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Sorption of Long-Lived Radionuclides onto Main Types of Rocks of the Novaya Zemlya Archipelago

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Abstract—The ability of black carbonaceous siltstones and silt sandstones, lime sandstones, gray limestones, carbon–silicon carbonate schists with pyrite, and other rocks that most widely occur on the Novaya Zemlya Archipelago to sorb ^{137}Cs, ^{90}Sr, $^{239+240}$Pu, and ^{241}Am was studied. The distribution coefficients K_d (cm^3 g^{-1}) are as follows: for $^{239+240}$Pu, 2.7×10^3–7.7×10^3; for ^{241}Am, 2.5×10^3–1.8×10^4; and for ^{137}Cs, 1.1×10^2–2.0×10^3. Strontium-85(90) it not noticeably sorbed (within the measurement uncertainty) by any of the rocks studied. $^{239+240}$Pu, ^{241}Am, and ^{137}Cs are strongly sorbed onto the rocks studied and are not noticeably desorbed from them with distilled water. The data obtained are required for predicting the migration of long-lived radionuclides generated by nuclear explosion with surface waters from test sites on the Novaya Zemlya Archipelago.

Keywords: Novaya Zemlya Archipelago, sorption, desorption, radionuclides, strontium-90, cesium-137, plutonium-239+240, americium-241, black carbonaceous siltstones, silt sandstone, lime sandstone, gray limestone, carbon–silicon carbonate schists with pyrite

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In the period from 1954 to 1989, 130 nuclear tests, including 85 atmospheric, 1 surface (1957), 2 overwater, 3 underwater, and 39 underground tests, have been performed at the Central Test Site of the Soviet Union, located on the Novaya Zemlya Archipelago [1, 2]. These tests resulted in radioactive contamination of some areas of the testing site. Because the islands of this archipelago are surrounded by the Barents and Kara Seas, in the period with temperatures higher than 0°C the radionuclides remaining after the explosions can migrate into the surrounding seas.

The migration of radionuclides is mainly determined by their physicochemical properties responsible for the sorption onto rocks or soils, desorption, and leaching, and also by the water flow intensity.

The most hazardous residual radionuclides after the lapse of several decades from the nuclear explosion are long-lived fission products ^{90}Sr and ^{137}Cs and residual nuclear fuel, $^{239+240+241}$Pu. The ^{241}Pu decay leads to accumulation of ^{241}Am ($T_{1/2}$ = 435 years). The ^{241}Am activity fraction gradually increases, reaching significant values (10% and more). Because the physicochemical behavior of Am in the environment can differ significantly from that of Pu, it is also necessary to have data on the distribution coefficients of ^{241}Am in the rock–water system.

The upper layer of the Earth crust on the Novaya Zemlya Archipelago is constituted by diverse rocks: quartzites, sandstones, quartzite sandstones, schists, limestones, siltstones, dolomites, etc. [2, 3].

The results of batch experiments on the ^{90}Sr distribution between fresh hydrocarbonate water and various soils (tundra soils, gray forest soil, medium podzol, kastanozems, chernozem), clayey rocks, sand, and natural sorbents have been reported [4]. The sorption behavior of ^{90}Sr and ^{137}Cs was studied on soils taken from the Hanford plant site (Washington State, the United States) [5] and on natural montmorillonite clay from the Polyana deposit (Shebekino raion, Belgorod oblast) [6]. Data on sorption of ^{90}Sr and ^{137}Cs, obtained in batch and column experiments with samples of granite, diorite, albitized granite, and quartz porphyry from tunnels of the Semilapatinsk Test Site are presented in [7, 8].

The behavior of Pu and Am in soils is largely determined by interaction with humic acids and their complexes with Ca, Fe, and Al, and also with iron and alu-

Table 1. Samples of rocks from the Novaya Zemlya Archipelago

Sample no.	Sampling site	Rock samples
1	Bashmachnyi Pen.	Black carbonaceous siltstones and silt sandstones
2	Bashmachnyi Pen.	Black lime–silt sandstones with calcite interlayers
3	Yuzhnyi Isl., coast of Chernaya Bay	Lime sandstones
4	Yuzhnyi Isl., coast of Chernaya Bay	Gray massive limestones
5	Severnyi Isl., coast of Gulf of Streams	Lime–silt sandstones
6	Severnyi Isl., coast of Gulf of Streams	Silky phyllite-like schists
7	Severnyi Isl., coast of Stepovoi Gulf	Dark gray siltstones
8	Coast of Matochkin Shar Strait	Carbon–silicon–carbonate schists with pyrite

minum oxides [9, 10]. However, we have found no data for rocks of the Novaya Zemlya Archipelago. Therefore, it is necessary to study the ability of these types of rocks to sorb the main artificial long-lived radionuclides: ^{239}Pu, ^{241}Am, ^{90}Sr, and ^{137}Cs.

EXPERIMENTAL

The samples taken for the experiments are listed in Table 1.

To determine the distribution coefficients of $^{239+240}$Pu, ^{241}Am, ^{137}Cs, and ^{90}Sr under laboratory conditions, we performed experiments on sorption and desorption of these radionuclides on various rocks constituting the mountain lands of the Novaya Zemlya Archipelago.

The rock samples were finely divided and fractionated on sieves. The fraction with the particle size in the range 0.25–0.13 mm was taken. The particles were elutriated with water to remove the dust and dried at 105 ± 5°C to constant weight, and weighed portions were taken for each experiment.

The radionuclide sorption was studied in batch experiments. Accurately weighed 2-g portions of each rock were taken for the analysis. The weighed portion was poured over in a flask with 100 mL of the initial solution containing $^{239+240}$Pu, ^{241}Am, ^{137}Cs, and ^{85}Sr.

The flasks, pipets, and beakers used were preliminarily saturated with radionuclides by filling with the initial radioactive solution until the adsorption on the vessel walls ceased.

The flasks were arranged in a laboratory shaker and kept there throughout the experiment. The pH of the solution was determined after the lapse of 24 h and then on the third and seventh days, after which the solution was analyzed by γ-ray and α-ray spectrometry and returned to the flasks to continue the experiment.

The amounts of γ-emitting nuclides were measured with a γ-ray spectrometer equipped with a DGDK-120V Ge(Li) detector. The measurement uncertainty was 7–15%.

The content of α-emitting isotopes, $^{239+240}$Pu and ^{241}Am, depending on the specific activity was determined with an α-ray spectrometer consisting of a surface-barrier silicon detector of 5 or 50 cm^2 area and a Nokia LP-4700 analyzer. The targets were prepared by applying the solution in drops. The measurement uncertainty was <25%.

The equilibrium in the solution was reached on the seventh day. For each sample of the rock, we calculated the distribution coefficient K_d:

$$K_d = [(A_0 - A_e)/A_e](V/m) , \quad (1)$$

where A_0 is the activity concentration of the initial solution, kBq kg^{-1}; A_e, activity concentration of the solution after the contact with the rock, kBq kg^{-1}; V, liquid phase volume, mL; m, solid phase weight, g; V/m = 50 mL g^{-1}.

After the equilibrium in the system was attained, for samples 1–4 we performed desorption experiments to evaluate the sorption reversibility. The initial radioactive solution was separated from the solid phase, distilled water was added in the ratio V/m = 50 mL g^{-1}, and the phases were shaken for 7 days. After that, the resulting solution was analyzed by γ- and α-ray spectrometry. The amount of the desorbed radionuclide in percents relative to the sorbed amount was calculated. For comparison and clearer presentation of the results, the radionuclide sorption values for samples 1–4 were also calculated in percents relative to the initial activity.

RESULTS AND DISCUSSION

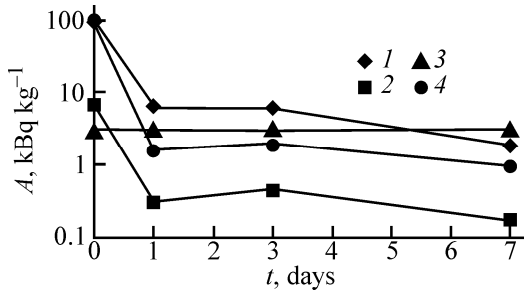
The results of solution analysis in the course of contact with the rock samples in sorption runs are

Table 2. Sorption of radionuclides onto samples from the Novaya Zemlya Archipelago

Radionuclide	Initial solution		1st day of contact		3rd day of contact		7th day of contact		K_d, $cm^3\ g^{-1}$
	A_0, kBq kg^{-1}	pH	A_e, kBq kg^{-1}	pH	A_e, kBq kg^{-1}	pH	A_e, kBq kg^{-1}	pH	
Sample 1									
$^{239+240}Pu$	98.0	2.40	0.95	6.55	1.00	7.55	0.72	8.15	6.8×10^3
^{137}Cs	6.5		0.26		0.28		0.25		1.3×10^3
^{85}Sr	3.05		3.11		3.28		3.21		–
^{241}Am	85.0		0.29		0.33		0.32		1.3×10^4
Sample 2									
$^{239+240}Pu$	98.0	2.40	2.65	7.10	3.72	7.57	1.05	8.00	4.6×10^3
^{137}Cs	6.45		0.30		0.30		0.16		2.0×10^3
^{85}Sr	3.05		3.06		2.87		3.03		–
^{241}Am	85.0		0.26		0.50		0.75		5.6×10^3
Sample 4									
$^{239+240}Pu$	98.0	2.40	3.23	7.80	2.82	8.30	0.86	8.35	5.6×10^3
^{137}Cs	6.45		2.63		2.55		1.98		1.1×10^2
^{85}Sr	3.05		3.21		3.09		3.27		–
^{241}Am	85.0		1.40		1.60		0.28		$1.5 \cdot 10^4$
Sample 5									
$^{239+240}Pu$	109.0	2.40	1.57	6.60	1.13	7.30	≤0.7	7.90	$\geq 7.7 \times 10^3$
^{137}Cs	4.9		0.41		0.33		0.31		7.4×10^2
^{85}Sr	0.70		0.77		0.80		0.80		–
^{241}Am	71.0		0.57		0.33		0.15		2.4×10^4
Sample 6									
$^{239+240}Pu$	109.0	2.40	1.81	2.90	0.47	2.90	≤0.7	2.90	$\geq 7.7 \times 10^3$
^{137}Cs	4.9		0.66		0.66		0.60		3.6×10^2
^{85}Sr	0.70		0.80		0.84		0.81		–
^{241}Am	71.0		2.10		1.60		1.40		2.5×10^3
Sample 7									
$^{239+240}Pu$	109.0	2.40	≤0.88	6.40	≤0.77	7.20	≤0.79	7.90	$\geq 6.8 \times 10^3$
^{137}Cs	4.9		0.36		0.30		0.29		7.8×10^2
^{85}Sr	0.70		0.795		0.84		0.83		–
^{241}Am	71.0		0.73		0.33		0.2		1.8×10^4
Sample 8									
$^{239+240}Pu$	109.0	2.40	3.67	7.00	2.61	7.80	1.12	7.90	4.8×10^3
^{137}Cs	4.9		1.17		1.00		1.33		1.3×10^2
^{85}Sr	0.70		0.86		0.90		0.75		–
^{241}Am	71.0		1.60		1.50		0.33		1.1×10^4

given in Table 2 and plotted in the figure. The calculated distribution coefficients for each rock are also presented.

For clearer presentation, we also plotted, using data on radionuclide sorption onto a sample of lime sandstones (sample 3), the dependences of the radionuclide activity concentrations in solution on the experiment time. We also calculated for the same tock the distribution coefficients K_d ($cm^3\ g^{-1}$): $^{239+240}Pu$ $\geq 2.7 \times 10^3$, ^{241}Am 4.4×10^3, and ^{137}Cs 1.8×10^2.



Activity concentrations of radionuclides in solution as functions of the contact time with a sample of lime sandstone (sample 3): (*1*) $^{239+240}Pu$, (*2*) ^{137}Cs, (*3*) ^{90}Sr, and (*4*) ^{241}Am.

Table 3. Distribution coefficients (K_d, $cm^3\ g^{-1}$) for samples of rocks of the Novaya Zemlya Archipelago

Sample	$^{239+240}Pu$	^{137}Cs	^{241}Am
1	6.8×10^3	1.3×10^3	1.3×10^4
2	4.6×10^3	2.0×10^3	5.6×10^3
3	2.7×10^3	1.8×10^2	4.4×10^3
4	5.6×10^3	1.1×10^2	1.5×10^4
5	$\geq 7.7 \times 10^3$	7.4×10^2	2.4×10^4
6	$\geq 7.7 \times 10^3$	3.6×10^2	2.5×10^3
7	$\geq 6.8 \times 10^3$	7.8×10^2	1.8×10^4
8	4.8×10^3	1.3×10^2	1.1×10^4

Because radionuclides were introduced as acid solutions, the initial solution had pH 2.4. The pH of the solution changed in the course of the experiment upon contact with rock samples (Table 2). An exception is sample 6, for which pH slightly increased relative to the initial solution and then remained unchanged up to the end of the experiment.

The major fraction of $^{239+240}Pu$, ^{241}Am, ^{137}Cs is sorbed by the rock already within the first 24 h, as indicated by the plots (see figure), whereas strontium is not noticeably sorbed (within the uncertainty of measuring the activity concentration).

Experiments on adsorption of cesium and strontium were performed previously at the Khlopin Radium Institute [11]. The data obtained show that cesium exhibits high distribution coefficient, with the cesium sorption onto the majority of inorganic sorbent samples being virtually independent of pH, which is in agreement with the results of this study. Strontium exhibits high affinity for many organic and inorganic sorbents at pH 8.6 [11]. In this study, pH of the solutions never reached 8.6. Strontium-85 was not sorbed by any of the rocks studied. Low distribution coefficients were also obtained in experiments on strontium sorption onto rocks of the Semipalatinsk Test Site [8].

$^{239+240}Pu$ and ^{241}Am exhibit high distribution coefficients in all the systems studied (Table 2). Data on the distribution coefficients are summarized in Table 3.

The results of the desorption experiments are given in Table 4.

As seen from Table 4, ^{239}Pu and ^{241}Am were desorbed from the rocks only slightly: Pu, to no more than 1%, and Am, to 0.1–4.7%, i.e., Am appeared to be more mobile than Pu. Such behavior of the radionuclides in the soil is influenced by properties of the rocks (absorption capacity of soil, composition of exchangeable cations, organic matter content, particle size, and mineralogical composition of the soil). The degree of desorption of ^{137}Cs from the rock samples studied ranged from 2 to 16%.

Experiments on sorption and desorption of ^{239}Pu, ^{241}Am, ^{137}Cs, and ^{85}Sr have shown that all the radionuclides except ^{85}Sr are tightly sorbed onto the examined rocks of the Novaya Zemlya Archipelago.

Thus, the laboratory study of the sorption and desorption of artificial long-lived radionuclides present among nuclear explosion products, performed for the first time with rocks from the Novaya Zemlya Archipelago, gave the following results. $^{239+240}Pu$, ^{241}Am, and ^{137}Cs exhibit high distribution coefficients in the systems studied ($cm^3\ g^{-1}$): $^{239+240}Pu$ 2.7×10^3–7.7×10^3, ^{241}Am 2.4×10^3–1.8×10^4, and ^{137}Cs 1.1×10^2–2.0×10^3. Strontium-85(90) is not sorbed (within the measurement uncertainty) by any of the rocks studied. The sorption is mainly complete within the first 24 h of the contact. The $^{239+240}Pu$, ^{241}Am, and ^{137}Cs radionuclides that fell out on the Novaya Zemlya Archipelago are tightly retained by the soils and can be transferred into the surrounding seas only with soil particles. The mobility of ^{90}Sr is considerably higher than that of the other radionuclides, and this fact can be responsible for the enrichment of water of some streams in the region of Novaya Zemlya test areas in ^{90}Sr relative to ^{137}Cs, although the activity concentration of ^{90}Sr is low (~5 Bq L^{-1}) [12]. The desorption of $^{239+240}Pu$ does not

Table 4. Sorption and desorption of radionuclides on samples of some rocks

Sample	Fraction of sorbed nuclide, %				Fraction of desorbed nuclide, %			
	$^{239+240}Pu$	^{137}Cs	^{85}Sr	^{241}Am	$^{239+240}Pu$	^{137}Cs	^{85}Sr	^{241}Am
1	99.3	96.2	–	99.6	0.03	2.1	–	0.1
2	98.9	97.5	–	99.1	0.06	3.3	–	0.8
3	98.2	97.4	–	98.9	ND[a]	7.1	–	2.5
4	99.1	69.3	–	99.7	0.65	15.9	–	4.7

[a] (ND) Not determined.

exceed 1%, that of ^{241}Am is 0.1–4.7%, and that of ^{137}Cs reaches 2–16%, depending on the rock type.

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