РАДІОБІОЛОГІЯ ТА РАДІОЕКОЛОГІЯ

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APPLICATION OF A COMPOSITE SORBENT BASED ON NATURAL AND SYNTHETIC ZEOLITES FOR CESIUM ION ELIMINATION FROM WATER SOLUTIONS

The study has been carried out to determine the effect of variations in the content of natural and synthetic zeolites, being the components of the composite sorbent, on the cesium sorption from the water solution.

Keywords: sorption, cesium, radioactive effluent, zeolites, clinoptilolite, synthetic zeolites, sorption coefficient.

Introduction

At present the part of nuclear energy reaches 17 % of the total world electricity production. Each year nuclear power generation facilities worldwide produce about 18 t. (or 27 t. by other estimates) of radioactive wastes and a major part of them (85 %) are radioactive effluent. The main tendency in managing of radioactive effluent is to minimize their volumes [1]. For this purpose different extraction and extraction-chromatographic methods are offered along with application of inorganic sorbents. Natural sorbents are characterized by the variability of mineral and chemical composition that eventually influences on the sorption properties. Synthetic sorbents are free from these disadvantages [1], however, a high cost of these materials implies additional expenditures for their application and subsequent disposal.

Therefore, to find sorbents for water radioactive decontamination is one of urgent problems in the present-day nuclear engineering. Besides, it should be taken into consideration that liquid radioactive wastes have a complex isotope composition. In this connection, the application of all available sorbents (natural and synthetic) presents some difficulties.

One of the most promising directions for this problem is the use of composite sorbents comprising natural and synthetic components, in particular, natural and synthetic zeolites. Natural and synthetic zeolites have similar elemental compositions, however there are significant differences in the crystal structure, percentage of basic elements etc., that influences on their sorption properties (Table 1) [2 - 5].

Table 1. **Characteristics of clinoptilolite and synthetic zeolites [2]**

Zeolite	Chemical formula of a zeolite cell	Si/Al	Crystallographic data		Exchange capacity, mole/kg
			symmetry	density, g/cm^3	
clinopTilolite (natural)	$Na_6[(AlO_2)_6(SiO_2)_{30}]\cdot 24H_2O$	4.25 - 5.25	monoclinic	2.16	2.2
Zeolite NaA (synthetic)	$Na_{12}[(AlO_2)_{12}(SiO_2)_{12}]\cdot 27H_2O$	0.7 - 1.2	cubic	1.99	5.5
Zeolite NaX (synthetic)	$Na_{86}[(AlO_2)_{86}(SiO_2)_{106}]\cdot 264H_2O$	1 - 1.5	cubic	1.93	4.7

As natural zeolites are mined in different geographic regions it is necessary to study additionally crystallographic data and determine more precisely their mineral and chemical compositions [3 - 5]. Among natural zeolites the most used, as sorbents, are mordenite, montmorillonite, clinoptilolite, phillipsite, chabazite [6]. Besides, natural zeolites are widely applied in the nuclear engineering as sorbents for radionuclide removal from water solutions [7].

In 90th years a series of composite aluminosilicate sorbents based on natural zeolites has been offered [8]. However, at that time the projects were limited by applications of only natural components, therefore, the sorption list for this sorbent was short despite its low cost. Subsequent investigations on the sorption properties of zeolites being under statistical conditions have shown that natural zeolites, in the case of strontium and cadmium, have low sorption properties [9 - 11]. Also it should be taken into account that clinoptilolite possesses a high-temperature stability and withstands the thermal action up to 700 ºC without appreciable structural changes [2]. Synthetic zeolites are unsuitable for use at > 200 ºC because during temperature rise the zeolite structure recrystalli-

zation takes place and a part of absorbed ions can escape from the crystal lattice [2]. Application of a composition comprising natural and synthetic zeolites permits to enlarge significantly the sorption list of elements and next to form a matrix for radioactive effluent disposal.

Research purpose definition

The purpose of this investigation is to determine the influence of sorbent composition content on the cesium sorption processes. The content of natural and synthetic zeolites in compositions has been varied that should lead to the change of sorption properties.

Materials and methods

In the course of experiments we have used natural and synthetic zeolites: natural zeolite – clinoplilolite (Ukraine), synthetic zeolites – zeolite NaX and NaA zeolite NaA (Russia).

The compositions (natural and synthetic zeolites were made in the following proportions:

1) natural zeolite – 100 % and synthetic zeolite – 0 %;
2) natural zeolite – 75 % and synthetic zeolite – 25 %;
3) natural zeolite – 50% and synthetic zeolite – 50 %;
4) natural zeolite – 25 % and synthetic zeolite – 75 %;
5) natural zeolite – 0 % and synthetic zeolite – 100 %.

The sorption subject was a water solution of cesium nitrate ($CsNO_3$). The sorption procedure has been carried out under dynamic conditions. To create dynamic conditions the authors designed a sorption device [12] comprising a pump, a sorption column with a cartridge, a tank and a batchbox. The sorption cartridge has a diameter of 8 mm and a height of 25 mm. The sampling was performed after 40 sorption cycles.

An analytic part of the experiment was conducted using an analytic nuclear-physical complex “Sokol” [13]. Targets for measurements were prepared of a solution solid residue on the carbon substrate. Cesium was activated by the beam of protons having an energy $E_p \approx 1600$ keV and average current $I_p \approx 150$ nA. An excited characteristic X-ray emission from L-series cesium atoms was recorded by means of a Si-pin detector with a resolution of 155 eV along the 6.4 keV line. The detector, placed at a distance of 7 mm from the target, was provided with a collimator of 2.5 mm in diameter and polyvinylchloride absorber of 150 μm thickness [14]. The relative measurement error was 5 %.

Results and discussion

For qualitative estimation of the sorbent-cesium interaction we have used the sorption coefficient (K_s, %), calculated by the formula of [12]

$$K_s = \frac{(C_0 - C_p)\cdot 100\,\%}{C_0},$$

where C_o and C_p are the initial and equilibrium solution concentrations, mole/dm^3.

The consideration of sorption properties in the clinoptilolite – zeolite NaX composition (Table 2) demonstrate that in the clinoptilolite (50 %) – zeolite NaX (50 %) composition they are significantly decreased (to 76 %). The cause is that the grains of each of sorbents are covered by the sorbent microparticles and when the solution passes through the sorbent composition these microparticles become to move and block the voids of the second sorbent being in the composition. In the clinoptilolite (75 %) – zeolite NaX (25 %) composition an insignificant cesium sorption decrease (80.69 %) is observed as compared to the pure clinoptilolite (82.46 %). The cesium sorption decrease does not exceed the measurement error.

In comparison with the pure zeolite NaX, the decrease of sorption properties in the composition containing 25 % of clinoptilolite does not exceed the measurement errors.

Table 2. **Cesium sorption in the clinoptilolite – zeolite NaX composition with different percentage of components**

Zeolite	Clinoptilolite – 100 % Zeolite NaX – 0 %	Clinoptilolite – 75 % Zeolite NaX – 25 %	Clinoptilolite – 50 % Zeolite NaX – 50 %	Clinoptilolite – 25 % Zeolite NaX – 75 %	Clinoptilolite – 0 % Zeolite NaX – 100 %
Sorption coefficient, %	82.46	80.69	76.00	79.60	82.45

Table 3 presents the data for the clinoptilolite – zeolite NaA composition. One can see a significant decrease (to 72 %) of sorption properties in the clinoptilolite (50 %) – zeolite NaA (50 %) composi-

tion. This decrease is due to the fact that the zeolite grains have a dust coating of finest zeolite particles. In the course of dynamic sorption, when the solution passes through the sorbent, the particles from the dust coating become to move and penetrate into the sorbent voids thus decreasing the sorption properties. In the clinoptilolite (75 %) – zeolite NaA (25 %) composition a cesium sorption decrease is insignificant (79.05 %) as compared to the pure clinoptilolite (82.46 %). The cesium sorption decrease does not exceed the measurement error.

Table 3. **Cesium sorption in the clinoptilolite – zeolite NaA composition with different percentage of components**

Zeolite	Clinoptilolite – 100 % Zeolite NaA – 0 %	Clinoptilolite – 75 % Zeolite NaA – 25 %	Clinoptilolite – 50 % Zeolite NaA – 50 %	Clinoptilolite – 25 % Zeolite NaA – 75 %	Clinoptilolite – 0 % Zeolite NaA – 100 %
Sorption coefficient, %	82.46	79.05	72.00	69.88	68.15

In the composition containing 25 % of clinoptilolite the decrease of sorption properties, as compared to the pure zeolite NaA does not exceed the measurement error.

Conclusion

The results of investigations on the composite sorbent comprising two components (natural zeolite and synthetic zeolite) show that the introduction of one of components in the amount more than 25 % exerts significant influence on the cesium sorption. When the composition components are in the ratio 50 to 50 % the sorption coefficient decreases nearly by 10 %. It should be noted that in comparison with the sorption properties of pure components (in the case of cesium): clinoptilolite, zeolite NaX and zeolite NaA, the composition containing clinoptilolite and zeolite NaX possesses higher sorption properties.

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ЗАСТОСУВАННЯ КОМПОЗИЦІЙНОГО СОРБЕНТУ НА ОСНОВІ ПРИРОДНОГО ТА СИНТЕТИЧНОГО ЦЕОЛІТІВ ДЛЯ ВИВЕДЕННЯ ІОНІВ ЦЕЗІЮ З ВОДНИХ РОЗЧИНІВ

Визначено вплив змін співвідношення компонентів у складі композиційного сорбенту на основі природного та синтетичного цеолітів на сорбцію цезію з водного розчину. До складу композиційного сорбенту входили природний і синтетичний цеоліт у різних співвідношеннях.

Ключові слова: сорбція, цезій, рідкі радіоактивні відходи, цеоліти, кліноптілоліт, синтетичні цеоліти, коефіцієнт сорбції.

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ПРИМЕНЕНИЕ КОМПОЗИЦИОННОГО СОРБЕНТА НА ОСНОВЕ ПРИРОДНОГО И СИНТЕТИЧЕСКОГО ЦЕОЛИТОВ ДЛЯ ВЫВЕДЕНИЯ ИОНОВ ЦЕЗИЯ ИЗ ВОДНЫХ РАСТВОРОВ

Определено влияние изменений соотношения компонентов в составе композиционного сорбента на основе природного и синтетического цеолитов на сорбцию цезия из водного раствора. В состав композиционного сорбента входили природный и синтетический цеолит в различных соотношениях.

Ключевые слова: сорбция, цезий, жидкие радиоактивные отходы, цеолиты, клиноптилолит, синтетические цеолиты, коэффициент сорбции.

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