SORPTION AND SPATIAL DISTRIBUTION OF RADIONUCLIDES ON FRACTURED ROCK MINERALS AT THE YENISEISKIY SITE

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The paper presents data on the distribution coefficients (K_d) of ^{137}Cs, ^{90}Sr/^{90}Y, ^{241}Am on a fractured rock sample taken from the exocontact zone of the Nizhnekanskiy granitoid massif. The study focuses on the micro-distribution of radionuclides on mineral phases of the fractured sample. Based on the comparative analysis of radiograms and SEM- images, the data on relative sorption efficiency (RSE) were obtained, which allowed to evaluate the contribution of an individual mineral phase of the fractured rock sample to the sorption of the studied radionuclides. It was noted that in terms of cesium and strontium retention, the secondary mineral, namely, the chlorite filling the fractured zones in the sample (RSE = 2) should be considered as the most effective mineral phase. Cesium and strontium sorption on zeolite and feldspars was less effective with RSE parameters ~ 1. Americium sorbed uniformly on the surface of the fractured sample, which was confirmed by similar RSE values on the mineral phases of the sample.

Keywords: *radioactive waste, sorption, micro-distribution of radionuclides, fractured rocks, Nizhnekanskiy granitoid massif, digital autoradiography.*

Currently, a final disposal facility designed for RW Class 1 and 2 disposal is being established in Russia, namely, at the Yeniseiskiy site in the exocontact zone of the Nizhnekanskiy granitoid massif (NGM) in the Krasnoyarsk Territory [1, 2]. The preliminary stage of this project involves underground research laboratory (URL) construction with relevant R&D being particularly focused on geochemical research, including radionuclide migration in fissure waters [3]. Sorption/desorption are seen as key processes governing radionuclide migration in the host rock environment. Therefore, special attention is paid to retention properties of crystalline rocks and their study.

The study of general patterns associated with radionuclide sorption by rocks should be supplemented by relevant knowledge on the role of individual mineral phases in the retention of mobilized waste components. Such information will support more detailed modeling of radionuclide migration in the repository area, since in the massif, the proportion of mineral phases predominantly retaining certain radionuclides varies significantly. Of particular importance are the mineral fillings of fractured zones, which may appear both the main migration pathways for the radionuclides and their retention zones in a porous rock matrix involving finely dispersed mineral phases [4, 5].

Experimental part

To study radionuclide microdistribution on the rock surface involving some fractured zones, a core sample was taken at a depth of 249 m from the R-11 well of the Yeniseiskiy section constituting to an exocontact zone of the Nizhnekanskiy granitoid massif. The sample was a skarnoid (calc-silicate hornfels) of a very complex inhomogeneous composition. The core with a diameter of 6.5 cm was cut into 6 mm thick disks, which were ground on one side for sorption and further radiography. Under these experiments, particular solutions were fabricated to simulate the underground natural water of the Yeniseiskiy site. Their composition was as follows: Cl^- — 36 mg/l, SO_4^{2-} — 15 mg/l, CO_3^{2-} — 18 mg/l, HCO_3^- — 79 mg/l, Na^+ — 32.6 mg/l, K^+ — 3.9 mg/l, Mg^{2+} — 10.2 mg/l, Ca^{2+} — 18.5 mg/l, solution pH 7—8, I=0.01 mol/l. Sorption was considered based on ^{137}Cs, $^{90}Sr/^{90}Y$, ^{241}Am radionuclides with a concentration of 10^{-9} M. The experiments were carried out in plastic dishes at a ratio of the solution volume to the surface area of the sample being equal to ~ 1 ml/cm^2 under static conditions for the time required to gain equilibrium. The concentration of radionuclides in solutions was measured by liquid scintillation spectrometry (Tri-Carb 2810 TR, Perkin Elmer).

Mineral composition of the R-11 sample was studied based on one of the core disks using scanning electron microscopy with X-ray spectral microanalysis (SEM with EPMA). To study the microdistribution of radionuclides over the surface of the discs, a digital radiography system Cyclone Storage System (Perkin Elmer) with flexible storage plates was used.

After the system has reached the equilibrium state, based on the following equation, distribution coefficients (K_a, ml/cm^2) per surface area of the disk were calculated for each radionuclide being in direct contact with the solution:

$$K_\alpha = \frac{I_0 - I_\infty}{I_\infty} \cdot \frac{V}{S},$$

where I_0 is the count rate (cpm) of the radionuclide in the initial solution, I_∞ is the count rate of the radionuclide in the solution at the moment of system equilibrium, V is the solution volume and S is the surface area of the disk being in contact with the solution.

The RSE parameter was calculated based on the following relationship:

$$\mathrm{RSE}_{i,j} = (I_{i,j}/I_{j,0})/(S_i/S_0),$$

where $I_{i,j}$ the photostimulated luminescence intensity (PLI) corresponding to the radionuclide j adsorbed on the mineral phase i; $I_{j,0}$ is the PLI intensity corresponding to the radionuclide j adsorbed on the entire surface of the disk (sample); S_i is the surface area occupied by the mineral phase i; S_0 is the disk surface area.

Results and discussion

As a result of the study, the distribution coefficients (K_a) were calculated for each of the studied radionuclides: these were calculated considering the surface area of the R-11 sample disks. For ^{137}Cs, $^{90}Sr/^{90}Y$, ^{241}Am these accounted for 6.6; 0.9; 26.1 (ml/cm^2) respectively. Thus, with respect to radionuclides, sorption capacity of the studied R-11 sample increases in the following series: $^{90}Sr/^{90}Y < ^{137}Cs < ^{241}Am$, where maximum retention is provided for americium. According to the distribution coefficients, it was possible to calculate the total sorption capacity of the sample with respect to the studied radionuclides, while the sample itself was rather heterogeneous and involved a number of mineral phases with different sorption capacities.

Based on the elemental analysis performed by SEM with EPMA, the mineral phases constituting to the R-11 skarnoid sample were identified. Accordingly, the following phases were identified: quartz, layered aluminosilicates (chlorite), nesosilicate (epidote), framework aluminosilicates (feldspars, zeolite), oxides (rutile), carbonates (calcite).

The microdistribution of ^{137}Cs, $^{90}Sr/^{90}Y$, ^{241}Am on the surface of R-11 sample was studied based on the obtained black-and-white radiogram images. It was found that ^{137}Cs and $^{90}Sr/^{90}Y$ radionuclides were distributed extremely unevenly over the surface of the R-11 skarnoid sample, while ^{241}Am was sorbed with similar efficiency on all mineral phases and slightly less on quartz and calcite ones.

Figure 1 shows the distribution of cesium on the surface of the R-11 sample. It was chloride belonging to the group of layered aluminosilicates that proved to be a most effective sorbent in this case.

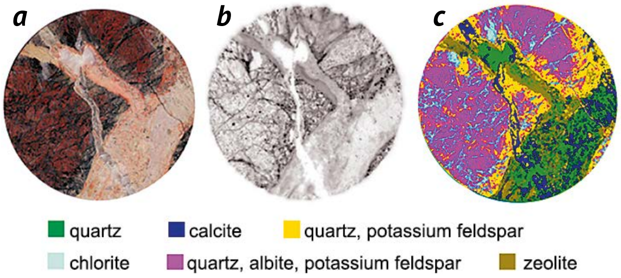

Figure 1. Distribution of cesium on the surface of the R-11 sample:
a — optical image of the R-11 well sample,
b — radiogram of cesium sorption on the R-11 sample,
c — optical image of the R-11 well sample with mineral phases

Zeolite had an average sorption capacity with respect to cesium, while other mineral phases did not produce any sufficient effect on this parameter, especially calcite, which has the lowest sorption capacity.

Based on SEM with EPMA, it was confirmed that strongly darkened areas on the radiogram (Figure 1b) corresponded to fracture zones filled with a secondary mineral, chlorite or crumbled mineral phases, which also featured chlorite.

The distribution of strontium over the mineral phases of the sample reproduced the behavior of cesium; strontium was also well sorbed on chlorite, less so on zeolite, and worst of all, on calcite. Such similarities in the behavior of strontium and cesium could be explained by similar strontium sorption mechanism on mineral phases.

Earlier in [6, 7], a method was described that could be used to calculate RSE parameter characterizing the contribution of each mineral phase of a heterogeneous system to the sorption of various radionuclides and could support quantitative sorption efficiency assessments considering individual mineral phases. This approach is based on a comparative analysis of a radiogram characterizing the microdistribution of radionuclides over the surface of a rock sample with a SEM image specifying the mineral phases. Comparative analysis was implemented in two ways: using the ImageJ software and the Python programming language (semi-automatic method). For ^{137}Cs and ^{90}Sr/^{90}Y, relative sorption efficiency was calculated based on the ImageJ software. The semi-automatic method based on the scikit-image (Python) package turned out to be the most suitable for ^{241}Am. Table 1 presents the RSE data. It should be noted that when the images were processed using the above methods, it was not possible to distinguish between all mineral phases since some of them were either finely mixed (quartz, feldspars, zeolite) or were falling into a same range of PLI values (quartz, calcite), therefore, a common RSE value was provided for them.

On the whole, the obtained RSE data did not contradict the earlier findings on the radionuclide behavior: ^{241}Am was distributed equally over all mineral phases with RSE values equal to 1, whereas chlorite turned out to be the most effective retaining phase for ^{137}Cs and ^{90}Sr/^{90}Y with relative sorption efficiency of 2 and 1.8, respectively, which is two times higher than the average values.

Table 1. Data on the relative sorption efficiency for ^{137}Cs, ^{90}Sr/^{90}Y, ^{241}Am on the R-11 sample

Mineral phases	Relative sorption efficiency		
	^{137}Cs	^{90}Sr/^{90}Y	^{241}Am
quartz, calcite	0.6	0.4	1
zeolite, feldspars, quartz	1.2	1	1
chlorite	2	1.8	1

Conclusions

This paper studied the sorption properties of an integral fractured rock sample taken from the R-11 well constituting to a zone of the Nizhnekanskiy granitoid massif with respect to Cs, Sr/Y, and Am. It was noted that the sorption capacity of the studied sample with respect to radionuclides increases in the following series Sr/Y < Cs < Am, where maximum retention is provided for americium. Considering the mineral phase surfaces of a fractured rock sample pertaining to the exocontact zone of the Nizhnekanskiy granitoid massif, RSE were calculated for cesium, strontium, americium. Based on the RSE calculated for each of the studied radionuclides, with the exception of americium, the most effective sorption phases were identified. It has been shown that cesium and strontium were predominantly retained in cracks filled with chlorite. Zeolite appeared to be a less effective sorbent in relation to cesium and strontium. Americium was sorbed with the same efficiency on all mineral phases.

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