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## Chemical and mineralogical aspects of clay-salt slimes of "Belaruskali" using for the preparation of nanostructured sorbents of radionuclides

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### Abstract

In the context of intensive nuclear-power engineering development there is an urgent need to solve a range of technological and environmental challenges associated with generation, treatment and disposal of radioactive waste. In this regards, the problems of radioactive waste safe management and rehabilitation of radioactively contaminated soils in the result of the radiation accidents at the Chernobyl and Fukushima Daiichi NPPs are especially significant. Concerning that, investigation of effective and low cost sorption materials for radionuclides immobilization has a special relevance.

In order to solve the above mentioned problems, it is supposed to develop a resource-saving technology for production of multi-purpose nanostructured sorbents of radionuclides (<sup>137</sup>Cs, <sup>90</sup>Sr) with predetermined physicochemical properties based on the waste of potash industry – clay-salt slimes (CSS) of the JSC "Belaruskali".

The performed research has shown that the CSS samples have a high fixing ability in relation to <sup>137</sup>Cs. The main sorption-active minerals in CSS are illite and montmorillonite. The degree of sorption is 99.6%,  $K_d$  is  $1.2 \times 10^5$  l/kg, RIP(K) is 6343 mmol/kg. The modification of the S-1 sample allows to enlarge the content of sorption-active minerals tentatively in 3.5 times, thereafter RIP(K) for the S-3 sample may be significantly increased.

Based on the obtained experimental data, CSS of the JSC "Belaruskali" can be estimated as a perspective initial material for production of multi-purpose nanostructured sorbents of radionuclides.

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**Keywords:** clay-salt slimes; montmorillonite; illite; radioactive waste; radiocaesium; immobilization; nanostructured sorbents; modification; soil amendments; rehabilitation

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## 1. Introduction

As a result of nuclear-power plants operation and the radiation accidents at the Chernobyl and Fukushima Daiichi NPPs, radioactive contamination of the environment occurs.

The main channels for radionuclides migration in the environment are radioactively contaminated water and soil solutions, which are usually characterized by a wide variety of chemical and radionuclide compositions. To clean the aqueous media from radionuclides the methods based on the processes of sedimentation and adsorption are mainly used. Application of natural sorption materials in these processes is attractive due to the fact that, in contrast to synthetic sorbents, they have a low cost and widely available in the environment. Environmentally safe natural aluminosilicates (zeolites, clays with layered structure etc.) are the most widely used in processes of purification of aqueous media from radionuclides [1].

Natural clay minerals with high cation exchange properties are mainly used for extraction of ionic forms of radionuclides, especially  $^{137}\text{Cs}$  and  $^{90}\text{Sr}$ .

Scientific-based and cost-efficient selection of clay materials that can selectively adsorb radionuclides is related to the search of available natural materials, chemical industry waste and studying of the possibility of their modifications to improve sorption properties.

The purpose of the research is to study physicochemical and sorption properties of clay-salt slimes of the JSC "Belaruskali" with the aim to develop fundamentally new and highly effective sorbents for the purification of aqueous media from radionuclides.

### Nomenclature

NPP	Nuclear Power Plant
CSS	Clay-salt slimes
RIP(K)	Radiocaesium Interception Potential

## 2. Objects and methods of research

The research objects are clay-salt slimes. Clay-salt slimes (CSS) are the industrial waste of the JSC "Belaruskali" formed in the result of sylvinitic ore reprocessing and accumulated in the special slimes storages (on January 1, 2015 the CSS volume is amounting to more than 105 mln tons). The CSS samples from the slimes storage of the 3<sup>rd</sup> mining factory of the JSC "Belaruskali" were selected for the experiments. The S-1 sample (the initial CSS sample) is a clay suspension in a saturated salt solution. It means that clay-salt slimes consist of 2 parts: water-soluble salts (KCl, NaCl) and water insoluble residue (i.r.).

The study of the initial CSS sample (S-1) was performed according to the fundamental principle of the physico-chemical analysis of materials, which determines the following interrelation: «composition – morphology (structure) – properties».

In order to study chemical and mineralogical composition as well as particle size distribution of insoluble residue of the S-1 sample, the S-2 and S-3 samples were used. The S-2 sample was prepared as follows: the S-1 sample was washed from water soluble salts NaCl and KCl and dried to constant weight (323K°, 6h). The S-3 sample was obtained on the base of the S-2 sample by acid treatment (0,1M HCl) causing disruption of carbonates, and then repeating the same procedures as for the S-2sample.

The free specific surface area ( $S_s$ ) of the S-2 sample was determined by the BET method by adsorption of  $\text{N}_2$  vapor at 78K° on the surface area analyzer ASAP-2010 (Micrometrics, USA). Grain size analysis of the S-2 and S-3 samples was carried out on the laser microprobe particle size analyzer Analysette 22 (Fritsch, Germany).

Morphological and elemental composition of the S-1 – S-3 samples were studied by the EDX method on the scanning electron microscope JSM-5610 LV with the system of microprobe chemical analysis EDX JED-2201 (accuracy 0.5%). Phase composition of the S-2 sample was analyzed by the XRD on the diffractometer D8 Advance Bruker AXS (Germany) with  $\text{CuK}_\alpha$  emitting. Content of  $\text{K}^+$  and  $\text{Na}^+$  ions in solution was determined by atomic

absorption spectrometry (AAS) on the spectrometer Solaar 6M. (Analytical lines:  $K^+$  – 766.5;  $Na^+$  – 586.8 nm. Relative error of determination – 15%).

Selective sorption of  $^{137}Cs$  at the S-2 sample was studied under the static conditions by the method of limited volumes [2].

In the sorption experiments distilled water was used as a liquid phase and  $^{137}Cs$  – as a radioactive label. A weighed portion of the air-dry S-2 sample (0,1 g) was suspended in 10 ml of radioactive solution within 24 hours. Concentration of  $Cs^+$  ions in the solutions ranged from  $10^{-10}$  to  $10^{-1}$  mol/l. Sorption capacity ( $C_s$ , mmol/kg) for the S-2 sample was calculated by the formula (1).

$$C_s = (C_{in} - C_{is}) \frac{V}{m}, \quad (1)$$

where  $C_{in}$  and  $C_{is}$  – initial and equilibrium concentration of  $^{137}Cs^+$  in the solution, mmol/l;  
 $V$  – volume of the solution, l;  
 $m$  – weight of the sample, kg.

The Radiocaesium Interception Potential (RIP(K)) was calculated by the formula (2).

$$RIP(K) = \frac{(A_{in} - A_{is})}{A_{is}} \cdot \frac{V}{m} \cdot [K^+]_{is} \quad (2)$$

where  $A_{in}$  and  $A_{is}$  – initial and equilibrium specific activity of  $^{137}Cs$  in the solution, Bq/l;  
 $[K^+]_{is}$  – concentration of  $K^+$  ions in the solution, mmol/l.

### 3. Results and discussion

The content of water-soluble salts (KCl, NaCl) was determined by atomic absorption spectrometry (AAS) for the sample S-1 is  $13.1 \pm 1.4$  and  $17.5 \pm 1.8$  wt.%, respectively; the content of the insoluble residue is 69.4 wt.%. Free specific surface area ( $S_s$ ) determined by the BET method for given sample is  $41.8 \pm 4.2$  m<sup>2</sup>/g.

According to the XRD data, the S-2 sample is characterized by multicomponent mineralogical composition and includes the following phases: calcite ( $13.3 \pm 1.1$ ), quartz ( $24.0 \pm 1.8$ ), potassium feldspar ( $27.7 \pm 2.1$ ), mixlayered minerals ( $34.9 \pm 2.2$ ) wt.%.

Chemical composition of the CSS samples is represented in the Table 1.

Table 1. Chemical composition of the CSS samples.

Sample	Content of chemical compound, wt.%											
	Na <sub>2</sub> O	MgO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	SO <sub>3</sub>	Cl	K <sub>2</sub> O	CaO	TiO <sub>2</sub>	FeO	CuO	ZnO
S-1	2,86	5,26	7,53	27,35	2,00	7,66	13,21	19,84	1,07	9,71	1,99	1,49
S-2	–	3,86	5,99	19,35	0,11	0,06	7,71	13,43	0,90	6,91	0,56	0,21
S-3	0,99	2,48	14,39	48,02	–	0,19	17,06	0,21	7,58	12,15	2,11	0,83

Having summarized and analyzed experimental data obtained by XRD and EDX methods for the S-2 sample, we can assume that the sample contains mix-layer minerals like “illite-montmorillonite”. The structure of illite is close to the montmorillonite structure. However, the charge of illite is located close to the surface of the structural layer

and falls on the unit cell. Because of these features, the adjacent layers in illite are tightly bounded by interlayer cations through ionic forces, and polar molecules can not penetrate between them preventing the lattice from expansion. Illite has a non-swellable crystal lattice (type 2 : 1), not allowing water molecules to pass through. However, as a result of chemical weathering, the inter-packet  $K^+$  ions in illite, which are directly in contact with a solution, are substituted by divalent cations  $Ca^{2+}$  and  $Mg^{2+}$ . This leads to formation of the swelling secondary phases of the montmorillonite type. As it is known from geochemistry, if the transformation processes are not profound and are limited by formation of the swelling phase "illite-montmorillonite" with high tetrahedral charge, the fixing ability of the mixlayer mineral will be high [3].

The integral and differential curves of particle size distribution for the CSS samples are shown in Fig. 1.

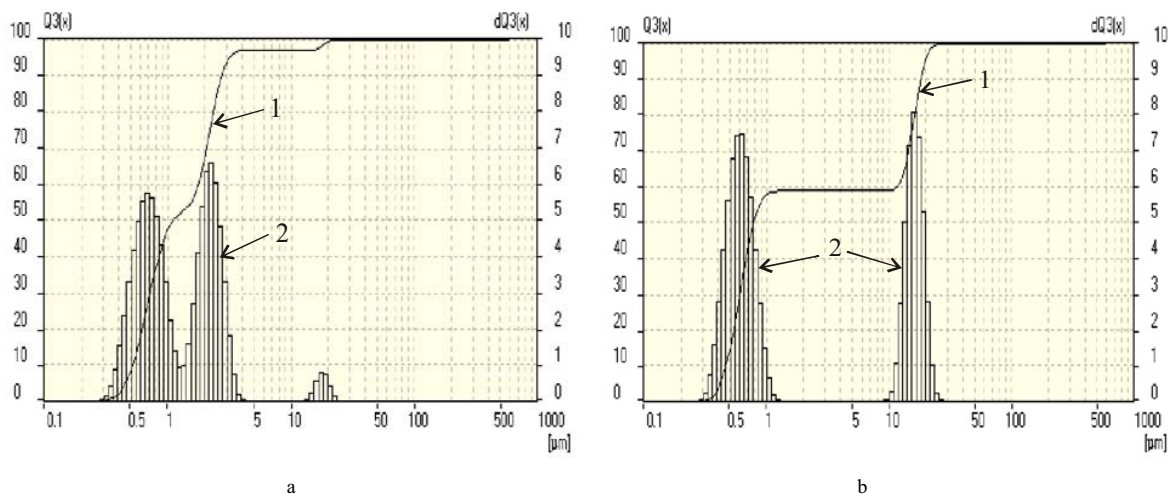


Fig. 1. Particle size distribution for the S-2 (a) and S-3 (b) samples: integral (1) and differential (2) form.

As follows from the presented data (Fig. 1), the particle size in the S-2 and S-3 samples varies from 0.25 to 25 microns. The content of the main fraction (0.25–1.5 microns) in the S-2 sample is 59 wt.%, and in the S-3 sample – 97 wt.%. The destruction of carbonates in the S-2 sample by treatment with 0,1M HCl allows to increase its dispersion in 1.7 times and to enlarge the content of sorption-active mixlayer mineral.

It is known that water-soluble salts significantly alter the structure of clay minerals. In the abstract [4] is shown, that NaCl-smectite tends to form microstructural units from closely packed lamellar elements. According to the results of the electron microscopic analysis, the morphological structure of the particles of the S-2 and S-3 samples is layered and consists of closely packed lamellar elements (Fig. 2), which agrees well with the available data [4].

The particles are presented as large and small flakes in the form of 10–40 nm thick sheet elements. These elements form ultramicrostructural units and microblocks with oriented locations. In addition to primary microporosity caused by the crystal lattice structure, the S-2 and S-3 samples have secondary transitional pores formed by the gaps between contacting particles. Such a structure of the S-2 and S-3 samples promotes the formation of large active surface for sorption.

In the paper [5] it is shown that clay minerals of the illite group are perspective natural materials for selective sorption of radiocaesium ions ( $^{137}Cs^+$ ) from solutions. Due to this, the "illite-montmorillonite" is sorption-active to  $^{137}Cs$  mineral in the S-2 sample. Considering the microstructure and phase composition of the S-1 sample, a series of sorption experiments was performed to assess the possibility of the insoluble residue of the S-2 sample application as a sorption material for selective fixation of  $^{137}Cs$  from solutions. The content of cations  $K^+$  and  $Na^+$  in the solution of the water-soluble part of the S-1 sample was 15.2 and 27.4 mmol/l, respectively, According to the experimental data, the equilibrium concentration of  $Cs^+$  in solution [ $C_s$ ] and its concentration in the solid phase [ $C_{Is}$ ] were calculated. The results obtained are shown in Fig. 3.

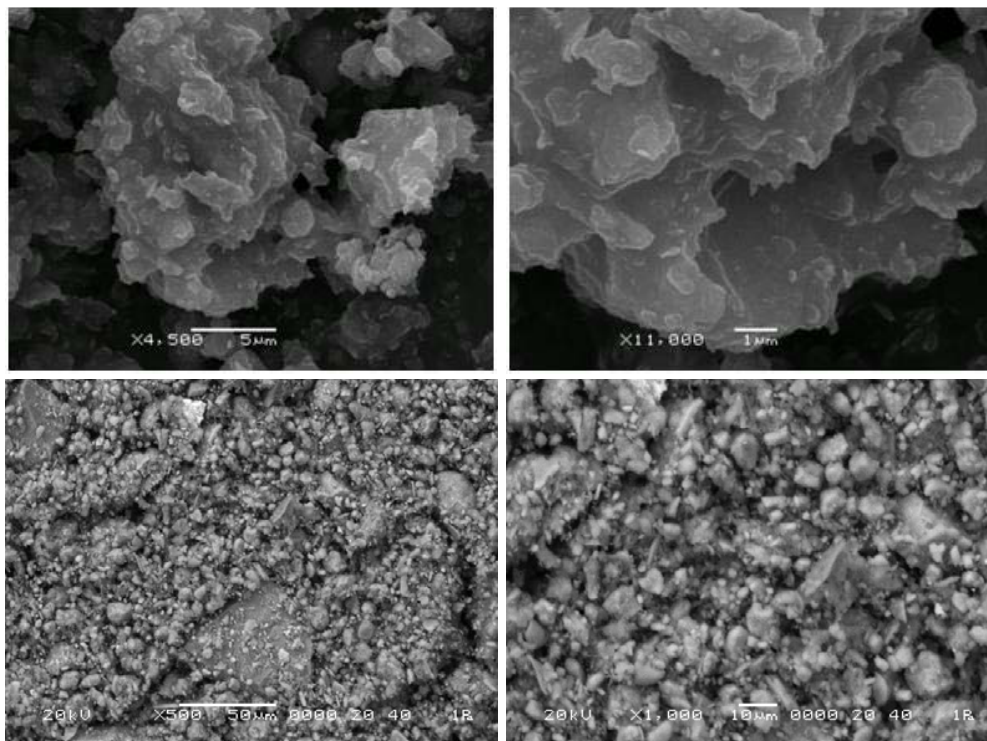


Fig. 2. The morphological structure of the S-2 sample.

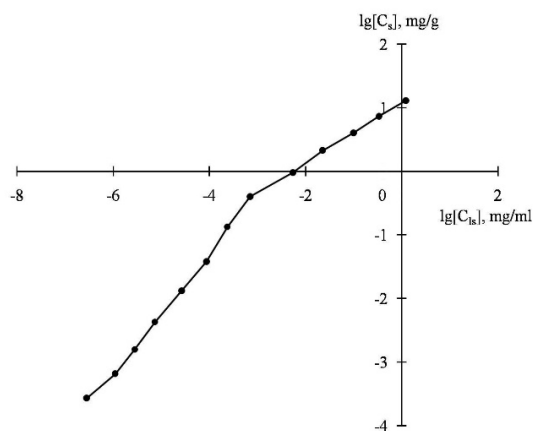


Fig. 3.  $^{137}\text{Cs}$  sorption isotherm on the S-2 sample.

Isotherm of  $^{137}\text{Cs}$  sorption on the S-2 sample (as the solid phase) was obtained over a wide range of concentrations and has a complicated form (Fig. 3). This indicates that in the structure of the S-2 sample several types of sorption centers with different distribution coefficients ( $K_d$ ) may present. Dependence of  $K_d$  on the initial concentration of  $\text{Cs}^+$  in solution  $[\text{C}_{\text{in}}]$  is shown in Fig. 4.

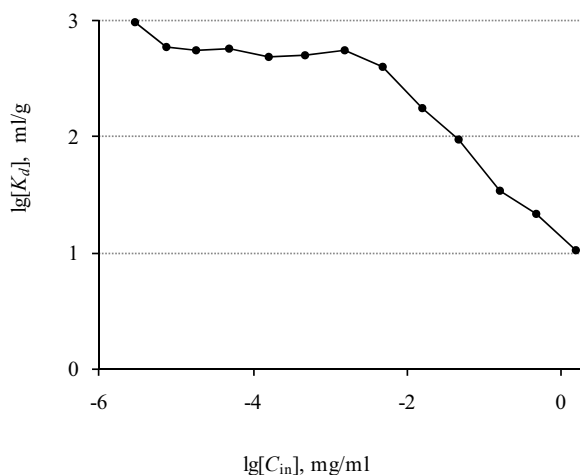


Fig. 4. Dependence of  $K_d$  on the initial concentration of  $\text{Cs}^+$  in the S-2 – solution system.

Analysis of the data obtained indicates that over  $\text{Cs}^+$  concentration range  $10^{-6}$ – $10^{-3}$  g/l the system obeys Henry's Law,  $^{137}\text{Cs}^+$  is a microcomponent and  $K_d$  is a constant (Fig. 4). Over this concentration range the S-2 sample exhibits high selectivity to  $^{137}\text{Cs}^+$  due to the presence of the active component “illite-montmorillonite” therein. Over  $^{137}\text{Cs}^+$  concentration range  $10^{-6}$ – $10^{-3}$  g/l there is a linear section of the isotherm:

$$\lg[C_s] = 2,63 + 0,95 \lg[C_{is}] \quad (3)$$

The angular coefficient of the linear section (0.95) is close to a unit which suggests that the selective sorption of  $^{137}\text{Cs}^+$  on the S-2 sample proceeds according to the ion exchange mechanism and is described by the equation:



The article [5] gives an equation for the sorbent–solution system, which binds selective sorption capacity [FES], radiocaesium selectivity coefficient ( $K_c(\text{Cs}^+/\text{K}^+)$ ),  $^{137}\text{Cs}$  distribution coefficient ( $K_d$ ) and competing ion ( $\text{K}^+$ ) concentration in the solution  $[\text{K}_{is}^+]$ :

$$K_c(\text{Cs}^+ / \text{K}^+)[\text{FES}] = K_d[\text{K}_{is}^+]. \quad (5)$$

$K_c(\text{Cs}^+/\text{K}^+)[\text{FES}]$  and  $K_d[\text{K}_{is}^+]$  are constant over a wide range of  $\text{K}^+$  concentration in solution, provided that under trace amounts of  $^{137}\text{Cs}^+$  the proportion of  $\text{K}^+$  on the sorption centers [FES] tends to unity.

The formula (3) defines such an indicator of selective sorption as radiocaesium interception potential (RIP(K)), which characterizes the ability of sorption materials to retain  $^{137}\text{Cs}^+$  in the conditions controlled by the selective sorption, i.e. in the presence of the competing cation ( $\text{K}^+$ ):

$$\text{RIP(K)} = K_c(\text{Cs}^+ / \text{K}^+)[\text{FES}] = K_d[\text{K}_{is}^+]. \quad (6)$$

The RIP(K) is used to compare the ability of various materials to sorb  $^{137}\text{Cs}$  from solutions [2]. For the S-2 sample the RIP(K) determined by the method [2] is  $6600 \pm 200$  mmol/kg, and  $K_d(^{137}\text{Cs})$  is  $1.3 \times 10^4$  l/kg ( $[\text{K}^+] = 0.5$  mmol/l).

The article [6] gives the RIP(K) value obtained in the similar conditions for a natural illite-based sorbent “Fithian” (Illinois, USA): RIP(K) = 3910±420 mmol/kg. Thus, RIP(K) of the S-2 sample is 1.7 times higher than RIP(K) of the sorbent “Fithian”.

To determine  $^{137}\text{Cs}$  forms and speciation in the S-2 sample, the selective sorption-desorption method was used. The experiment was held under pH = 7.2, after reaching the sorption equilibrium in the system sorbent–solution,  $^{137}\text{Cs}$  was desorbed consistently by the following reagents: distilled water, KCl, 1M HCl. The degree of  $^{137}\text{Cs}$  sorption ( $F_s(^{137}\text{Cs})$ ) is about 98 %. The content of  $^{137}\text{Cs}$  water-soluble forms in the S-2 sample is rather small (~1%). Nearly 14% of  $^{137}\text{Cs}$  is desorbed by KCl solution and 1 % – by 1M HCl solution. Thus, the common content of  $^{137}\text{Cs}$  exchangeable forms in the S-2 sample is about 15 %. The rest of  $^{137}\text{Cs}$  ( $^{137}\text{Cs}$  fixed forms) is firmly fixed in the interlayer space of the sorbent. The similar results were obtained when  $^{137}\text{Cs}$  was in contact with the desorption reagent (0.01 M KCl solution) for 10 days.

#### 4. Summary and conclusions

The S-2 sample (the insoluble residue of the initial CSS sample (S-1)) was subjected to a comprehensive research. It was determined that in the S-2 sample the particle size ranges from 0,25 to 25 microns, and the content of the main fraction (0.25–1.5 microns) is 59 wt.%. The specific surface area ( $S_s$ ) of the given sample is 41.8±4.2 m<sup>2</sup>/g. It is shown that destruction of carbonates in the S-2 sample (with 0.1M HCl) allows to enrich it with sorption-active mineral “illite-montmorillonite” and to increase dispersion in 1.7 times. SEM revealed that the S-2 particles have a layered structure and consist of closely packed lamellar elements about 10–40 nm thick.

The S-2 sample is characterized by high selectivity to  $^{137}\text{Cs}$  at its concentration 10<sup>-6</sup>–10<sup>-3</sup> g/l. The RIP(K) of the S-2 sample is 6600±200 mmol/kg, and  $K_d(^{137}\text{Cs})$  is 1.3 × 10<sup>4</sup> l/kg ([K<sup>+</sup>] = 0.5 mmol/l). The studies have shown that the S-2 sample has a high fixing ability in relation to  $^{137}\text{Cs}$  (up to 84% of the sorbed  $^{137}\text{Cs}$ ).

Given the availability of large volumes of clay-salt slimes (CSS) in the Republic of Belarus which are the industrial waste of the JSC “Belaruskali” and their high sorption properties as well as the ability to use traditional methods and technologies of their reprocessing, this material can be regarded as a secondary mineral resource for production of the nanostructured sorbents of radionuclides.

#### References

1. Rjabchikov B.E. Purification of liquid radioactive waste. Moscow, DeLiprint Publ., 516 p. (in Russian).
2. Wauters J., Elsen A., Cremers A., Konoplev A.V., Bulgakov A.A., Comans R.N.J. Prediction of solid/liquid distribution coefficients of radiocaesium in soils and sediments. Part one: A simplified procedure for the solid phase characterization. Applied Geochemistry, 1996. Vol. 11, pp. 589–594.
3. Popov V.G., Abdrahmanov R.F. Introduction to the exchange-adsorption concept of underground waters formation: structure and ion-exchangeable properties of clay minerals, kinetics of the processes. Geological compilation. Information materials, 2014. Vol. 11, pp. 233–242. (in Russian).
4. Kharitonova G. V., Manucharov A. S., Chernomorchenko N. I., Konovalova N. S. Clay minerals of soils - the natural nanosystems. Abstracts of the II All-Russian scientific and practical conference with international participation "Fundamental advances in soil science, ecology, agriculture towards innovation". Moscow, 2008, pp. 127–128. (in Russian).
5. Cremers A. A., Elsen A., De Preter P., Maes A. Quantitative analysis of radiocaesium retention in soils. Nature, 1988. Vol. 335, № 6187, pp. 247–249.
6. Popov V.E., Il'icheva N.S., Maslova K.M., Stepina I.A. The study of kinetics of selective sorption of  $^{137}\text{Cs}$  by dynamic method with measurement of radioactivity in the solid phase of soil. Pedology, 2011. Vol. 5, pp. 556–563. (in Russian).