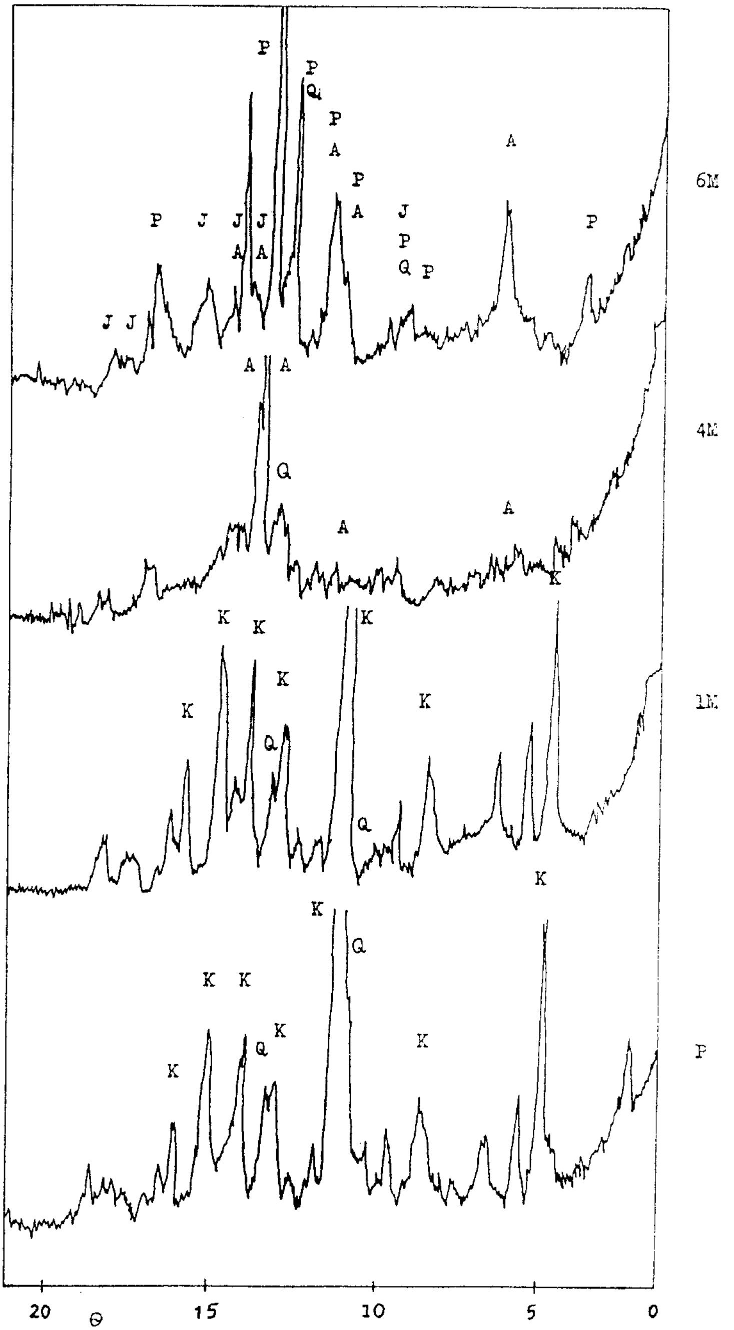

Fig. 1 Phase composition of natural and modified zeolitic materials; K - clinoptilolite, Q - quartz, A - albite, J - jadeite, P - paragonite

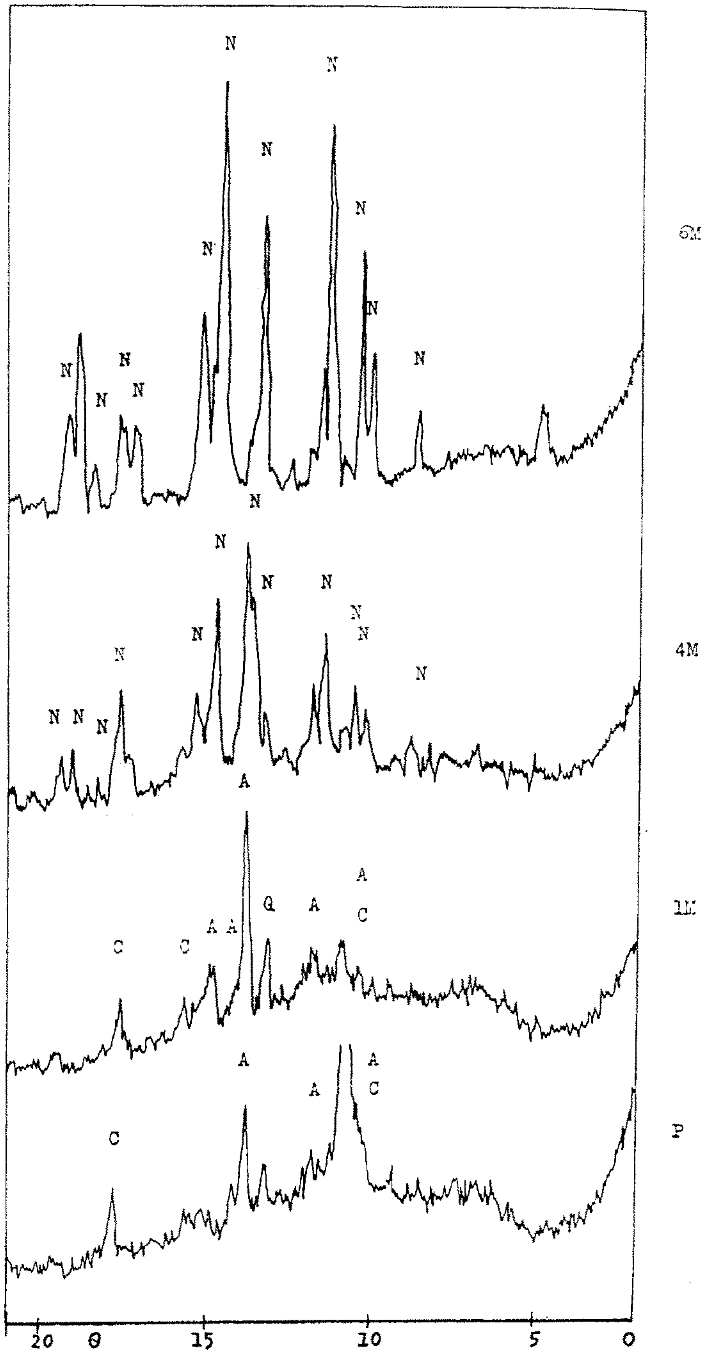

Fig. 2 Phase composition of natural and modified zeolites after annealing up to the temperature 1000°C; Q - quartz, A - albite, C - cristobalite, N - nepheline

Table 3 Thermogravimetric data on zeolites used

Type of zeolite	Loss in mass / %	First loss in mass/temperature/ %/°C	Second loss in mass/temperature/ %/°C	Maximum of endotherm. effect/ °C
P*	11.0	10.4/450	0.6/740	–
1 M**	13.3	13.3/740	–	–
4 M**	24.6	22.4/460	2.2/760	800
6 M**	30.4	28.2/320	2.4/790	810

*P = natural zeolitic material

** natural zeolitic material modified by treatment with 1 *M*, 4 *M* or 6 *M* NaOH

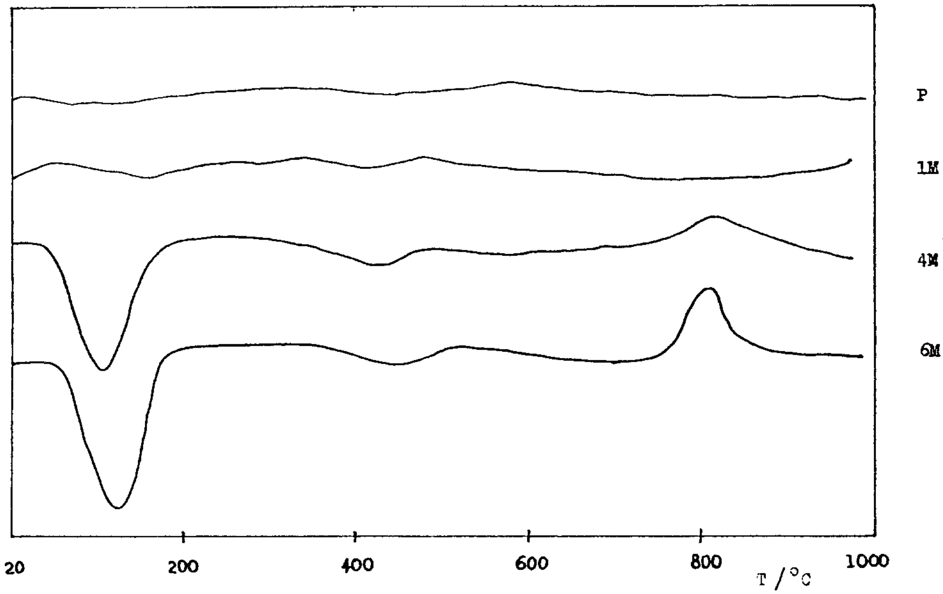

Fig. 3 DTA curves of natural and modified zeolites; P - natural zeolite, 1 *M* - zeolite modified with 1 *M* NaOH solution, 4 *M* - zeolite modified with 4 *M* - zeolite modified with 4 *M* NaOH solution, 6 *M* - zeolite modified with 6 *M* NaOH solution

For both materials, the loss in mass is evident only up to 750°C. The DTA curves for both materials show only a broad expressionless endothermic effect.

Table 4 lists the phase compositions of the samples before and after annealing up to the 1000°C. The phase compositions of the samples after annealing up to 1000°C are very similar according to the XRD analysis.

It may be assumed that the high-temperature stable form of SiO_2 (cristobalite) persists together with a very small amount of quartz and albite ($NaAlSi_3O_8$). The pattern indicates a significant amount of the amorphous form.

Table 4 Phase compositions of natural and treated zeolites

Type of zeolite	Composition of zeolite before annealing	after annealing up to 1000°C
P*	clinoptilolite, quartz	quartz, (cristobalite), albite, amorphous part
1 M**	clinoptilolite, quartz	quartz, (cristobalite), albite, amorphous part
4 M**	albite, quartz	nepheline, amorphous part
6 M**	albite, quartz, paragonite, jadeite	nepheline, amorphous part

*P = natural zeolite

** natural zeolitic material modified by treatment with 1 *M*, 4 *M* or 6 *M* NaOH

The chemical treatment of natural zeolite with more concentrated solutions of NaOH (4 *M* or 6 *M*) caused more marked changes. Thermogravimetric calculations revealed losses in mass of 25–30%.

The DTA curves of these modified zeolites demonstrate an endothermic process at about 100°C, and an exothermic process from 750 up to 800°C, obviously relating to a process in the solid state.

XRD analysis points to changes caused by heating up to 1000°C: the original zeolite modified with 4 *M* NaOH displays very low crystallinity: only albite and quartz. Annealing changes it to a unique crystalline phase, nepheline ($NaAlSiO_4$), together with an amorphous part.

The sample modified with 6*M* NaOH contains a mixture of crystalline forms: albite, quartz, jadeite ($NaAlSi_2O_6$) and probably also paragonite $\{NaAl_2(AlSi_3O_{10})(OH)_2\}$. On annealing at 1000°C, the structure of this sample changes to nepheline (as in the case of zeolite treated with 4 *M* NaOH), and some amorphous material is probably also formed.

All the results show that the effects of NaOH on natural zeolite lead to changes in phase composition and microstructure which result in increased Cs and Co uptakes (from aqueous solution).

This experience could be useful in the immobilization of radionuclides present in waste waters from nuclear power plants.

References

1 A. Dyer and F. H. Kadhim, J. Radioanal. Nucl. Chem., 131 (1989) 161.
2 J. Kozač, D. Očenáš, D. Rusnák and J. Hoffman, Miner. Slovaca, 14 (1982) 124.
3 A. Sopková and J. Bubanec, Chem. Průmysl, 38 (1988) 11.
4 L. L. Ames, Amer. Mineral., 45 (1960) 689.
5 P. Hložek, M. Földesová and P. Lukáč, J. Radioanal. Nucl. Chem., Lett., 165 (1992) 175.
6 P. Lukáč, P. Hložek and M. Földesová, Geologica Carpatica - Series Clay, 2 (1992) 125.
7 P. Lukáč and M. Földesová, J. Radioanal. Nucl. Chem., Lett., 188 (1994) 427.
8 V. Tomková, P. Lukáč, M. Földesová and J. Majling, Slovak Patent. Appl.: PV 0005 - 95, Bratislava, 1995.
9 Selected Powder Diffraction Data for Minerals, Philadelphia, 1974.