STUDYING SORPTION PROPERTIES OF A MIXTURE OF NATURAL AND SYNTHETIC ZEOLITES IN RESPECT OF RADIONUCLIDES ^{137}Cs AND ^{90}Sr

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Sorption properties of a mixture of zeolites (natural and synthetic) in respect of radionuclides ^{137}Cs and ^{90}Sr are studied. The influence of additions on the sorption properties of clinoptilolite and mixture of zeolites (natural and synthetic) is studied.

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1. INTRODUCTION

Operation of nuclear power plants requires the safety measures to protect plant personnel from radiation and, in particular, from contamination by radioactive material that consists in decontamination of working clothes, working places with subsequent utilization of radioactive waste for storage and disposal.

Recently one widely applies decontaminant cleaning agents (detergents) based on materials with adsorption properties suitable for decontamination. These detergents are universal in using for working surfaces of equipment and materials and can significantly decrease a number of liquid-waste drains. Decontaminants contain, besides active materials, possessing adsorption, ion-exchanging properties, a number of admixtures. The admixtures contained in the detergent used for decontamination should fulfill the following functions:

- to decrease the surface tension of the decontaminating solution;
- to promote the processes of slurrying, emulsification and foam formation that in whole improves the detergent washing off from the surface after contamination removing.

A mass fraction of admixtures should not exceed 50-80 %. Besides, it is very important to determine which influence the admixtures exert, how much they decrease adsorption and ion-exchanging properties necessary for decontamination.

The purpose of the work was to investigate the sorption interaction of natural and synthetic zeolites in the composition prepared by mixing the components, and then to determine how the admixtures, used in the form of filling agents, influence on this composition. Therefore, firstly we investigated the change of the sorption activity of clinoptilolite in the composition of clinoptilolite and synthetic zeolite obtained by mixing them to formation of a homogeneous mixture.

The next stage of investigations consisted in determining the sorption activity of mixtures of additions with a composition (clinoptilolite - synthetic zeolite) which revealed the best results of radionuclide sorption.

2. MATERIALS AND METHODS

Materials used for investigations were natural zeolite - clinoptilolite and synthetic zeolites such as NaA, NaX, NaY. This choice was conditioned by a necessity to combine zeolite, with different content of silicon, and aluminum (SiO_2/Al_2O_3), as this ratio essentially influences on the exchange capacitance and selectivity to ^{137}Cs and ^{90}Sr. Clinoptilolite belongs to high-silicon zeolite ($SiO_2/Al_2O_3 = 4 \dots 10$), and synthetic zeolites NaA, NaX, NaY belong to low-silicon zeolites ($SiO_2/Al_2O_3 = 2 \dots 3$).

In experiments we used the solution of radionuclide ^{137}Cs with a specific activity of $3.18\Delta \cdot 10^6$ Bq/dm^3 without a carrying agent and the solution of ^{90}Sr with a specific activity of $76 \cdot 10^6 Bq/dm^3$ without a carrying agent.

Clinoptilolite was preliminary crushed. Such a preparation sharply increases the contact sorbent- solution surface and raises its efficiency. The sorption ability of the zeolite system in respect of radionuclides was studied under statistic conditions as a function of pH (pH range was from 2 to 8.5). The acidity was regulated by addition of HCl- and NaOH solutions. The filling material, used as admixture, was a detergent base (including surface-active material -SAM).

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Table 1. *Coefficients of radionuclide sorption (Ks,%) by the clinoptilolite- synthetic zeolite compositon at different pH values*

Mixture of sorbents	Coefficient of ^{137}Cs sorption (Ks), %			Coefficient of ^{90}Sr sorption (Ks), %		
	pH =2	pH =7	pH =8.5	pH =2	pH =7	pH =8.5
Clinoptilolite - NaA						
2.5 - 7.5	78.0±2.3	80.0±2.4	81.0±2.4	12.0±0.4	72.0±2.2	70.0±2.1
5.0 - 5.0	46.0±1.4	48.0±1.4	50.0±1.5	10.0±0.3	39.0±1.2	44.0±1.3
6.8 - 3.2	62.0±1.9	65.0±1.9	68.0±2.0	12.0±0.4	57.0±1.7	62.0±1.9
7.5 - 2.5	74.0±2.2	77.0±2.3	79.0±2.4	13.0±0.4	69.0±2.0	74.0±2.2
8.2 - 1.8	80.0±2.4	86.0±2.6	86.0±2.6	14.0±0.5	76.0±2.3	79.0±2.4
9.0 - 1.0	86.0±2.5	88.0±2.6	88.0±2.6	14.0±0.5	70.0±2.1	76.0±2.3
Clinoptilolite - NaY						
2.5 - 7.5	72.0±2.2	74.0±2.2	74.0±2.2	12.0±0.4	70.0±2.1	56.0±1.7
5.0 - 5.0	45.0±1.4	47.0±1.4	48.0±1.4	8.0±0.2	37.0±1.1	42.0±1.3
6.8 - 3.2	60.0±1.8	64.0±1.9	67.0±2.0	10.0±0.3	55.0±1.6	60.0±1.8
7.5 - 2.5	70.0±2.1	72.±2.2	74.0±2.2	11.0±0.3	63.0±1.9	68.0±2.0
8.2 - 1.8	76.0±2.3	77.0±2.3	78.0±2.4	12.0±0.4	68.0±2.0	72.0±2.2
9.0 - 1.0	84.0±2.5	87.0±2.6	86.0±2.6	12.0±0.4	67.0±2.0	70.0±2.1
Clinoptilolite - NaX						
2.5 - 7.5	65.0±1.9	69.0±2.1	71.0±2.1	11.0±0.3	69.0±2.0	58.0±1.7
5.0 - 5.0	45.0±1.4	47.0±1.4	48.0±1.5	8.0±0.2	36.0±1.1	42.0±1.3
6.8 - 3.2	59.0±1.8	64.0±1.9	67.0±2.0	10.0±0.3	54.0±1.6	60.0±1.8
7.5 - 2.5	70.0±2.2	72.0±2.2	74.0±2.3	11.0±0.3	62.0±1.8	68.0±2.0
8.2 - 1.8	75.0±2.3	77.0±2.4	78.0±2.4	12.0±0.4	67.0±2.0	71.0±2.1
9.0 - 1.0	84.0±2.5	86.0±2.6	86.0±2.6	12.0±0.4	65.0±1.9	70.0±2.2

The SAM falling entering with composition of washing basis were: nonionic substance (polyoxyethylene ethers, alkylphenol, amine and other compounds with the reactives atoms of hydrogen), cation substance (derivatives of alkylamine), anionic substance (salts of carboxylic acids, alkylsulphate, alkylsulphonate, fluorinealkylsulphate).

The mixture of zeolites and fillers was prepared by thorough mechanical mixing. For investigation of the sorption the mixture sample was mixed with the solution being studied by means of a magnetic stirrer [1-3].

Radiometric measurements of a solid residue were carried out using an automatic $\alpha - \beta$-weigher NRR-610 "Tesla".

The relative error of radioactivity measurements does not exceed 3%.

A statistical error at plenty of measurings (for different compositions, ph, various of zeolite) lay in sidealtar 3-5%. The total error of measurings taking into account a hard error did not exceed 10%.

3. RESULTS AND DISCUSSION

In the preliminary tests of sorbents we used, as a qualitative characteristic, the coefficient of radionuclide sorption (Ks, %) calculated by formula (1):

$$\mathrm{K}_s = \frac{\mathrm{I}_o - \mathrm{I}_p}{\mathrm{I}_o} \cdot 100\,, \qquad (1)$$

where I_o and I_p are the initial and equilibrium radioactivity of the solution, $pulse/s$.

Table 2. *Coefficients of radionuclide sorption (Ks,%) by the mixture of zeolites with fillers at different pH values*

Mixture of sorbents with fillers	Coefficient of ^{137}Cs sorption			Coefficient of ^{90}Sr sorption		
	pH =2	pH =7	pH =8.5	pH =2	pH =7	pH =8.5
clinoptilolite - zeolite NaA (8.2 - 1.8) / detergent base (including SAM)						
10 - 90	13.0±0.4	15.0±0.5	15.0±0.5	4.0±0.1	8.0±0.2	12.0±0.4
15 - 85	32.0±0.9	35.0±1.1	35.0±1.1	6.0±0.2	21.0±0.6	26.0±0.8
25 - 75	38.0±1.2	40.0±1.2	40.0±1.2	8.0±0.2	32.0±1.0	35.0±1.1
35 - 65	46.0±1.4	48.0±1.5	48.0±1.5	10.0±0.3	40.0±1.2	46.0±1.4
45 - 55	67.0±2.0	69.0±2.1	69.0±2.1	12.0±0.4	61.0±1.8	66.0±1.9
65 - 35	*	*	*	*	*	*
75 - 25	*	*	*	*	*	*
85 - 15	*	*	*	*	*	*
*-the layering of the sorbent system hampering the exact measurement of the sorption was observed						

Table 3. *Coefficients of radionuclide sorption (Ks,%) by the mixture of clinoptilolite with fillers at different pH values*

Mixture of clinoptilolite with fillers	Coefficient of ^{137}Cs sorption			Coefficient of ^{90}Sr sorption		
	pH =2	pH =7	pH =8.5	pH =2	pH =7	pH =8.5
Clinoptilolite / detergent base (including SAM)						
10 - 90	**	**	**	**	**	**
15 - 85	7.0±0.2	9.0±0.3	9.0±0.3	**	7.0±0.2	8.0±0.2
25 - 75	12.0±0.4	15.0±0.5	15.0±0.5	4.0±0.1	16.0±0.5	20.0±0.6
35 - 65	23.0±0.7	25.0±0.8	25.0±0.8	6.0±0.2	24.0±0.7	30.0±0.9
45 - 55	33.0±1.0	35.0±1.1	35.0±1.1	8.0±0.2	30.0±0.9	36.0±1.1
65 - 35	*	*	*	*	*	*
75 - 25	*	*	*	*	*	*
85 - 15	*	*	*	*	*	*
*-the layering of the sorbent system hampering the exact measurement of the sorption was observed						
**- measurements are impossible as the sorption values do not exceed the background indices						

Analysis of the results obtained on the sorption for compositions with different ratios of clinoptilolite and synthetic zeolites (table 1) has shown that for clinoptilolite - synthetic zeolite compositions the main physical-chemical laws are remained being characteristic for both clinoptilolite and synthetic zeolites. The system with low clinoptilolite content, despite high sorption coefficients (table 1), requires the introduction of additional components for system stabilization [4-7]. In the case of a high clinoptilolite content the composition loses its universality, i.e. applicability for different radionuclides, not only for ^{137}Cs.

The results given in table 1 show that, unlike the preliminary results [1-3], the sorption coefficients are decreased in all the compositions. It is related to tem, that the examined system of sorption changed. Along with interaction each of sorbents with isotopes, takes place and interaction between sorbentami due to the liquid phase of isotope, that results in the forced locking of centers of exchanges, with corking of superficial pores and channels. Here the dependence of the radionuclide sorption on pH was observed. The best results were obtained in the compositions of clinoptilolite and synthetic zeolite NaA. Clinoptilolite and the composition (clinoptilolite and zeolite NaA) were considered under interaction with admixtures (fillers). The results obtained are given in Tables 2 and 3. The clinoptilolite-and-zeolite NaA system combines with fillers most effectively. However, in the case of a high clinoptilolite content and the composition in combination with admixtures (from 46 to 85% of sorbing components) we observed the layering of the sorbent system that hampered exact measurement of the ^{137}Cs and ^{90}Sr sorption. Table 3 presents the results obtained for the admixture influence on the of ^{137}Cs and ^{90}Sr sorption by clinoptilolite.

As is seen from the results given in Tables 2 and 3, the use of clinoptilolite alone in combination with admixtures does not give an effective sorption of ^{137}Cs and ^{90}Sr. With a zeolite content of 10% the effective sorption of ^{137}Cs and ^{90}Sr is impossible as the sample radioactivity values do not exceed the background indices. Application of the sorbent composition (clinoptilolite-synthetic zeolite) is characterized by higher values of ^{137}Cs and ^{90}Sr sorption. It should be noted that according to the data obtained (Tables 1, 2, 3) the before-mentioned dependence [1,2] of the radionuclide sorption on pH of the initial solution is remained. The improvement of sorption properties with pH increasing in the range from 2 to 8.5 is observed.

CONCLUSIONS

- Experiments have shown that the sorption activity of a composition prepared by mixing clinoptilolite and synthetic zeolite is decreased. In the clinoptilolite-synthetic zeolite compositions the sorption dependence on pH is remained. An optimum proportion (8.2 : 1.8) of the clinoptilolite-synthetic zeolite NaA composition, at which the sorption of ^{137}Cs and ^{90}Sr is maximum (86% and 76% respectively), was determined.

- It has been found that the mixture of clinoptilolite with additions (fillers) has the sorption coefficient lower than that of the mixture of admixtures with a composition (clinoptilolite-synthetic zeolite).

- An optimum proportion (45 : 55) of the zeolite-admixture composition at which the sorption of ^{137}Cs and ^{90}Sr is maximum (69% and 61% respectively) was determined.

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ИЗУЧЕНИЕ СОРБЦИОННЫХ СВОЙСТВ СМЕСИ ПРИРОДНОГО И СИНТЕТИЧЕСКИХ ЦЕОЛИТОВ В ОТНОШЕНИИ РАДИОНУКЛИДОВ ^{137}Cs И ^{90}Sr

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Изучались сорбционные свойства смеси цеолитов (природного и синтетического) в отношении радионуклидов ^{137}Cs и ^{90}Sr. Исследовано влияния вспомогательных веществ на сорбционные свойства клиноптилолита и смеси цеолитов (природного и синтетического).

ВИВЧЕННЯ СОРБЦІОННИХ ВЛАСТИВОСТЕЙ СУМІШІ ПРИРОДНОГО І СИНТЕТИЧНИХ ЦЕОЛІТІВ ВІДНОСНО ДО РАДІОНУКЛІДІВ ^{137}Cs ТА ^{90}Sr

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Вивчалися сорбційні властивості суміші цеолітів (природного і синтетичного) відносно радіонуклідів ^{137}Cs і ^{90}Sr. Досліджено впливи допоміжних речовин на сорбційні властивості кліноптілоліту і суміші цеолітів (природного і синтетичного).