

INVESTIGATION OF RADIONUCLIDE ^{137}Cs SORPTION BY NATURAL AND SYNTHETIC ZEOLITES

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Sorption-selective properties of natural zeolite-clinoptilolite, from the Sokirnitsky deposit of Ukraine, and synthetic zeolites relatively to radionuclide ^{137}Cs and depending on pH and temperature were studied. A high sorption ability of clinoptilolite relatively to ^{137}Cs was determined.

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1. INTRODUCTION

The problem of natural and technical water purification from radionuclides is of importance for improvement of the ecological situation in the regions with increased man-caused antropogenic radiation.

The work was aimed to studying of sorption properties of natural zeolite-clinoptilolite (from the Sokirnitsky clinoptilolite deposit of the Khustsk district of the Zakarpatye region) and synthetic zeolites (erionite, NaA, NaX, NaY) (given by the Research Institute of Basic Chemistry of Kharkov) relatively to radionuclide ^{137}Cs contained in the water solution.

2. MATERIALS AND METHODS

Investigations of sorption-selective properties of natural zeolite and clinoptilolite were carried out on the base of the Radiochemistry and Radioecology Department of the Research Institute of Chemistry at the Kharkov National University.

Synthetic zeolites are high-quality and comparatively cheap sorbents. At present more than 100 synthetic zeolites are known [1]. The technology of sorption water purification uses zeolites of two structural types: A and X. In this respect, erionite and zeolite NaY are much less studied (Table 1).

Table 1. Physico-chemical and structured characteristics syntetic zeolites

Zeolite	Chemical formula	Crystalline structure	Parameters of elementary cell, nm	Dimension of windows, nm
NaA	$\text{Na}_2\text{O}\cdot\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2\cdot 4.5\text{H}_2\text{O}$	Cubic	$a=2,464$	0,42 in 8-element; 0,22 in 6-element;
NaX	$\text{Na}_2\text{O}\cdot\text{Al}_2\text{O}_3\cdot 2.5\text{SiO}_2\cdot 6\text{H}_2\text{O}$	Cubic	$a=2,502\dots 2,486$	0,74 in 12-element; 0,22 in 6-element
NaY	$\text{Na}_2\text{O}\cdot\text{Al}_2\text{O}_3\cdot 4.8\text{SiO}_2\cdot 8.9\text{H}_2\text{O}$	Cubic	$a=2,486$	0,74 in 12-element; 0,22 in 6-element
Erionite	$0.65\text{K}_2\text{O}\cdot 0.45\text{Na}_2\text{O}\cdot\text{Al}_2\text{O}_3\cdot 7\text{SiO}_2\cdot 6\text{H}_2\text{O}$	Hexagonal	$a=1,326$	0,36-0,52 in 8- element rings

Zeolites are the most important representatives of natural ion exchangers. They constitute a group of aluminosilicate minerals, which are distinguished by the regular spatial structure. In the silicate lattice a part of Si^{4+} ions is replaced by Al^{3+} ions, consequently, the lattice of zeolite has some residual negative charge that is compensated by cations of alkaline- and rare-earth metals (Fig. 1). Cations are located in internal lattice voids, and just by this factor the ion-exchanging properties of zeolite are conditioned [1,2].

Depending on the composition of exchanging cations, zeolites manifest such properties as thermal stability, ability to absorption reactions, ion exchange, taking part in catalytic reactions [3-6].

An important characteristic of zeolites is the Si/Al ratio. By the value of this ratio zeolites can be divided into high-siliceous ones ($\text{SiO}_2/\text{Al}_2\text{O}_3=4\dots 10$) – clinop-

tilolite, erionite and low-siliceous ones ($\text{SiO}_2/\text{Al}_2\text{O}_3= 2\dots 3$) – NaA, NaX, NaY.

Unlike zeolites A, X and Y, synthetic zeolite has a more complex chemical composition. In its lattice, besides sodium, a significant amount of K^+ ions is contained.

High-siliceous zeolites possess a high thermal stability, chemical resistance.

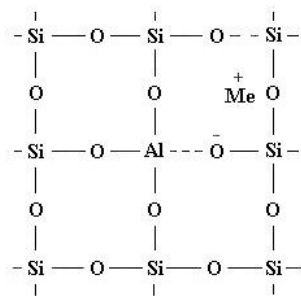


Fig. 1. Localization of univalent cations of a large size (Me^+) in silicon-oxygen rings, relating to the zeolite structure

The sorption ability of zeolites relatively to ^{137}Cs was studied in static conditions depending on pH (pH range from 2 to 8.5) and on temperature (temperature range from 293.15...318.15 K). For experiments a radionuclide ^{137}Cs solution with a specific activity $3.18 \cdot 10^6$ Bq/dm³ without carrier was used. Clinoptilolite was preliminary grinded to the grain diameter from 0.3...0.4 mm. Such preparation increases sharply the surface of sorbent contact with solution and decreases significantly the extent of using it.

To study the sorption, the 0.05 g portions of sorbents were mixed with 10 ml of the solution being investigated by means of a magnetic mixer. Radiometric measurements of a dry residue of samples were conducted at the α - β automatic machine NRR-610 "Tesla". The relative error of radioactivity measurements was not higher than 2%.

3. RESULTS AND DISCUSSION

As quantitative characteristics of sorbent interaction with radionuclides we used the coefficients of radionuclide distribution (K_d , ml/g), and sorption coefficients (K_s , %) which were calculated by

$$K_d = \frac{(I_0 - I_p) \cdot V}{I_p \cdot m}, \quad (1)$$

$$K_s = \frac{(I_0 - I_p) \cdot 100\%}{I_0}, \quad (2)$$

where I_0 and I_p are the initial and equilibrium radioactivity of the solution, pulse/s; V is the total volume of the solution, ml; m is the sorbent mass, g.

The relative error of values in the range of their values $1 \cdot 10^2 \dots 1 \cdot 10^4$ was calculated with a relative error of 2...5%, and in the range less than $1 \cdot 10^2$ the error was 10%.

Analysis of obtained kinetic curves of the radionuclide ^{137}Cs sorption with clinoptilolite (Fig. 2) has shown that the radionuclide sorption on clinoptilolite practically does not depend on pH of the initial solution, and the equilibrium between clinoptilolite and ^{137}Cs is getting in 20...30 min.

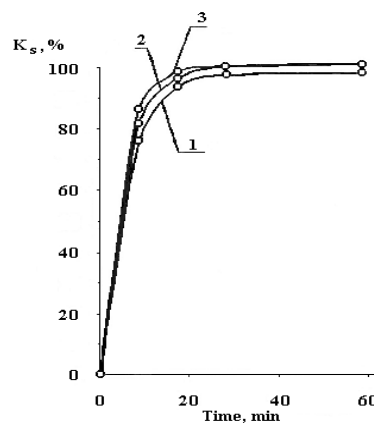


Fig. 2. Kinetic curves of ^{137}Cs sorption on clinoptilolite at different pH values: 1-2.0; 2-7.0; 3-11.0

Analysis of obtained kinetic curves of the radionuclide ^{137}Cs sorption with synthetic zeolites (Fig. 3) showed that the equilibrium between zeolite and ^{137}Cs is getting in 20...60 min.

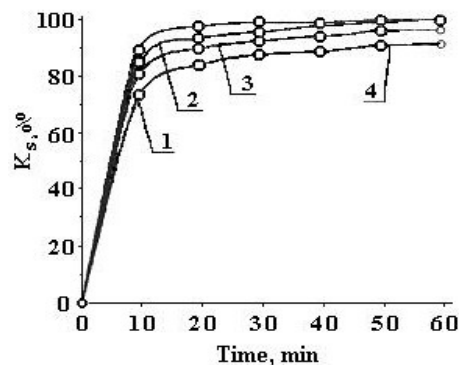


Fig. 3. Kinetic curves of ^{137}Cs sorption on synthetic zeolites at pH=7.0: 1 - erionite; 2 - zeolite NaY; 3 - zeolite NaA; 4 - zeolite NaX

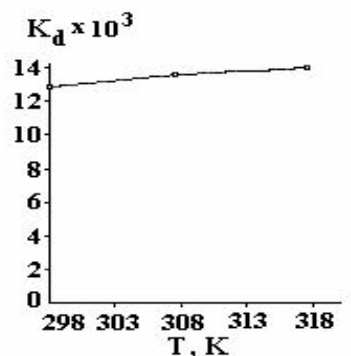


Fig. 4. Temperature influence on the radionuclide ^{137}Cs distribution (K_d)

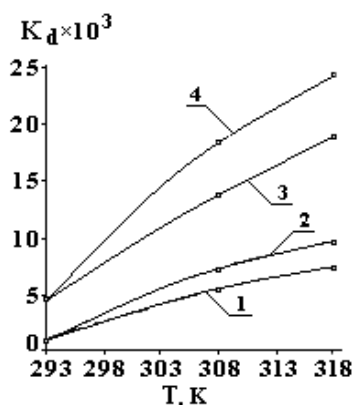


Fig. 5. Temperature dependence of coefficients of radionuclide ^{137}Cs distribution (K_d): 1-NaX; 2-NaA; 3-NaY; 4-erionite

The process of ion exchange consists of two stages: rapid and slow. Each of them depends on the features of the zeolite structure and physical-chemical characteristics of exchanging ions.

The temperature has different influence on the sorption properties of zeolites relatively to ^{137}Cs (Fig. 4,5). In the investigated temperature range the ^{137}Cs sorption by clinoptilolite is almost independent on the temperature. It means that all sodium ions of clinoptilolite, capable to be exchanged, take part in the exchange by caesium already at 293.15 K.

The sorption ability of synthetic zeolites relatively to ^{137}Cs increases with temperature increasing.

The data obtained shows that clinoptilolite (Tables 2,3) is specified by high sorption characteristics relatively to radionuclide ^{137}Cs at all pH values (from 97 to 99.5% of capture), and in the range of pH values from 7 to 11 they depend slightly on the solution acidity. Selectivity of synthetic zeolites to ^{137}Cs , including high-siliceous ones (erionite, zeolite NaY), was found significantly lower.

Table 2. Values of coefficients of radionuclide ^{137}Cs distribution (K_d) on zeolites at different pH values at a temperature of 293.15 K

Zeolite	Coefficient of radionuclide ^{137}Cs distribution (K_d), ml/g			
	pH=2	pH=5	pH=7	pH=8,5
Clinoptilolite	1681	8592	1284	9084
Erionite	3276	3534	4552	2230
NaA	755	803	865	1000
NaY	1719	2722	3249	3192
NaX	817	904	990	502

Table 3. Values of coefficients of radionuclide ^{137}Cs sorption ($K_s, \%$) on zeolites at different pH values at a temperature of 293.15 K

Zeolite	Coefficient of radionuclide ^{137}Cs sorption (K_s), %		
	pH=2	pH=7	pH=8,5
Clinoptilolite	97	99	99
Erionite	99	99	98
NaA	95	95	96
NaY	97	99	98
NaX	90	94	96

The presence of large cavities and big channels in the clinoptilolite structure determines its sharply defined selectivity to coarse feebly hydrated cations of univalent and bivalent metals. In the structure of clinoptilolite there are four-, five-, six- and eight-element rings of oxygen atoms. The cause of the high selectivity of clinoptilolite relatively to univalent cations of large size is their localization in eighth-element rings the size of which are close to the sizes of incoming cations.

Clinoptilolite has a high Si/Al ratio and possesses a weak force field. Therefore, it exhibits a high selectivity to the coarse feebly hydrated caesium ion.

4. CONCLUSIONS

The investigations performed resulted in showing up the high sorption ability of clinoptilolite to ^{137}Cs that is almost independent on pH values and temperature.

The well-defined dependence of absorption properties of synthetic zeolites relatively to ^{137}Cs on pH values and temperature was established.

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Изучены сорбционно-селективные свойства природного цеолита клиноптилолита Сокирницкого месторождения Украины и синтетических цеолитов относительно радионуклида ^{137}Cs в зависимости от pH и температуры. Установлена высокая сорбционная способность клиноптилолита в отношении ^{137}Cs .

**ДОСЛІДЖЕННЯ СОРБЦІЇ РАДІОНУКЛІДА ^{137}Cs
ПРИРОДНИМИ І СИНТЕТИЧНИМИ ЦЕОЛІТАМИ**

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Вивчено сорбційно-селективні властивості природного цеоліту кліноптілоліта Сокирницького родовища України і синтетичних цеолітів щодо радіонукліда ^{137}Cs у залежності від pH і температури. Установлено високу сорбційну здатність кліноптілоліту у відношенні до ^{137}Cs .