INFLUENCE OF DIFFERENT FACTORS ON SORPTION OF ^{90}Sr BY NATURAL AND SYNTHETIC ZEOLITES

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The paper researches into factors influencing sorption and selective properties of natural zeolite clinoptilolite from the Sokirnitsky deposit of Ukraine and synthetic zeolites in relation to radionuclide ^{90}Sr. It also studies the effect of competing ions on the sorption of ^{90}Sr by zeolites.

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1. INTRODUCTION

In the last years there has been an increase in the usage of zeolites in different compositions to delete and bury different radio-contaminations [1-3]. A paper published earlier researched the interaction of clinoptilolite and synthetic zeolites with a radionuclide ^{137}Cs [4]. It was established, that clinoptilolite exhibits a considerable selectivity to a cesium ion.

Sorption properties of zeolites in relation to ^{90}Sr have a number of differences. This can be explained by a higher hydration energy and considerably smaller ionic radius of Sr^{2+} in comparison with Cs^{+} (Table 1) [5].

Therefore, the paper is meant to study how sorption and selective properties of zeolites in relation to ^{90}Sr depend on different solution pH values, temperature, and presence of extraneous ions.

Table 1. *Ionic radii, electronic configuration, thermodynamic characteristics of a hydration, and thermodynamic exchange constants (K_T) of Cs^{+} and Sr^{2+} ions on clinoptilolite*

Ions	Electronic configuration	Ionic radius, nm	$-\Delta H^0_{hydrat}$, κJ/mol	$-\Delta S^0_{hydrat}$, κJ/(mol·K)	$-\Delta G^0_{hydrat}$, κJ/mol	K_T $Na^+ - M^{n+}$
Cs^+	$6S^1$	0.167	280	10.03	275	63.1
Sr^{2+}	$4S^2$	0.127	1475	163.03	1425	3.3

2. MATERIALS AND METHODS

The research into sorption and selective properties of natural zeolite and clinoptilolite was hosted by the Department for Radiochemistry and Radioecology of the Research Institute of Chemistry at Kharkov National University.

The following synthetic zeolites were used as sorbents: erionite, NaA, NaX, NaY with the grain diameter of 0.3…0.5 mm, and also natural zeolite – clinoptilolite with the particles 0.3…0.5 mm in size.

Sorption ability of zeolites in relation to ^{90}Sr was studied in static conditions as functions of pH (pH range 2 to 8.5) and temperature (temperature range 293.15 K to 318.15 K). Solution acidity was adjusted by adding the solutions of HCl and NaOH.

A solution of NaCl (with NaCl=0.05 mol/dm^3, T=293.15 K) was used to study the effect that extraneous ions have on the sorption ability of zeolites. The experiments used a solution of ^{90}Sr with the specific activity of 1.76·106 Bq/dm^3, without a carrier.

To study sorption, batches of sorbents, 0.05 gram each, were mixed using a magnetic stirrer with 10 ml of the researched solution.

Radiometric measurements were performed using NRR-610 "Tesla" α-β automatic machine. The relative error of radioactivity measurements did not exceed 2%.

Quantitative characteristics of sorbent interaction with radionuclides were expressed using radionuclide distribution coefficients (Kd, ml/g), and sorption coefficients (Ks, %), which were calculated under Formulas 1 and 2:

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

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

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

The relative error of values in the range of $1\cdot10^2$ … $1\cdot10^4$ was calculated with a relative error of 2…5%, whereas below $1\cdot10^2$ with an error of 10%.

The previously published paper offers evidence of a high sorption ability of clinoptilolite to ^{137}Cs (K_s=97… 99%), practically not affected by pH and temperature values, and establishes a clear dependence of sorption properties of synthetic zeolites to ^{137}Cs upon pH and temperature values [4].

The analysis of the obtained kinetic curves for the sorption of ^{90}Sr by clinoptilolite and synthetic zeolites at miscellaneous pH values (Fig. 1,2) showed that the equilibrium between clinoptilolite and ^{90}Sr occurs after 48…240 hours, whereas between synthetic zeolites and ^{90}Sr it occurs after 96-240 hours and depends on the pH of the medium.

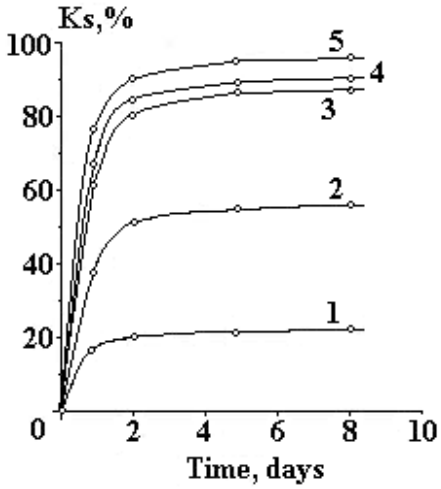

Fig. 1. *Kinetic curves of ^{90}Sr sorption on clinoptilo-lite at different pH values: 1-2; 2-5; 3-7; 4-8.5; 5-11*

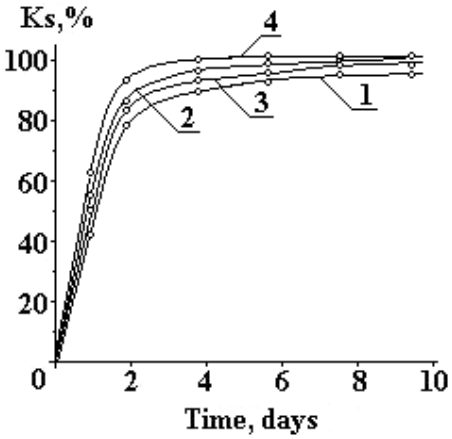

Fig. 2. *Kinetic curves of the ^{90}Sr sorption on synthetic zeolites at pH=7.0: 1 – erionite; 2 – NaY; 3 – NaA; 4 – NaX*

As the work proceeded, it was established that the sorption ability of zeolites in relation to ^{90}Sr essentially depends on pH and temperature. Also, it was found that higher concentration of an extraneous electrolyte dramatically decreases the sorption of ^{90}Sr.

Tables 2 and 3 list the values for distribution coefficients (K_d, ml/g) and sorption coefficient (Ks, %) for ^{90}Sr on zeolites. The obtained data testify to a considerable effect, which the pH value of the solution has on sorptive absorption of ^{90}Sr by zeolites.

The sorption characteristics of zeolites in relation to ^{90}Sr are considerably lower and change significantly within a researched range of pH values.

This effect of pH on the sorption ability of zeolites is stipulated by the fact that these sorbents, as well as other aluminum silicates, are multifunctional subacid ionites [6,7].

Therefore, in the acid environment the exchange of different cations on the sorbent also involves competing hydrogen ions.

The coefficient of ^{90}Sr sorption for zeolites grows as temperature increases. It has to do with an increased pH of the solution caused by ions of sodium, which underwent a transition to the solution from a solid phase.

Table 2. *Distribution (K_d) of ^{90}Sr radionuclide on zeolites at different pH values, at 293.15 K*

Zeolite	Distribution coefficient (K_d) of ^{90}Sr radionuclide, ml/g			
	pH=2	pH=5	pH=7	pH=8.5
clinoptilolite	11.2	144	340	850
erionite	18.0	301	580	283
NaA	7.0	749	1223	471
NaY	5.0	623	1195	220
NaX	21.0	530	842	520

Table 3. *Values of coefficients of radionuclide ^{90}Sr sorption ($K_{s,\%}$) on zeolites at different pH values at a temperature of 293.15 K*

Zeolite	Coefficient of ^{90}Sr radionuclide sorption (K_s), %		
	pH=2	pH=7	pH=8.5
Clinoptilolite	23	89	94
Erionite	26	91	88
NaA	14	97	92
NaY	12	96	81
NaX	32	94	85

The interaction of hydrogen ions with an oxygen radical of the zeolite body generates hydroxyl groups and lowers the charge of the matrix, which is accompanied by a decrease in the sorption ability of zeolites in relation to ^{90}Sr. Besides, a higher sorption of the radionuclide due to increasing pH shows that in the solution they are in an ionic state.

Temperature impacts the sorption of ^{90}Sr by clinoptilolite and synthetic zeolites (Figs. 3,4).

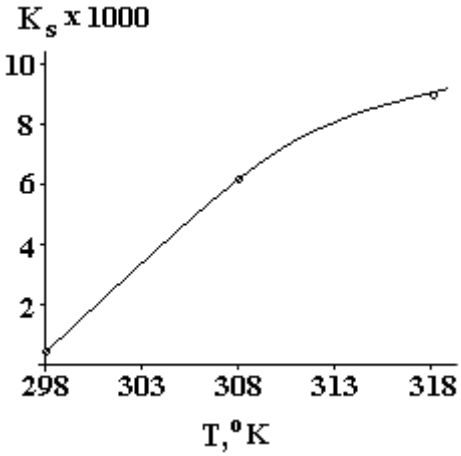

Fig. 3. *The effect of temperature on the coefficient of ^{90}Sr sorption (K_d) by clinoptilolite*

Besides, as temperature increases, the hydrate sheath of a Sr ion decreases. This enables ^{90}Sr to penetrate cuboctahedron units and to replace ions of sodium inside zeolite structure, which contributes to the completeness of ion exchange and results in a higher sorption coefficient.

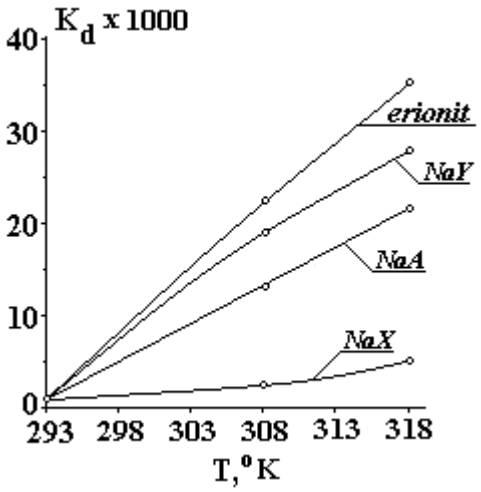

Fig. 4. *Distribution coefficient (K_d) of ^{90}Sr on synthetic zeolites versus temperature*

A considerable effect on the sorption ability of clinoptilolite and synthetic zeolites is produced by the presence of extraneous ions. As can be seen from Table 4, an increase in the ionic strength of a solution created by sodium chloride significantly reduces the distribution coefficient (Kd, ml/g) for ^{90}Sr.

Table 4*. Effect of sodium chloride on the distribution coefficient (Kd, ml/g) for ^{90}Sr on zeolites at pH=7 and temperature 293.5 K*

Zeolite	K_d, ml/g	
	$C_{Na\ Cl}$=0 mol/dm^3	C_{NaCl}=0,1 mol/dm^3
Clinoptilolite	340	89
Erionite	580	120
NaA	1223	78
NaX	842	82
NaY	1195	63

The following summary conclusion can be made: synthetic zeolites have a higher absorbing capacity in relation to ^{90}Sr than clinoptilolite.

3. CONCLUSIONS

The research established the effect of pH on the sorption of ^{90}Sr by clinoptilolite and synthetic zeolites. Higher pH values in the range of 2 to 8.5 result in increased sorption properties of zeolites.

It was found that higher temperature led to a considerable increase in the sorption of ^{90}Sr by zeolites.

It was established that the presence of extraneous ions in the solution reduces the sorption of ^{90}Sr by zeolites.

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ВЛИЯНИЕ РАЗЛИЧНЫХ ФАКТОРОВ НА СОРБЦИЮ ^{90}Sr ПРИРОДНЫМИ И СИНТЕТИЧЕСКИМИ ЦЕОЛИТАМИ

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Исследованы факторы, влияющие на сорбционно-селективные свойства природного цеолита клиноптилолита Сокирницкого месторождения Украины и синтетических цеолитов относительно радионуклида ^{90}Sr. Показано, что при наличии конкурирующих ионов существенно снижается сорбция ^{90}Sr цеолитами.

ВПЛИВ РІЗНИХ ФАКТОРІВ НА СОРБЦІЮ ^{90}Sr ПРИРОДНИМИ ТА СИНТЕТИЧНИМИ ЦЕОЛІТАМИ

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Досліджено фактори, що впливають на сорбційно-селективні властивості природного цеоліту клиноптилолита Сокирницького родовища України і синтетичних цеолітів щодо радіонукліда ^{90}Sr. Показано, що наявність конкуруючих іонів суттєво знижує сорбцію ^{90}Sr цеолітами.