

## Radionuclide Sequential Extraction from Reservoir R-17 Bottom Sediments of the Mayak Production Association

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**Abstract**—The extraction parameters and speciation of <sup>137</sup>Cs and <sup>241</sup>Am in bottom sediments of reservoir R-17 of the Mayak Production Association were studied. The extraction was performed with four solutions with different pH values (water simulating in its composition the groundwater from the investigated area, 0.1 M Na<sub>2</sub>CO<sub>3</sub>, acetate buffer solution, and 1 × 10<sup>−3</sup> M HNO<sub>3</sub>). With the first solution, the degree of extraction of <sup>137</sup>Cs and <sup>90</sup>Sr becomes constant in 24 h. The desorption percentage did not depend on pH. The <sup>137</sup>Cs distribution coefficients were calculated. The lowest values were observed in the buffer solution (27) and sodium carbonate solution (21), and the highest values, in water (9250). As shown by sequential extraction, the major fraction of cesium (90%) occurs in the insoluble form. Incorporation into the crystal lattice of clay minerals was found to be the main sorption mechanism. The <sup>241</sup>Am sorption mainly occurs by the mechanism of complexation with carbonates.

**Keywords:** sequential extraction, bottom sediments, cesium-137, americium-241, radioactively contaminated reservoir

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Reservoir R-17 (“Old Swamp”) of the Mayak Production Association is used as an intermediate-level waste repository. A project for conservation of the repository and radiation remediation of the adjacent territory has been developed. Its implementation will allow the surface contamination of the territory to be stopped, but the release of radionuclides into the underground aquifer will continue. Bottom sediments play the role of a “geochemical barrier” to radionuclide migration. The mobility/availability of radionuclides in bottom sediments depends on the strength of their binding, which is determined by the chemical properties of the radionuclides, their speciation in the sediments, and physicochemical features of the bottom sediments. Determination of the parameters of radionuclide extraction from solid technogenic sludge of the reservoir allows evaluation of the radionuclide fixation in the bottom sediments, monitoring of their migration in the reservoir, evaluation of the possibility of the sediment de-

contamination, and determination of the probability of transfer between the abiotic and biotic components.

Reservoir R-17 (water surface area 0.13 km<sup>2</sup>, maximal depth 6.5 m [1]) is in operation since 1949. The total activity in the reservoir is about 74 × 10<sup>15</sup> Bq. The major fraction of radionuclides is deposited in technogenic and natural sludge [2]. The near-bottom suspended material consists to 90% of inorganic substances supplied from the reservoir banks and hydrate-slime slurries and to 10% of organic residues. The radioactivity is mainly due to <sup>90</sup>Sr and <sup>137</sup>Cs [3].

Stukalov and Simkina [4] summarized the results of a comprehensive R-17 study and of studies of the radionuclide desorption from the Old Swamp bottom sediments since the 1950s. In the first steps of the study, experiments were performed with tap and distilled water; tap water extracted radionuclides more efficiently (by 5–15%). The total amount of the extracted activity of β-emitting radionuclides was 47–

**Table 1.** Characteristics of solutions studied

Solution composition	pH	Ionic strength	Concentration, M
Sodium carbonate ( $\text{Na}_2\text{CO}_3$ )	11.1	0.3	0.1
Water of composition simulating the groundwater of the given region <sup>a</sup>	8.1	0.018	$\text{NaHCO}_3$ $4.6 \times 10^{-3}$ , $\text{CaSO}_4$ $1.4 \times 10^{-3}$ , $\text{MgSO}_4$ $2.0 \times 10^{-3}$ , $\text{KCl}$ $2.0 \times 10^{-4}$
Acetate buffer solution ( $\text{CH}_3\text{COONa} + \text{CH}_3\text{COOH}$ ) <sup>b</sup>	5.6	6.66	$\text{Na}^+$ 6.63, $\text{CH}_3\text{COO}^-$ 6.68
Acid ( $\text{HNO}_3$ )	3.0	$1 \times 10^{-3}$	$1 \times 10^{-3}$

<sup>a</sup> The solution was prepared by standard procedure [5] with respect to pH (8.0–8.4).

<sup>b</sup> The solution was prepared by standard procedure [6].

54% depending on the procedure of desorption experiments. In addition, a model experiment on the extraction of  $^{90}\text{Sr}$ ,  $^{137}\text{Cs}$ , and  $^{144}\text{Ce}$  with tap and distilled water from artificially contaminated sludge was performed. The total amount of the  $^{137}\text{Cs}$  activity extracted from the simulated contaminated sludge was 12–46%. An important role of ion exchange for cesium was noted.

In the 1970s, the coefficients of the  $^{137}\text{Cs}$  and  $^{90}\text{Sr}$  desorption with a solution simulating water from reservoir R-17 were calculated:  $15.6 \times 10^{-4}$  and  $8.2 \times 10^{-3} \text{ kg L}^{-1}$ , respectively. The experiment was performed with an 0.1 M  $\text{NH}_4\text{Cl}$  solution. The desorption coefficients were found to be somewhat higher than that for the simulated water ( $^{137}\text{Cs}$   $22.7 \times 10^{-4}$ ,  $^{90}\text{Sr}$   $10.4 \times 10^{-3} \text{ kg L}^{-1}$ ). The strontium desorption coefficient was by approximately an order of magnitude higher than that of cesium, suggesting higher mobility of  $^{90}\text{Sr}$  compared to  $^{137}\text{Cs}$ .

More detailed analysis was performed in 2008: The initial sediment activity was calculated, and the composition of the groundwater used for the radionuclide washout from the sediment was studied. Desorption with natural water (pH 7.3) resulted in removal of 7.2% of  $^{137}\text{Cs}$  and 48.5% of  $^{90}\text{Sr}$  relative to the initial activity. Desorption with nitrate-containing groundwater ( $1.7 \text{ g L}^{-1} \text{ NO}_3^-$ ) resulted in removal of 13.2% of cesium and 50.7% of strontium relative to the initial activity. The  $^{137}\text{Cs}$  and  $^{90}\text{Sr}$  distribution coefficients were calculated for the nitrate solution (9.7 and  $1.2 \text{ m}^3 \text{ kg}^{-1}$ , respectively) and natural water (15.0 and  $1.4 \text{ m}^3 \text{ kg}^{-1}$ , respectively). Three main conclusions were made in these studies.

(1) The dependences of the extracted activity on the number of the desorbing solution portion for  $^{137}\text{Cs}$  and  $^{90}\text{Sr}$  have a descending exponential shape. A fraction of  $^{90}\text{Sr}$  (50%) and  $^{137}\text{Cs}$  (7–13%) is present in technogenic sludge in mobile forms and is washed out even with fresh water at increased salt content. Trans-

uranium elements are not noticeably washed out from technogenic sludge.

(2) The nitrate solution extracts  $^{137}\text{Cs}$  from sludge considerably better (by a factor of 2) than the pure groundwater does.

(3) For  $^{137}\text{Cs}$  and  $^{90}\text{Sr}$ , the desorption coefficient regularly increases in the course of the experiment, which suggests the presence of a significant amount of fixed (unextractable) forms of these radionuclides (approximately 40–50% for  $^{90}\text{Sr}$  and 90% for  $^{137}\text{Cs}$ ) [4].

Ten years have passed since publication of the last data. The dynamics of variation of the radionuclide mobility with time is of interest. This study was aimed at determining the desorption parameters of  $\gamma$ -emitting  $^{137}\text{Cs}$  and  $\alpha$ -emitting  $^{241}\text{Am}$  and their variation in time, and also at identifying the radionuclide sorption mechanisms on R-17 bottom sediments. To achieve this aim, we performed sequential extraction experiments.

## EXPERIMENTAL

In 2013, bottom sediment samples from reservoir R-17 were taken. The sampling site was chosen in the immediate vicinity of the radioactive waste discharge site.

To determine the parameters of radionuclide extraction from R-17 reservoir sludge, four solutions (Table 1) of different compositions with different pH values were prepared.

A vessel with a weighed portion of the bottom sediment (0.1 g) and the solution (45 mL) was placed on a shaker (155 rpm). 1.5-mL aliquots were taken after 1, 3, and 5 h and then at 24-h intervals and were centrifuged (20 min, 21 000 rpm). The solution was separated from the precipitate and measured with a  $\gamma$ -ray spectrometer (GC 3818 Canberra, equipped with an HPGe semiconductor detector), after which the total  $\alpha, \beta$ -activity was measured with a liquid scintillation

spectrometer (Tri-Carb 2700TR). The precipitate was also measured with the  $\gamma$ -ray spectrometer to calculate the distribution coefficients. After a week, the whole vessel with the precipitate was centrifuged (20 min, 8000 rpm), the spent solution was replaced by a fresh portion, and the experiment was repeated.

To analyze and compare the radionuclide extraction parameters, we calculated the extraction percentage by the following equation:

$$K_{\text{extr}} = (A/A_{\text{in}}) \times 100\%,$$

where  $A$  [ $\text{Bq mL}^{-1}$ ] is the aliquot activity and  $A_{\text{in}}$  [ $\text{Bq g}^{-1}$ ] is the initial activity of the sediment.

The initial activity of  $\gamma$ -emitting radionuclides in the sediment was preliminarily calculated for a specific weighed portion of the sludge, taken for each experiment. The initial activity of  $\alpha, \beta$ -emitting radionuclides was evaluated relative to the total activity of the sediment in accordance with the data of [7].

The distribution coefficient of radionuclides in extraction ( $K_d$ ,  $\text{mL g}^{-1}$ ) under the conditions of our experiment for each  $i$ th portion of the extracting solution was calculated using the equation

$$K_d = (S_{i-1} - C_i V)/(m C_i),$$

where  $S_{i-1}$  is the radionuclide activity in the sludge weighed portion after treatment with the preceding portion of the extracting solution ( $i - 1$ ), Bq;  $C_i$ , activity concentration of the radionuclide in the  $i$ th portion of the desorbate,  $\text{Bq mL}^{-1}$ ;  $V$ , volume of one portion of the extracting solution, mL; and  $m$ , sludge sample weight, g.

The extraction percentage was determined in a single run for each point. The experimental error includes the random error of counting (device error) of 0.2–2%, detection efficiency of 2.5–4.5%, and volume measurement error of 1–3%. The total error did not exceed 5% of the results obtained.

The errors of the distribution coefficients were calculated using statistical processing. The sample was sufficient for determining the rms deviation and calculating the errors on the  $3\sigma$  level.

After analyzing the desorption parameters, we performed experiments on sequential extraction of radionuclides from bottom sediments using Tessier's procedure [8]. An 0.05-g portion of bottom sediment from reservoir R-17 of the Mayak Production Associa-

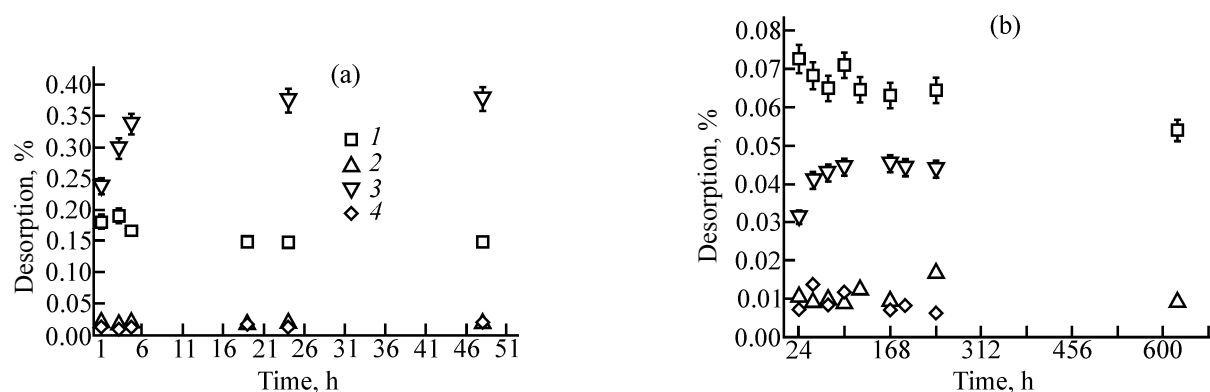
tion was placed in a vial; the solid-to-liquid ratio was 1 : 20. The exchangeable fraction was obtained by stirring a mixture of 0.05 g of the bottom sediment and 1 mL of a 1 M  $\text{MgCl}_2$  solution (pH 7.5) at room temperature for 1 h. The fraction associated with carbonates was obtained by mixing for 3.5 h at room temperature the precipitate from the previous step with 1 mL of a 1 M NaAc solution acidified to pH 4.7 with glacial  $\text{CH}_3\text{COOH}$ . To obtain the fraction associated with iron–manganese oxides, the precipitate from the previous step was extracted for 6 h at 96°C with an 0.04 M  $\text{NH}_2\text{OH}\cdot\text{HCl}$  solution acidified to pH 2.1 with 25% HOAc. The fraction associated with the organic matter was prepared by stirring the residue from the previous step with 2 mL of 30%  $\text{H}_2\text{O}_2$  solution acidified to pH 1.8 with 0.02 M  $\text{HNO}_3$  and heating at 85°C for 2 h. The precipitate from the previous step was extracted by further addition of 2 mL of 30%  $\text{H}_2\text{O}_2$  (pH 1.8) and heating at 85°C for 3 h. The solid-to-liquid ratio in the steps of treatment with  $\text{H}_2\text{O}_2$  was 1 : 40, because  $\text{H}_2\text{O}_2$  is a strong oxidant decomposing on heating (1 mL is insufficient for the extraction). To obtain the insoluble fraction, the precipitates from the previous step were transferred from vials into Teflon beakers for the subsequent dissolution in concentrated acids ( $\text{HF}$ ,  $\text{HNO}_3$ ,  $\text{HCl}$ ). The insoluble residue was broken down in hydrofluoric acid; concentrated  $\text{HNO}_3$  and  $\text{HCl}$  were added in small portions until the precipitate completely dissolved. To dissolve the residual organic matter,  $\text{H}_2\text{O}_2$  was added dropwise. After the precipitate dissolution, the solution was evaporated to wet salts. The salts were dissolved in 1 mL of 3 M  $\text{HNO}_3$ , and the resulting solutions were measured with a  $\gamma$ -ray spectrometer.

To evaluate the random error, experiments were performed with three samples. After each step, the vials were centrifuged (16000 rpm, 25 min). The solution was separated from the precipitate and transferred into a separate Eppendorf test tube.

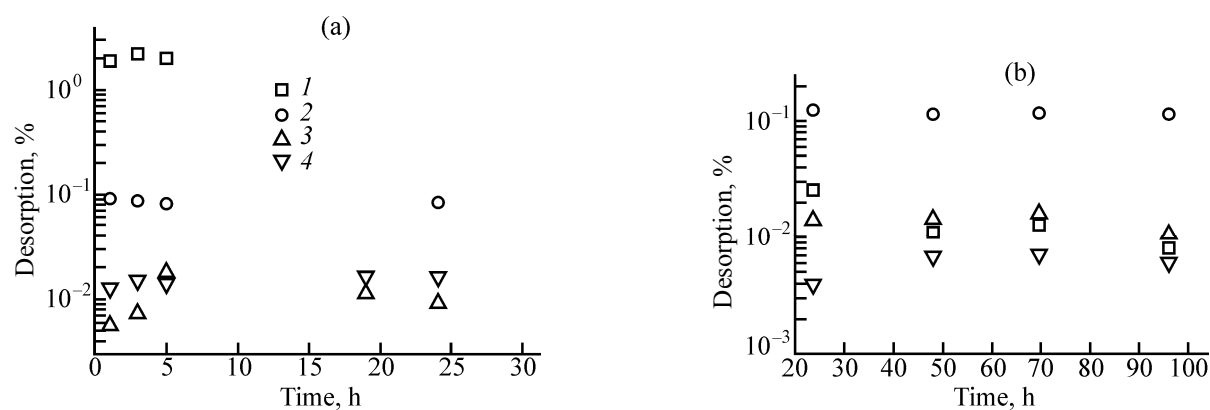
## RESULTS AND DISCUSSION

### *Radionuclide Desorption from R-17 Bottom Sediments*

Figure 1 shows how the  $^{137}\text{Cs}$  desorption percentage for two solutions varies with time (the solution was replaced weekly). For all the four solutions, the  $^{137}\text{Cs}$  desorption percentage in the first extraction cycle becomes constant in 24 h. For the second cycle, the pattern is different: The desorption ceases in 94 h in



**Fig. 1.** Kinetics of  $^{137}\text{Cs}$  desorption with the (a) first and (b) second solution portions. (1) Sodium carbonate solution, (2) water, (3) buffer solution, and (4) acid.



**Fig. 2.** Kinetics of  $^{90}\text{Sr}$  desorption with the (a) first and (b) second solution portions. (1) Buffer solution, (2) acid, (3) sodium carbonate solution, and (4) water.

the buffer solution and acid, in 160 h in water, and in 24 h in the sodium carbonate solution.

Experiments on the  $^{90}\text{Sr}$  desorption kinetics showed (Figs. 2a, 2b) that the desorption ceased in 24 h in both the first and the second solutions.

Treatment of the sediment with the first solution results in relatively rapid washout of the radionuclides from the surface. In treatment with the second solution, the radionuclide desorption occurs during a longer time. To determine the desorption mechanism, we studied the pH dependence of the process. On the whole, Sr is desorbed to a greater extent than Cs.

As seen from Fig. 3, the degree of desorption of  $^{137}\text{Cs}$  and  $^{90}\text{Sr}$  is independent of pH. Therefore, the sediment decontamination can be performed using the solution with pH 8.6, which is the environmentally friendliest value for the reservoir studied, because even minor changes in pH strongly affect the cells of species living in the reservoir.

The independence of the radionuclide desorption from pH allows us to make assumptions concerning the sorption mechanism. For the single-charged  $^{137}\text{Cs}$  cation, the ion-exchange mechanism is typical and is the most probable. The ionic strength of the buffer solution is higher compared to the other solutions tested (Table 1); hence, in the case of the ion-exchange mechanism the highest desorption percentage could be expected in the acetate buffer solution, and this is the case.

For  $^{90}\text{Sr}$ , complexation with acetate anions could be expected. High concentration of  $\text{CH}_3\text{COO}^-$  favors the interaction with  $\text{Sr}^{2+}$  cations, characteristic of the  $\text{Sr(II)}$  chemistry.

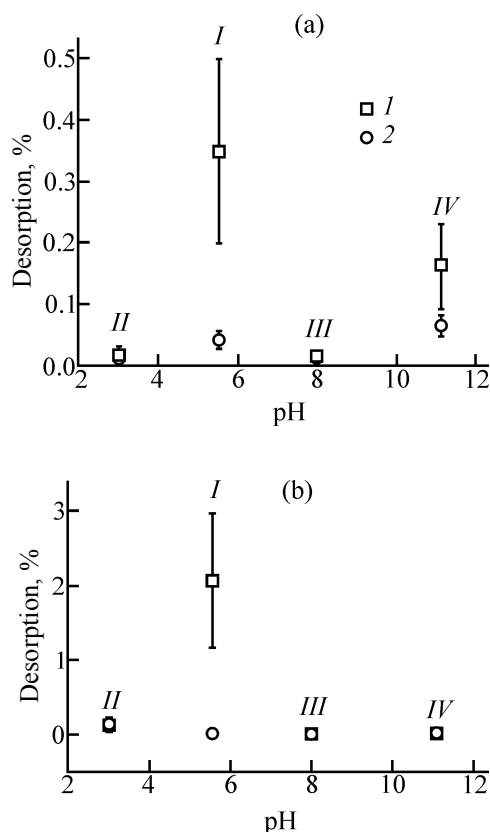
The  $^{137}\text{Cs}$  distribution coefficients are plotted in Fig. 4. The lowest distribution coefficient is observed in the buffer and sodium carbonate solutions, demonstrating easier desorption of  $^{137}\text{Cs}$  from bottom sediments with these solutions than with the other solu-

**Table 2.** Activity concentration of  $^{137}\text{Cs}$  in extracts

Solution	First portion		Second portion	
	activity concentration, $\text{Bq mL}^{-1}$	desorption percentage	activity concentration, $\text{Bq mL}^{-1}$	desorption percentage
Buffer solution	$920 \pm 127$	$0.348 \pm 0.007$	$109 \pm 12$	$0.042 \pm 0.022$
Acid	$38 \pm 14$	$0.014 \pm 0.008$	$22 \pm 7$	$0.009 \pm 0.008$
Water	$42.0 \pm 1.0$	$0.017 \pm 0.001$	$29 \pm 6$	$0.011 \pm 0.008$
Sodium carbonate	$413 \pm 60$	$0.160 \pm 0.014$	$169 \pm 15$	$0.065 \pm 0.011$

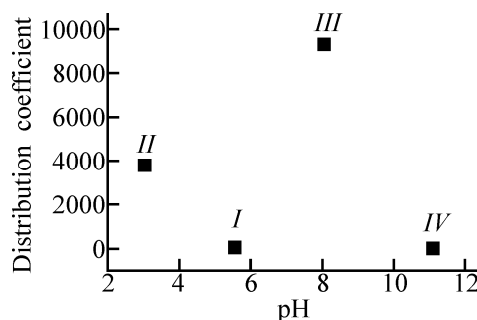
**Table 3.** Activity concentration of  $^{90}\text{Sr}$  in extracts

Solution	First portion		Second portion	
	activity concentration, $\text{Bq mL}^{-1}$	desorption percentage	activity concentration, $\text{Bq mL}^{-1}$	desorption percentage
Buffer solution	$3086 \pm 90$	$2.06 \pm 0.22$	$21 \pm 5$	$0.010 \pm 0.008$
Acid	$128 \pm 9$	$0.090 \pm 0.017$	$175 \pm 5$	$0.120 \pm 0.009$
Water	$21.7 \pm 1.9$	$0.010 \pm 0.003$	$12 \pm 8$	$0.010 \pm 0.001$
Sodium carbonate	$13 \pm 5$	$0.010 \pm 0.009$	$24 \pm 9$	$0.020 \pm 0.001$

**Fig. 3.** Degree of desorption of (a)  $^{137}\text{Cs}$  and (b)  $^{90}\text{Sr}$  as a function of pH. Solution portion: (I) first and (2) second; (I) buffer solution, (II) acid, (III) water, and (IV) sodium carbonate solution.

tions. With water, on the contrary, the distribution coefficient is maximal; i.e., the desorption of radiocesium with water is inefficient.

The data on the desorption percentage and activity concentrations are given in Tables 2 and 3. Despite very low desorption percentage, the activity concentrations of radionuclides in each sample are high, allowing calculation of thousandth fractions of percent. According to NRB-99/2009 document [9], the interference levels ( $\text{Bq mL}^{-1}$ ) are  $11 \times 10^{-3}$  for  $^{137}\text{Cs}$  and  $4.9 \times 10^{-3}$  for  $^{90}\text{Sr}$ . The Cs contamination of the sample exceeds this level by 3–4 orders of magnitude, and the Sr contamination, by 4–6 orders of magnitude. The contamination of the aqueous solution simulating the groundwater, for which the distribution coefficient is

**Fig. 4.** Distribution coefficients of  $^{137}\text{Cs}$ : (I) buffer solution, (II) acid, (III) water, and (IV) sodium carbonate solution.

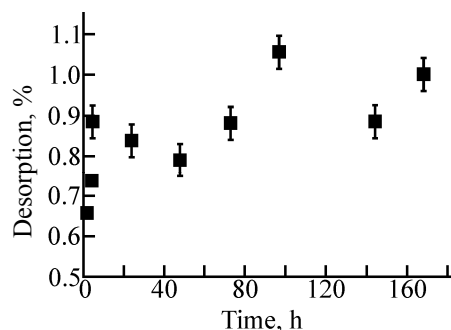


Fig. 5. Desorption of  $^{241}\text{Am}$  with the first portion of the buffer solution.

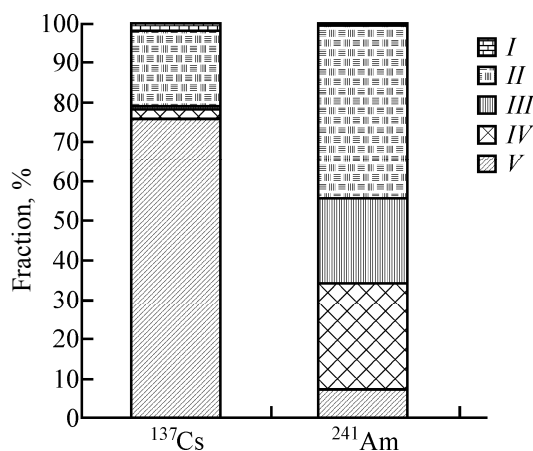


Fig. 6. Percent distribution of  $^{137}\text{Cs}$  and  $^{241}\text{Am}$  between fractions of the bottom sediment of reservoir R-17. Fractions: (I) exchangeable, (II) carbonate, (III) iron-manganese oxides, (IV) associated with organic matter, and (V) residual.

the lowest, exceeds the above level by 3 orders of magnitude. This means that measures should be taken to monitor the situation and exclude the penetration of these radionuclides into groundwater.

#### Desorption of $\alpha$ -Emitting Radionuclides

Figure 5 shows the kinetics of the  $^{241}\text{Am}$  desorption with the buffer solution. Americium-241 was detected only in the first solution, which suggests the  $^{241}\text{Am}$  washout from the sediment particle surface. The error

of calculating the desorption percentage is also relatively high; therefore, it is impossible to judge on actual degree of the  $^{241}\text{Am}$  desorption. In the other solutions tested (sodium carbonate solution, acid solution, water) and the second acetate buffer solution, no  $\alpha$ -emitting radionuclides were detected. This conclusion was confirmed by liquid scintillation spectrometry.

The  $^{241}\text{Am}$  activity and desorption percentage for several successively taken aliquots of the first buffer solution are compared in Table 4. The sample activity exceeds the interference levels (NRB-99/2009) for this radionuclide ( $6.9 \times 10^{-4} \text{ Bq mL}^{-1}$ ) by 6 orders of magnitude.

#### Sequential Extraction of $^{137}\text{Cs}$ and $^{241}\text{Am}$ from V-17 Bottom Sediments

For speciation studies, we chose two radionuclides,  $^{137}\text{Cs}$  and  $^{241}\text{Am}$ . Their activity concentrations were determined using the  $\gamma$ -lines at 661 keV for  $^{137}\text{Cs}$  and at 59 keV for  $^{241}\text{Am}$ . Cesium-137 is the main dose-producing radionuclide of the reservoir and is well detected even at low desorption percentages. Americium-241 is the only  $\alpha$ -emitting radionuclide detected in the desorption experiment; it is biologically available to hydrobionts of the aquatic medium.

The first three fractions, water-soluble, exchangeable, and carbonate, are the most mobile and biologically available; therefore, the content of radionuclides in these fractions is of most interest for evaluating the hazard of the contamination of bottom sediments and migration of radionuclides with reservoir hydrobionts. The desorption experiment showed that the content of  $^{137}\text{Cs}$  in the water-soluble fraction was less than 1% of the total sediment activity;  $^{241}\text{Am}$  was not detected.

The results of the experiment (Fig. 6) showed that the  $^{137}\text{Cs}$  content was the highest in the residual fraction, 43.3%. This suggests the possibility of the incorporation of Cs atoms into the structure of clay minerals, which could be broken down by the action of strong acids such as HF,  $\text{HClO}_4$ , HCl, and  $\text{HNO}_3$ .

Let us consider the state and content of the radionuclides under consideration in each fraction (Table 5).

**Exchangeable fraction.** Exchangeable cations are retained in a sample by weak electrostatic interactions, and their behavior is determined by ion-exchange processes. Changes in the ionic composition of the medium and a decrease in pH of the solution lead to mo-

Table 4. Activity concentration of  $^{241}\text{Am}$  in extracts

Extraction time, h	Activity concentration in extract, $\text{Bq mL}^{-1}$	Desorption, %
1	34.7	0.66
5	46.6	0.88
97	55.6	1.06

bilization of exchangeable ions [10]. This fraction is mobile and biologically readily available. Low Cs percentage and the absence of Am in this fraction show that the transfer of these radionuclides from the sediment to water is low. However, even at low content of  $^{137}\text{Cs}$  in the exchangeable fraction, 1.0% of the total activity of  $^{137}\text{Cs}$  in the sediment, the specific activity of the solution is as high as  $365 \text{ Bq mL}^{-1}$ ; i.e., the solution is radioactively contaminated, and its contamination level exceeds the limits prescribed by NRB-99/2009 [9].

**Carbonate fraction.** In some sequential extraction procedures, this fraction is also termed acid-soluble [11, 12]. Metals coprecipitated with carbonates and adsorbed on the surface of compounds extracted in the subsequent steps are extracted in this step. Metals are extracted from the samples at pH close to 5. The content of metals in this fraction can depend on the bottom sediment composition; namely, it can vary depending on the amount of carbonate minerals [10, 13]. For the bottom sediment sample studied, 11.0% of radiocesium is in the carbonate fraction. The content of Am in this fraction is maximum (32.7%). Complexation of Am with carbonates is a characteristic feature of the Am chemistry and is used for Am separation in other fields of radiochemistry [14]. The maximum amount of Am associated with carbonate complexes was confirmed by many researchers [15, 16].

**Fraction associated with iron–manganese oxides.** The fraction is readily or moderately reducible; manganese oxides and amorphous iron and aluminum oxides are extracted in this fraction. Such compounds are moderately or difficultly mobile and exhibit moderate bioavailability. The reducible material of the soil mainly consists of iron and manganese oxides, in particular, of those known from the viewpoint of fixing trace amounts of metals [17]. Fe–Mn oxides are unstable under reducing conditions. The extraction of metals associated with iron–manganese oxides is performed at low pH values (pH 2), which suggests low bioavailability of radionuclides associated with these oxides. The content of Am in this fraction was significant (15.4%). The highest content of Am is usually observed in the fractions associated with carbonates (prevalent), iron–manganese oxides, and organic matter. On the average, the amount of Am in the fractions associated with Fe–Mn oxides and with the organic matter is approximately equal. The content can differ depending on the chemical composition of soil.

**Table 5.** Relative content of  $^{137}\text{Cs}$  and  $^{241}\text{Am}$  in R-17 reservoir bottom sediment fractions

Fraction	$^{137}\text{Cs}$ , %	$^{241}\text{Am}$ , %
Exchangeable	$1.0 \pm 0.1$	Not detected
Carbonate	$11.0 \pm 0.7$	$32.7 \pm 2.6$
Iron–manganese oxides	$0.5 \pm 0.1$	$15.4 \pm 0.9$
Associated with organic matter	$1.3 \pm 0.1$	$19.5 \pm 1.1$
Residual	$43 \pm 3$	$5.6 \pm 0.3$

**Fraction associated with the organic matter** (oxidizable fraction). Twofold treatment with an  $\text{H}_2\text{O}_2$  solution acidified with  $\text{HNO}_3$  to pH 2 at S : L = 1 : 40 results in extraction of stable organic compounds and sulfides, humic acid salts, and fulvic acids. The fraction is difficultly available biologically and difficultly mobilizable. Binding in complexes with organic compounds of bottom sediments is untypical of cesium [18]. The americium percentage in this fraction is approximately the same as in the fraction associated with iron–manganese oxides.

**Residual fraction.** The largest amount of cesium is in the residual fraction, suggesting isomorphous substitution of sodium and potassium in the crystal structure of clay minerals. The fraction is immobile and biologically unavailable, which demonstrates efficient sorption of cesium by bottom sediments as a “geochemical barrier.”

Thus, we have performed experiments on the radionuclide desorption from bottom sediments of reservoir R-17 of the Mayak Production Association and determined the  $^{137}\text{Cs}$  and  $^{241}\text{Am}$  speciation. The desorption experiments revealed 0.009–0.348%  $^{137}\text{Cs}$  desorption and 0.01–2.06%  $^{90}\text{Sr}$  desorption. The desorption kinetic parameters were determined: The first washout occurs within 24 h for  $^{137}\text{Cs}$  and  $^{90}\text{Sr}$  in all the solutions studied; the second portion of the solution extracts  $^{137}\text{Cs}$  in the time from 24 to 160 h and  $^{90}\text{Sr}$  in 24 h. The distribution coefficients ( $\text{mL g}^{-1}$ ) were calculated for four solutions: sodium carbonate 20, water 9000, buffer solution 27, and acid 3800. The  $^{137}\text{Cs}$  and  $^{90}\text{Sr}$  desorption did not depend on pH but did depend on the solution composition and ionic strength. The specific activity of the final solutions exceeds the interference level (NRB-2009/99) for  $^{137}\text{Cs}$  ( $11 \text{ Bq L}^{-1}$ ) by at least 3 orders of magnitude, that for  $^{90}\text{Sr}$  ( $4.9 \text{ Bq L}^{-1}$ ) by at least 4 orders of magnitude, and that for  $^{241}\text{Am}$  ( $0.69 \text{ Bq L}^{-1}$ ) by 6 orders of magnitude.

The sequential extraction by Tessier’s technique [8]

furnished detailed information on the radionuclide speciation. Cesium can be converted to the soluble form only under the action of strong acids and oxidants. The major fraction of  $^{137}\text{Cs}$  was found in the residual fraction (43%), which suggests that the main mechanism of the sorption onto bottom sediments is incorporation into the structure of clay minerals. In bottom sediments, the  $^{241}\text{Am}$  sorption occurs by the mechanism of complexation predominantly with carbonates and, to a lesser extent, with the organic matter and with iron–manganese oxides. The results obtained agree with the results of studies concerning other reservoirs near the Mayak Production Association territory. In particular, studies of the radionuclide speciation in reservoirs R-10 and R-11 showed that the difficultly soluble fraction contained the maximum amount of Cs and the minimum amount of Am [19].

The results of sequential extraction always depend on numerous factors and can be interpreted differently; however, the occurrence of cesium in the biologically unavailable and physicochemically immobile fraction shows that decontamination of bottom sediments is unfeasible. At high specific activities of bottom sediments, despite low desorption percentage (<1%) with any solution (except strong acids and 1 M NaAc), the specific activity of the contacting solution will also exceed the permissible level (NRB-99/2009) by several orders of magnitude.

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#### CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

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