

EFFECT OF COMPETING IONS ON MULTISORPTION (Cs^+ , Sr^{2+}) BY COMPOSITE SORBENTS BASED ON NATURAL AND SYNTHETIC ZEOLITES[†]

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In the course of the research, the effect of competing ions (Na^+) on multisorption (Cs^+ , Sr^{2+}) by composite sorbents based on natural and synthetic zeolites under static conditions was studied. It was found that the maximum concentration of competing ions (0.4 g of NaCl per 100 ml of solution) leads to a decrease in cesium sorption by 20%, and strontium sorption decreases by 10%. At the same time, high rates of sorption of cesium and strontium are preserved. Thus, for a composite sorbent (clinoptilolite -30%: zeolite NaX - 70%), the sorption of cesium was 67.9%, and the sorption of strontium was 87.6%. The analytical technique was developed on the basis of the PIXE (Proton Induced X-ray Emission) method and made it possible to qualitatively and quantitatively determine the content of isotopes. The work was performed at the analytical nuclear-physical complex "Sokil". The energy range of the electrostatic accelerator is 200-2000 keV. The complex made it possible to carry out all the main methods of analysis using ion beams. The targets were placed in the exit, at the Chamber for PIXE. To carry out measurements, a vacuum with a pressure of 10^{-4} Pa was created in the chamber. To excite the atoms of cesium, strontium, a proton beam with an energy of $E_p \approx 1400$ keV was used. The characteristic X-ray radiation of the L-series of cesium atoms and K-series of strontium atoms was recorded by two detectors: XR-100CR Si-PIN X-Ray and Ge(HP). The sorption coefficient (Sorption, %) was used as a quantitative characteristic of the interaction of sorbents with cesium, strontium.

Keywords: cesium; strontium; liquid radioactive waste; zeolites; static sorption

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One of the main problems in the further development of nuclear energy is the management of radioactive waste. Radioactive waste is divided by activity (high activity, medium activity, low activity), by physical state (solid, liquid and gaseous). A significant part of radioactive waste is liquid radioactive waste. Thus, in 2020, 8783 m³ of liquid radioactive waste was accumulated at Ukrainian NPPs [1,2]. For the purification and subsequent processing of liquid radioactive waste, thermal, sorption, and membrane methods are used, and they also include filtration, coprecipitation and coagulation of sediments and suspensions, ion exchange, osmosis and reverse osmosis, electrodialysis, and evaporation of solutions [3–8]. The most promising is the sorption method, which includes various directions of sorption. When choosing a sorbent for purification of liquid radioactive sorbents, the following factors are taken into account: sorption efficiency, structural stability (radiation resistance, chemical resistance, and thermal stability), cost, and production conditions [9].

Numerous studies have shown the effectiveness of natural ion-exchange sorbents in experiments. This group includes bentonite, vermiculite and clinoptilolite. When using them, it must be taken into account that natural sorbents are characterized by a narrow spectrum of sorbed radionuclides. The most effective use of clinoptilolite is for sorption of cesium. In this case, it should be taken into account that, depending on the deposit and the depth of occurrence, the composition of the exchange ions of the zeolite and the content of crystalline water may change. A change in these factors can have a significant effect on the sorption properties of the zeolite.

Synthetic zeolites are distinguished by a stable composition of exchange ions, which is set during the synthesis process. As well as a more developed structure with a large number of exchange centers. This is due to the predominance of Al ions in the structure of synthetic zeolites. Al ions are the basis for the formation of an excess negative charge. The negative charge is formed due to the interaction with the fourth O atom, which is included in the tetrahedral structure of the zeolite [10-12].

Therefore, the most promising is the use of composite sorbents, which include a natural component and a synthetic component in their composition. Such a composition significantly expands the list of sorbed radionuclides. The most promising is the composition based on natural zeolite (clinoptilolite) and synthetic zeolite.

When conducting model experiments on the sorption of radionuclides from liquid radioactive waste, the following factors must be taken into account: a complex radionuclide composition and the presence of competing ions.

In the work published earlier, the processes of multisorption on clinoptilolite and composite sorbent based on zeolites were considered, but the effect of competing ions on sorption processes was not considered in this work [13].

The issues of studying of sorption Cs^+ and Sr^{2+} are very relevant and are reflected in modern publications [14-18].

Therefore, in this work, multisorption (Cs^+ , Sr^{2+}) by sorbents in the presence of an increasing content of competing ions (Na^+) was considered.

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MATERIALS AND METHODS

Research objects

Nitric acid salts CsNO_3 and $\text{Sr}(\text{NO}_3)_2$ served as sources of cesium and strontium ions. 100 ml of a solution containing Cs^+ ions (0.02 g CsNO_3 per 100 mL solution) and Sr^{2+} ions (0.02 g $\text{Sr}(\text{NO}_3)_2$ per 100 mL solution) was prepared. Taking into account the fact that the interaction of Sr^{2+} with CO_3^{2-} forms a poorly soluble compound, NaCl was used as a source of competing ions. This made it possible to consider the influence of sorption processes competing without harm. When considering the influence of competing ions, different concentrations of NaCl in the test solution were considered: 0.02 g of NaCl per 100 mL of solution; 0.04 g NaCl per 100 ml solution; 0.2 g NaCl per 100 mL solution; 0.4 g NaCl per 100 ml solution.

Natural zeolite (clinoptilolite) and synthetic NaX zeolite in the following compositions were used as the composite sorbents considered in the work:

1. clinoptilolite - 100% : zeolite NaX - 0%;
2. clinoptilolite - 50%: zeolite NaX - 50%;
3. clinoptilolite - 25%: zeolite NaX - 75%.

The choice of compositions 2 and 3 is due to the studies conducted earlier [19]. These studies made it possible to determine the optimal compositions based on natural and synthetic zeolites.

Sorption experiment (sorption)

Sorption was carried out under static conditions using sorbent fractions of 0.1 mm. The weight of the sorbent used in the experiment was 0.1 g. A weighed portion of the sorbent was placed in 20 mL of the test solution. Periodically, the solution with the sorbent was forcibly mixed.

The experiment lasted 24 hours with periodic sampling. Sorption equilibrium in the zeolite-cesium system occurs within 1 hour. The increase in the time of the experiment was carried out taking into account the time of onset of sorption equilibrium in the zeolite-strontium system, which occurs within 24 hours [20].

Targets preparation

The targets were prepared on a carbon substrate. The carbon substrate was prepared from carbon rods. The carbon substrate had a length of 10.00 mm and a thickness of 2.00 mm.

A solution in an amount of 0.05 mL containing a mixture of isotopes (cesium, strontium) was deposited on a carbon substrate and dried by heating to 35°C.

The targets prepared in this way were preserved after the initial use and could be subjected to further studies under the conditions given below [20-22].

ANALYTICAL PART OF THE EXPERIMENT

The analytical part of the work was performed on the analytical nuclear-physical complex "Sokol" [20-22]. The energy range of the electrostatic accelerator is 200-2000 keV. The complex made it possible to carry out all the main methods of analysis using ion beams. The complex made it possible to irradiate the objects under study with singly and doubly charged gas ions from hydrogen to xenon. The complex had 5 outputs, on which various nuclear physics techniques were implemented: an output for recording characteristic X-ray emission (the Chamber for PIXE (Proton Induced X-ray Emission)); the beam exit to atmosphere; the output for the determination of Rutherford backscattering (the Chamber RBS); the Nuclear Microbeam and the ion irradiation channel.

The targets were placed in the exit, at the Chamber for PIXE. To carry out measurements, a vacuum with a pressure of 10^{-4} Pa was created in the chamber. To excite the atoms of cesium, strontium, a proton beam with an energy of $E_p \approx 1400$ keV was used. This energy made it possible to excite the characteristic X-ray radiation of the L-series of cesium atoms and the K-series of strontium atoms. The characteristic X-ray radiation was measured using XR-100CR Si-PIN X-Ray detector with an energy distribution of 155 eV along the 6.4 keV line. The detector was placed at a distance of 7 cm from the target, at an angle of 135 ° to the proton beam, outside the window with beryllium foil 25 μm thick. XR-100CR Si-PIN X-Ray the detector was equipped with a \varnothing 1.5 mm collimator and a 56 μm thick mylar absorber [20-22]. The choice of the collimator and absorber took place taking into account the parameters of the detector when measuring the dead time and the intensity of the characteristic X-ray radiation.

The characteristic X-ray radiation of the K series of strontium atoms was recorded by two detectors: XR-100CR Si-PIN X-Ray and Ge(HP). The second detector was used to increase the detection efficiency of the K-series radiation of strontium atoms (14.164 keV).

Ge(HP) the detector was based on an ultrapure germanium crystal with a crystal thickness of 8.5 mm and a sensitive surface area of 25 mm². When working with a Ge (HP) detector, the SBS-75 pulse signal board was used as a spectrometric amplifier, a multichannel amplitude analyzer, and a spectrometric pulse accumulator.

RESULTS AND DISCUSSION

The sorption coefficient (Sorption, %) was used as a quantitative characteristic of the interaction of sorbents with cesium, strontium, and was calculated by the formula (1):

$$\text{Sorption, \%} = \frac{(C_0 - C_{eq}) \cdot 100\%}{C_0} \quad (1)$$

where C_0 and C_{eq} are the initial and equilibrium concentration of the solution, mg/ml.

The obtained results are presented in Tables 1-3.

For clinoptilolite, the effect of competing ions in small amounts (0.02 g of NaCl per 100 ml of solution; 0.04 g of NaCl per 100 mL of solution) does not lead to a significant decrease in the sorption of cesium and strontium (Table.1). An increase in the content of competing ions (0.2 g NaCl per 100 mL of solution; 0.4 g NaCl per 100 mL of solution) leads to a decrease in the sorption of cesium and strontium by ~20%.

For composite sorbent № 2, an unusual effect of competing ions was observed. This is due to the introduction of NaX zeolite into the composition of the sorbent. At low concentrations of competing ions (0.02 g of NaCl per 100 mL of solution; 0.04 g of NaCl per 100 mL of solution), an increase in the sorption of cesium and strontium by 40% was observed during the first hour of sorption. However, by the time the sorption equilibrium was reached (24 hours), the change in sorption did not exceed 5% (Table 2).

Table 1. Sorption coefficients of cesium and strontium from a mixture of solution by clinoptilolite under static conditions in the presence of competing ions

Sorption time, h	Competing compound	The number of competing compounds per 100 mL of solution, g.	Cesium sorption coefficients, %	Strontium sorption coefficients, %
1	-	-	86.0	38.0
6	-	-	97.7	38.0
24	-	-	97.8	53.3
1	Sodium chloride	0.02	81.5	28.5
6	Sodium chloride	0.02	93.7	34.6
24	Sodium chloride	0.02	94.5	50.8
1	Sodium chloride	0.04	73.1	12.0
6	Sodium chloride	0.04	91.6	29.7
24	Sodium chloride	0.04	94.4	50.3
1	Sodium chloride	0.2	50.0	8.5
6	Sodium chloride	0.2	80.6	35.0
24	Sodium chloride	0.2	81.8	43.9
1	Sodium chloride	0.4	35.4	5.7
6	Sodium chloride	0.4	61.4	8.5
24	Sodium chloride	0.4	75.4	34.6

Table 2. Sorption coefficients of cesium and strontium from a mixture of solution by a composite sorbent 50/50 under static conditions in the presence of competing ions

Sorption time, h	Competing compound	The number of competing compounds per 100 mL of solution, g.	Cesium sorption coefficients, %	Strontium sorption coefficients, %
1	-	-	24.3	13.6
6	-	-	76.3	76.8
24	-	-	89.1	93.7
1	Sodium chloride	0.02	63.9	50.0
6	Sodium chloride	0.02	87.6	90.9
24	Sodium chloride	0.02	88.9	93.6
1	Sodium chloride	0.04	66.1	49.4
6	Sodium chloride	0.04	86.7	86.0
24	Sodium chloride	0.04	88.0	88.4
1	Sodium chloride	0.2	33.7	35.4
6	Sodium chloride	0.2	68.2	76.6
24	Sodium chloride	0.2	79.3	86.5
1	Sodium chloride	0.4	26.0	28.5
6	Sodium chloride	0.4	61.5	73.3
24	Sodium chloride	0.4	64.3	85.4

An increase in the content of competing ions (0.2 g NaCl per 100 mL of solution; 0.4 g NaCl per 100 mL of solution) leads to a decrease in cesium sorption by ~20%, while strontium sorption decreased by ~10%.

For composite sorbent № 3, an unusual effect of competing ions was also observed. This is due to the introduction of NaX zeolite into the composition of the sorbent. At low concentrations of competing ions (0.02 g of NaCl per 100 mL of solution; 0.04 g of NaCl per 100 mL of solution), an increase in the sorption of cesium and strontium by 30% - 35% was observed during the first hour of sorption. However, by the time the sorption equilibrium was reached (24 hours), the change in sorption did not exceed 2 - 3% (Table 3).

An increase in the content of competing ions (0.2 g NaCl per 100 mL of solution; 0.4 g NaCl per 100 mL of solution) leads to a decrease in cesium sorption by ~20%, while strontium sorption decreased by ~10%.

The results obtained indicate that the introduction of a high content of competing ions into the solution (0.4 g of NaCl per 100 mL of solution) leads to a decrease in the sorption of cesium by clinoptilolite and composite sorbents by 20%.

Table 3. Sorption coefficients of cesium and strontium from a mixture of solution by a composite sorbent 30/70 under static conditions in the presence of competing ions

Sorption time, h	Competing compound	The number of competing compounds per 100 mL of solution, gr.	Cesium sorption coefficients, %	Strontium sorption coefficients, %
1	-	-	27.8	27.1
6	-	-	81.2	94.7
24	-	-	87.3	95.8
1	Sodium chloride	0.02	55.2	66.9
6	Sodium chloride	0.02	84.7	98.1
24	Sodium chloride	0.02	85.5	98.1
1	Sodium chloride	0.04	59.3	63.9
6	Sodium chloride	0.04	83.6	95.4
24	Sodium chloride	0.04	84.6	97.8
1	Sodium chloride	0.2	31.4	45.6
6	Sodium chloride	0.2	52.9	82.6
24	Sodium chloride	0.2	69.5	89.6
1	Sodium chloride	0.4	27.5	35.3
6	Sodium chloride	0.4	48.2	61.8
24	Sodium chloride	0.4	67.9	87.6

The inclusion of synthetic zeolite in the composition of the composite sorbent significantly changes the situation of sorption of strontium in the presence of competing ions (0.4 g of NaCl per 100 mL of solution). Thus, for clinoptilolite, strontium sorption decreases by 20%, while for composite sorbents, the presence of competing ions (0.4 g NaCl per 100 mL of solution) leads to a decrease in strontium sorption by only 10%.

CONCLUSIONS

The results obtained indicate that during multisorption (cesium, strontium), clinoptilolite exhibits high sorption properties for cesium (Ks - 97.8%), and strontium sorption is only 53.3%.

At the same time, composite sorbents exhibit higher strontium sorption (Ks (50/50) - 93.4%, Ks (30/70) - 95.8%). And the sorption of cesium decreases slightly (Ks (50/50) - 89.1%, Ks (30/70) - 87.3%). This fact significantly expands the use of composite sorbents based on zeolites.

The concentration of competing ions in a solution significantly affects multisorption. At the maximum concentration of competing ions (0.4 g of NaCl per 100 ml of solution), cesium sorption decreases by 20%, and strontium sorption by 10%.

At the same time, high rates of sorption of cesium and strontium are preserved. So, for a composite sorbent (clinoptilolite - 50%: zeolite NaX - 50%), the sorption of cesium was 64.3%, and the sorption of strontium was 85.4%. For the composite sorbent (clinoptilolite - 30%: zeolite NaX - 70%), the cesium sorption was 67.9%, and the strontium sorption was 87.6%.

The results obtained confirm the effectiveness of using composite sorbents based on natural and synthetic zeolites for the purification of liquid radioactive waste.

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ВПЛИВ КОНКУРУЮЧИХ ІОНІВ НА МУЛЬТИСОРБЦІЮ (Cs^+ , Sr^{2+}) КОМПОЗИЦІЙНИМИ СОРБЕНТАМИ НА ОСНОВІ ПРИРОДНОГО ТА СИНТЕТИЧНИХ ЦЕОЛІТІВ

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У ході досліджень вивчався вплив конкуруючих іонів (Na^+) на мультисорбцію (Cs^+ , Sr^{2+}) композиційними сорбентами на основі природних і синтетичних цеолітів у статичних умовах. Встановлено, що максимальна концентрація конкуруючих іонів (0,4 г NaCl на 100 мл розчину) призводить до зниження сорбції цезію на 20%, а сорбції стронцію – на 10%. При цьому зберігаються високі показники сорбції цезію та стронцію. Так, для композиційного сорбенту (кліноптилоліт – 30%: цеоліт NaX – 70%) сорбція цезію становила 67,9%, а сорбція стронцію – 87,6%. Аналітична методика була розроблена на основі методу PIXE (Індуковане протонами рентгенівське випромінювання) і дозволила якісно та кількісно визначати вміст ізотопів. Робота була виконана на аналітичному ядерно-фізичному комплексі «Сокіл». Енергетичний діапазон електростатичного прискорювача 200-2000 кеВ. Комплекс дозволяв проводити всі основні методи аналізу за допомогою іонних пучків. Мішені розміщувалися на виході, в камері для PIXE. Для проведення вимірювань в камері створювався вакуум з тиском 10^{-4} Па. Для збудження атомів цезію, стронцію використовувався пучок протонів з енергією $E_p \approx 1400$ кеВ. Характеристичне рентгенівське випромінювання L-серії атомів цезію та K-серії атомів стронцію реєструвалося двома детекторами: XR-100CR Si-PIN X-Ray та Ge(NP). Як кількісну характеристику взаємодії сорбентів з цезієм, стронцієм використовували коефіцієнт сорбції (Sorption, %).

Ключові слова: цезій; стронцій; рідкі радіоактивні відходи; цеоліти; статична сорбція