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### SYNTHESIS AND PROPERTIES OF THE COMPOSITE SORBENTS ON THE BASIS OF ALUMOSILICATES SEPARATED FROM THE CLAY-SALT SLIMES

The composite sorbent, including an active inorganic component (alumosilicates derived from clay-salt slimes) in the quantity of more than 80 wt % and the polymer binder (polyacrylamide) was obtained. The influence of various factors on its sorption and mechanical properties were studied. It is established that the content of polyacrylamide in the composite sorbent should be in the range of 10–15 wt %. It is shown that quasi-equilibrium of  $^{137}\text{Cs}$  in the system "sorbent – solution" is reached within 80 min. The distribution coefficient ( $K_d$ ) is  $2.4 \cdot 10^4 \text{ cm}^3/\text{g}$ . The obtained data of kinetic parameters (diffusion coefficient and during sorption half-time) show that the received sorbent can be referred to sorbents with high rate of  $^{137}\text{Cs}$  sorption.

**Introduction.** Development of new types of selective sorbents, study of their physical, chemical and sorption properties is an actual problem, the solution of which will determine the ways of improving the technology for processing of liquid radioactive waste (LRW) of low and intermediate level.

Recently, much attention is paid to the use of inorganic sorbents for clearing of radioactive solutions out from radionuclides [1–3]. These materials are superior to organic resins in their mechanical, thermal and radiation resistance, and exhibit high selectivity for different radionuclides. Unfortunately, most of inorganic sorbents are amorphous and fine-grained sediments, that is why it is difficult to use them for treatment of large volumes of liquid radioactive waste in dynamic conditions because of the high hydrodynamic resistance. In this regard, the possibility of effective practical application of inorganic ion exchange materials will be largely determined not only by their chemical properties, but also by their hydromechanical resistance. As a rule, for inorganic ion exchange materials an adequate hydromechanical stability is achieved through the development of composite sorbents [4–9]. In this case, such inorganic materials as silica gel, zeolites, zirconium hydroxide, etc are generally used in the quality of binders or carriers.

In today's world, there are various technologies of composite materials production based on inor-

ganic ion-exchange materials, comparisons are shown in Table 1.

As can be seen from the Table 1, high hydro-mechanical stability of the composite sorbent is provided by a significant reduction in the proportion of active component in the sorbent, which leads to a decrease of its sorption capacity. So, development and production of the compositional sorbent with a high degree of active component and high hydromechanical stability is an important task.

In connection with the above, the aim of this work was to obtain a composite sorbent with a share of the active component in a composition equal to more than 80 wt %, and to study its sorption-kinetic properties.

Thanks to the analysis of published data on the physical and chemical properties of polymer materials and the understanding of the mechanism of stress generating in granules of composite sorbents [3, 10], it is possible to make a conclusion that there is a possibility to use organic polymers as part of the composite sorbent and these polymers will carry out a binding function. Among a number of organic polymer binders (polyacrylamide, polyvinyl acetate and carboxymethyl cellulose) available for the synthesis of compositional sorbent, such material as polyacrylamid has been chosen since it is very soluble in water and is strong enough to wear.

Table 1

Comparison of different technologies of composite materials production based on inorganic ion-exchange materials

Technology of production	Proportion of the active ingredient, %	Hydromechanical stability, %
Drying-out	100	20–50
Impregnation into finished media	up to 20	75–80
Co-precipitation with silica gel	up to 50	85–90
The sol-gel method	up to 30	85–95

**Objects and methods.** For the synthesis of composite sorbent samples there were used clay-salt slimes (CSS) – waste of potassium production of the JSC “Belaruskali” which contain in their composition 30–35 wt % of water-soluble chloride salts of potassium and sodium, and about 40–50 wt % of superfine aluminosilicates (illite, feldspar and others).

Aluminosilicates of CSS were extracted by filtering the suspension through a sintered metal membrane “Trumem” with a pore size of 1.0 and 0.2  $\mu\text{m}$  with the ratio of the solid : the liquid phase equal to 1 : 30.

Synthesis of composite sorbents was carried out by mixing of a solution of aluminosilicates (pH = 9–11) and an organic polymer solution, followed by stirring of the mixture for 1–2 h. Then the precipitate was detached and annealed at 150–200°C for 2–4 h. This approach provides a combination of two processes: curing of the composition and molding of pellets.

According to the experimental data presented in the paper [11], aluminosilicates belonging to the CSS exhibit selective properties with respect to radionuclide  $^{137}\text{Cs}$  and effectively remove it from the radioactive solutions with salt content up to 30 g/l.

To study the sorption and transport properties of composite sorbents (CS) based on aluminosilicate (AS) and polyacrylamide (PA) the following samples were used. The description of the samples is presented in Table 2.

Table 2

Characterization of composite sorbents

The title of samples	The components of the CS, wt %	
	AC	PA
CS-1	95	5
CS-2	90	10
CS-3	85	15
CS-4	70	30

Static sorption capacity of the samples of composite sorbents was determined with the use of the following procedure [12]. The weighed portion of a sorbent sample with the fraction size equal to 0.25–0.50 mm and a mass of 0.2 g was brought into contact with 10  $\text{cm}^3$  of a solution of radioactive  $^{137}\text{Cs}$ . Mixing of phases is effectuated by mechanical stirrer at a speed of 300 rev/min.

In this work radionuclide  $^{137}\text{Cs}$  was used, which acted as a radioactive label. The specific activity of  $^{137}\text{Cs}$  solution was  $2 \cdot 10^5$  Bq/l. The distribution of  $^{137}\text{Cs}$  between the phases was determined by the change in the activity of the aqueous phase before and after the sorption on the gamma-beta spectrometer (RUS-91M).

Sorption isotherms of  $^{137}\text{Cs}$  in the samples of the composite sorbent were obtained by changing

the concentration of the non-active cesium in solution in the range of 0.1 to 5.0 meq/l. Duration of the contact phase was 24 h at  $(20 \pm 1)$  °C.

To calculate the concentration of inactive cesium adsorbed on the composite sorbents the following relations are used:

$$K_d = \frac{a_0 - a}{a} \frac{V}{m}, \quad (1)$$

where  $K_d$  – distribution ratio  $^{137}\text{Cs}$ ;  $a_0$  and  $a$  – specific activity of  $^{137}\text{Cs}$  in the initial solution before and after adsorption, respectively, Bq/ $\text{sm}^3$ ;  $V$  – volume of solution,  $\text{sm}^3$ ;  $m$  – mass of sorbent, g.

$$C_e = \frac{C_0}{1 + K_d \frac{V}{m}}, \quad (2)$$

where  $C_e$  and  $C_0$  – respectively the equilibrium and the initial concentration of inactive cesium ions in solution, meq/ $\text{sm}^3$ .

$$Q = \frac{C_0 K_d}{1 + K_d \frac{V}{m}}, \quad (3)$$

where  $Q$  – concentration of inactive cesium, meq/g.

Hydromechanical stability (HMS) assessment of the composite sorbents was performed by the following procedure. 50  $\text{cm}^3$  of distilled water was poured into a plastic cup with the sorbent sample (its mass 5 g). To enhance the mechanical impact on the sorbent, fluoroplastic balls with the size of 2 mm and a weigh of 15 g were added into the cup. Then, the mixture was stirred up during 5 h with the frequency equal to 10 Hz and amplitude equal to 20 mm. According to the number of pellets which remained undistorted, hydromechanical stability assessment was identified [10].

Kinetic parameters of sorption by the sorbent CS-2 were investigated by the method of “limited volume” according to the following procedure [2]. Into a thermostated glass cell, equipped with a mechanical stirrer, a solution  $\text{NaNO}_3$  was poured with the concentration 0.1 mol/l, pH = 6, containing tracer amounts of the radionuclide  $^{137}\text{Cs}$  ( $2 \cdot 10^5$  Bq/l). The experiment was carried out at  $(20 \pm 1)$  °C and repeated twice.

Into the cell there was loaded 0.2 g of the weighed portion of a sorbent with the fraction size 0.25–0.50 mm. Then, the mixing was turned on at a speed suitable to ensure full turbulence of the sorbent grains in the solution. At regular intervals, the specific activity of  $^{137}\text{Cs}$  in the solution was measured by microsampling (0.2  $\text{cm}^3$ ).

The degree of sorption ( $S_i$ ) and the degree of the sorption equilibrium achievement ( $F$ ) were calculated using the following formulas:

$$S_t = \frac{a_0 - a}{a_0} 100\%, \quad (4)$$

$$F = \frac{S_t}{S_e}, \quad (5)$$

where  $a_0$  and  $a$  – specific activity of  $^{137}\text{Cs}$  in the initial solution and the solution at time  $t$ , respectively,  $\text{Bq}/\text{sm}^3$ ;  $S_t$  and  $S_e$  – the degree of sorption of  $^{137}\text{Cs}$  on the sorbent at time  $t$  and in the quasi-equilibrium conditions, respectively.

**Results and discussion.** Maximum concentration of inactive cesium was taken as static sorption capacity by the sorbent sample in relation to the ions of cesium. The dependence of the static sorption capacity (CEC) for the composite sorbents on the polyacrylamide content is shown in Fig. 1.

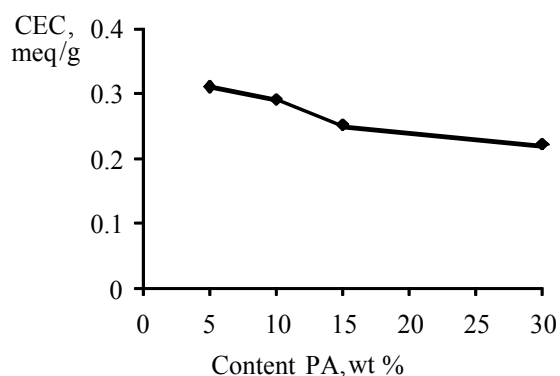


Fig. 1. The static sorption capacity for the composite sorbent depends on the content of polyacrylamide

As can be seen from Fig. 1, the increase in the content of polyacrylamide in the composition leads to an almost linear decrease in its static sorption capacity with respect to the ion of cesium.

The experimental results are used for elaboration of dependence of hydro-based stability of the composite sorbents on the content of polyacrylamide in them. The nature of this dependence is shown in Fig. 2.

As shown in Fig. 2, dependence of the hydro-mechanical stability of the sorbent on the content of polyacrylamide has a pronounced stepwise character. Thus, when the concentration of polyacrylamide is more than 15 wt %, the value of HMS is almost constant. This apparently indicates that within this very concentration the formation of a solid polymer frame of a granule occurs.

The experimental data show that for the composite sorbent based on aluminosilicates extracted out from CSS, the optimal content of polyacrylamide is that of 10–15 wt %. In this case, the composite sorbent remains the high value of the sorption capacity for cesium ion and, thus, it is

provided a strong enough packaging resistant to deformation.

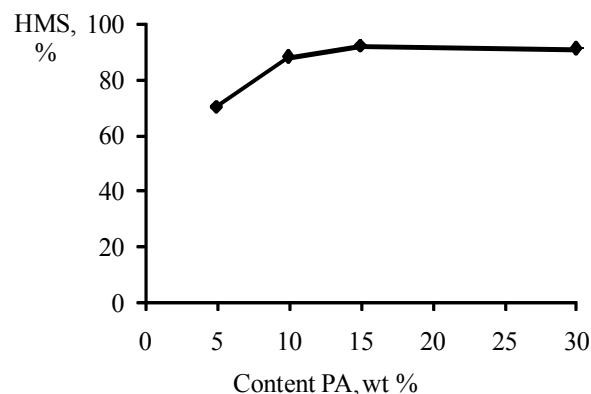


Fig. 2. Hydromechanical stability of the composite sorbent depends on the content of polyacrylamide

Currently, it is established the fact that the high sorption capacity of soils and sediments is determined by the presence of layered minerals of illite type even in small amounts (10 Å) [13–15].

According to the theory of selective sorption, the behavior of  $^{137}\text{Cs}$  in the solution is determined by its specific sorption and fixation on the layered minerals (illite, montmorillonite, vermiculite, etc.) with the crystal lattice of 2 : 1. Radiocesium irreversibly adsorbed on selective sorption sites, so-called FES (Frayed Edge Sites), located between the layers of the crystal lattice of the extended ends. The specific location of FES causes their high selectivity for cesium ions and other monovalent cations with low hydration energy ( $\text{K}^+$ ,  $\text{NH}_4^+$ ,  $\text{Rb}^+$ ). At these centers, the sorption of  $\text{Cs}^+$  tens and hundreds times higher compared with major competing cations of potassium ( $\text{K}^+$ ) and ammonium ( $\text{NH}_4^+$ ) [16, 17].

As it is shown in the papers [16, 17], the capacity of the selective sorption sites (FES) are located between the layers of the crystal lattice in their extended edges, which determines the ability of layered minerals to sorb  $^{137}\text{Cs}$  specifically, and the number of FES is only 1–8% of the total sorption capacity (CEC) for different minerals [18]. When placed on the selective sorption sites (FES) there occurs hindering in the procedure of exchange of  $^{137}\text{Cs}$  for ions  $\text{Na}^+$  and  $\text{Ca}^{2+}$  which predominate in the liquid radioactive waste.

Maximum capacity of selective sorption (FES) was determined for the sorbent CS-2 by processing of the experimental data on the initial section of the sorption isotherm with the use of Langmuir equation in the linear form [12]:

$$\frac{I}{Q} = \frac{I}{[FES]} + \frac{K}{[FES]} \frac{I}{[C_e]}, \quad (6)$$

where  $Q$  – number of non-active cesium ions sorbed by the sorbent, meq/g;  $[FES]$  – selective sorption capacity, meq/g;  $K$  – empirical constant, which is a characteristic of the binding force of the sorbent sorption centers in respect to the cesium ions;  $C_e$  – concentration of inactive cesium ions in the solution, meq/sm<sup>3</sup>.

According to the experimental data, the selective sorption capacity (FES) of the sorbent CS-2 was  $(0.065 \pm 0.012)$  meq/g, which is comparable with the specific sorption capacity of the ferrocyanide sorbent “Termoksid-35” (0.1 meq/g) [3].

The kinetics of sorption of <sup>137</sup>Cs on a sorbent CS-2 has shown that the time of reaching of the quasi-equilibrium (i.e. independence in time at the specific activity of a test solution) in the “solid phase – solution” is about 80 min. The kinetic value of <sup>137</sup>Cs sorption for the composite sorbent CS-2 is shown in Fig. 3.

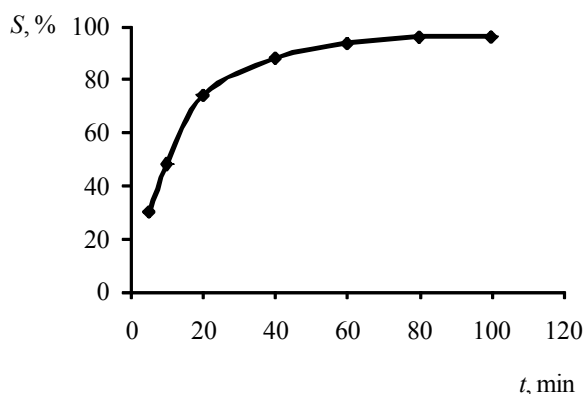


Fig. 3. Sorption kinetics of <sup>137</sup>Cs for the sorbent CS-2

On the curve two places can be identified, where the process of sorption of <sup>137</sup>Cs upon the sorbent runs at different speeds. As can be seen from Fig. 3, the sorption of <sup>137</sup>Cs upon the sorbent CS-2 is fast enough. During the first 40 min it is sorbed up to 92% of <sup>137</sup>Cs of its equilibrium quantity, then the sorption rate decreases bitterly. The degree of quasi-equilibrium sorption of <sup>137</sup>Cs upon the sorbent CS-2 out of 0.1 mol/l NaNO<sub>3</sub> solution was 96%.

The calculation of the diffusion coefficient ( $D$ ) was performed by the processing of experimental dependence of the degree of sorption equilibrium achievement ( $F$ ) on the time ( $t$ ) by the method of least squares with  $F < 0.4$ .

The experiments showed that the dependence of  $F - t$  at  $F < 0.4$  upon the investigated sample of the sorbent CS-2 is satisfactorily approximated by linear dependence in the coordinates  $F - \sqrt{t}$ , indicating that the internal diffusion kinetics of the process takes place.

Diffusion coefficient ( $D$ ) was calculated by the equation, provided that  $F < 0.4$  [19]:

$$F = \frac{6}{R_{av}} \frac{a_0}{a_0 - a_e} \sqrt{\frac{Dt}{\pi}} \quad (7)$$

The time of semi-exchange of the sorption was determined according to the following formula:

$$t_{0.5} = 0.03 \frac{R_{av}^2}{D}, \quad (8)$$

where  $R_{av}$  – average radius of granules, m;  $a_0$  and  $a_e$  – specific activity of <sup>137</sup>Cs in the initial and equilibrium solutions, respectively, Bq/sm<sup>3</sup>;  $D$  – diffusion coefficient, m<sup>2</sup>/s.

Sorption values of <sup>137</sup>Cs on the composite sorbent CS-2 from NaNO<sub>3</sub> solution with the concentration 0.1 mol/l and pH = 6 are shown in Table 3.

Table 3

**Sorption values of <sup>137</sup>Cs  
on the composite sorbent CS-2**

Indices of sorption	Value of indices
Fractional composition, mm	0.25–0.50
$R_{av}$ , m	$1.88 \cdot 10^{-4}$
$D$ , m <sup>2</sup> /s	$(175 \pm 65) \cdot 10^{-14}$
$t_{0.5}$ , min	10
$K_d$ , cm <sup>3</sup> /g	$(24 \pm 4) \cdot 10^3$
$S_e$ , %	96

The data presented in the Table 3 show that according to the following kinetic characteristics: the diffusion coefficient ( $D$ ) and the time of sorption semi-exchange ( $t_{0.5}$ ), the sorbent CS-2 with the following composition (AS + PA = 90 + 10 wt %) in the context of the classification proposed in this paper [2], can be referred as a sorbent with high sorption capacity in respect to <sup>137</sup>Cs.

**Conclusion.** Based on the research results, it was established that for the synthesis of the composite sorbent based on aluminosilicates separated from CSS, the optimal content of polyacrylamide is 10–15 wt %. This content of polyacrylamide provides a high value of the static sorption capacity relative to <sup>137</sup>Cs and a strong enough structure resistant to deformation.

The obtained values of the kinetic parameters (diffusion coefficient and sorption half-time of the cesium sorption) show that the sorbent with the composition (AS + PA = 90 + 10 wt %) can be referred to sorbents with high sorption of <sup>137</sup>Cs.

Thus, the composite sorbents with a share of the active component of more than 80 wt % can be considered as perspective for clean-up of liquid radioactive waste (medium and low level activity).

From the practical point of view, the advantages of the developed sorbents are the following: good kinetic and capacity characteristics, simple technology of production and the availability of

large volumes of CSS in Belarus which is the co-product of potassium fertilizers production at the JSC "Belaruskalii".

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