Sorption of ^{137}Cs , ^{90}Sr , Se , ^{99}Tc , $^{152(154)}\text{Eu}$, $^{239(240)}\text{Pu}$ on fractured rocks of the Yeniseysky site (Nizhne-Kansky massif, Russia)

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Abstract. The study demonstrates the effect of sorption properties of fractured host rocks from the Yeniseysky site (Nizhne-Kansky rock massif, Krasnoyarsk region) on the migration of dissolved radioactive components (^{137}Cs , ^{90}Sr , ^{79}Se , ^{99}Tc , $^{152(154)}\text{Eu}$, $^{239(240)}\text{Pu}$) in the deep geological conditions of a high-level radioactive waste repository. Estimates of radionuclide distribution coefficients between the aqueous solution and fractured rocks obtained from sorption experiments. The influence of various petrographic types and fracture-filling substances on the retardation of radioactive components has been investigated. Based on the results of sorption experiments, we concluded that the type and attributes of rock discontinuities, as well as the mineral composition of the material in fractures, are crucial for the immobilization of radionuclides during their migration through a geological environment.

1 Introduction

There is a project plan for the construction of a deep underground research facility in the gneissic Nizhne-Kansky rock massif (Krasnoyarsk region, Russia) to investigate the physical-chemical processes in the system “vitrified high-level radioactive waste–artificial barriers–surrounding host rock”. Particularly, there is the problem of prediction of dissolved radioactive components' behavior during their migration from the repository to the biosphere through geological formations. There are scarce and unstructured data about the sorption properties of the host rocks at the Yeniseysky site of the Nizhne-Kansky massif and there is no comprehensive comparison of the retention capacities of rocks in this region. The aim of our study is to obtain data of sorption experiments with the interaction of contaminated groundwater with host rocks at the Yeniseysky site and to understand how these rocks govern the behavior of radionuclides. It was assumed that the preferential pathways of contaminated groundwater flows are areas with high permeability, i.e. fractured rocks. Therefore, we considered an area confined to faults and fractures in rocks, assuming that the sorption of radionuclides is occurring predominantly on fracture surfaces or on the material which fills the interspace of fractures and on brecciated and mylonitized material from shear zones. Thus, the mineral composition of fracture material was carefully

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determined by using available strip logs and photographic logs of excavated core samples during the borehole drilling (14 research wells, approx. 7600 m of cores) [1]. The sorption of dissolved radionuclides onto fractured rocks was estimated by applying two experimental approaches: (1) the sorption onto the crushed material and (2) sorption onto fracture's surfaces. The study demonstrated that both mechanisms must be taken into account through effective (combined) retardation coefficients (factors) for application in solute transport modeling.

2 Methods

2.1 Sampling

The sampling was based on photos of excavated core, and strip logs made by geologists of JSC Krasnoyarskgeologiya. Samples should meet the criteria: (1) have no indications of exogenous influence and the interval of sampling should be below 200 m; (2) taken from the depths that show increased fracture index (FI) (> 10 per meter of a core); (3) represent the rock diversity (gneisses, dolerites, etc.). It was observed that 60% of fractured rocks (FI > 10) corresponded to intrusions of dolerite dikes and 40% were in gneisses. The mineral composition of the fractures was determined by examining the strip logs. Carbonate identified in 64.2% of all fractures. The part of chlorite, quartz, kaolinite, and clay minerals were 17.7, 5.7, 5.0, and 4.0%, respectively. Dark-color mineral, K-feldspar, and an unknown mineral were found in 1.3, 1.3, and 0.67%, respectively. Finally, 10 samples of rocks were selected for sorption experiments. They represented two kinds: monolithic rock fragments and disintegrated material. It allowed developing two types of experiments: the sorption of radionuclides onto surfaces of fractures and the sorption of radionuclides onto the matrix of the rocks from shear zones.

2.1 Sorption experiments

Prior to sorption experiments, aqueous solution with the composition of the groundwater from the Yeniseysky site was prepared from salts dissolved in distilled water. The initial activities of dissolved radionuclides were $3.00 \cdot 10^4$, $2.17 \cdot 10^6$, $1.03 \cdot 10^6$, $3.79 \cdot 10^5$, and $9.24 \cdot 10^3$ Bq/L for ^{152}Eu , ^{137}Cs , ^{239}Pu , ^{90}Sr , and ^{99}Tc , respectively. The source of Se ($9.98 \cdot 10^{-7}$ mol/mL) was Na_2SeO_3 . Samples for sorption onto matrix material were crushed, powdered, the fraction < 0.5 mm was separated and dried. For surface sorption samples were prepared from monolithic pieces, which were divided into fragments, such that at least one surface corresponded to the fresh surface of a tight fracture. Then, fragments (excluding fresh fracture surface) were covered by a sealant in order to avoid contact with the radioactive solution. Sorption experiments were carried out at stirring for 1 week at room temperature. The solid-liquid ratio in batch sorption experiments was equal to 1 g per 40 mL. In the case of sorption on the fracture surfaces, the ratio of liquid volume to the surface area of tight fracture was 4.2 cm.

3 Results

After experiments, the activities of dissolved radionuclides were measured. The sorption distribution coefficient (K_d , [cm^3/g]) of radionuclides on fractured rocks from shear zones was estimated:

$$K_d = \left[\frac{C_i - C_o}{C_o} \right] \cdot \frac{V}{m} \quad (1)$$

where C_i , C_o are the activities of dissolved radionuclides before and after sorption; V is the volume of aqueous solution, m is the mass of the solid sample.

For the sorption of radionuclides onto the surfaces of tight fractures in monolithic rock fragments, the surface sorption distribution coefficient (K_a , [cm]):

$$K_a = \left[\frac{C_i - C_o}{C_o} \right] \cdot \frac{V}{S} \quad (2)$$

where S is the surface area of the tight fracture in contact with the radioactive solution.

From estimated K_d - coefficients we concluded that ^{239}Pu and ^{137}Cs are associated with each other (Fig. 1a). They sorb onto dolerite and gneiss from the shear zones and altered dolerite, where the fracture substance is clay, chlorite, and carbonate. The lowest K_d -values of ^{137}Cs and ^{239}Pu were in dolerite from shear zones, higher K_d were in altered and cataclastic rocks. The highest K_d were in biotite plagiogneiss. The retention of ^{152}Eu and ^{90}Sr correlated with each other as well (Fig. 1b). However, the dependence on the rock-type and on fracture mineral for the retention of these components was not apparent. The lowest K_d of ^{152}Eu and ^{90}Sr detected in brecciated dolerite and shear zone of dolerite. Intermediate K_d was in plagiogneiss from the shear zones and altered dolerite on the contact with cordierite-biotite plagiogneiss. The highest K_d were in brecciated dolerite and cataclastic gneiss. The correlations between K_d for ^{137}Cs - ^{239}Pu and ^{90}Sr - ^{152}Eu can indicate the sorption of both pairs on two different minerals. The co-sorption of Cs and Pu can be explained by the content of biotite in rocks (biotite plagiogneiss). This result is in agreement with previous studies [2-4].

Fig. 1. Correlations between experimentally obtained sorption distribution coefficients of radionuclides on the powdered fractured rock samples: (a) ^{137}Cs - ^{239}Pu and (b) ^{90}Sr - ^{152}Eu . The error bars reflect the relative uncertainty of 10%. The dashed lines delimit the fields of different rock types. The dotted lines indicate the 95% confidence interval of the linear approximation.

Considering the results of sorption onto fracture surfaces we concluded that: (1) radionuclides sorb predominantly on the fracture surfaces of biotite plagiogneiss from shearing zones (clay and carbonate are the main minerals of fractures), while the sorption was weakest on the fractures in dolerites (fracture material is calcite); (2) considerable sorption of ^{90}Sr is on carbonate fracture surfaces in gneisses and plagiogneisses confirming the substitution of Ca by ^{90}Sr in carbonates [5]; (3) ^{239}Pu is often sorbed onto clay in fracture surfaces, and generally it is attracted to rocks from shear zones. At the same time, ^{152}Eu becomes immobile in the contact with fracture surfaces containing carbonates.

Radionuclide retardation factors were estimated assuming that the fractured massif consists of two typical structural domains: (a) intact (host) rock (HR) blocks and (b) large-scale linear shear zones (SZ). The intact rock blocks are represented by randomly distributed fractures, open or filled with secondary minerals (or alteration products), and a porous matrix. The open fractures and porous matrix in gneiss differ in permeability but similar storage capacities with respect to nonreactive species. The shear zones are complex assemblages of fault rocks (gouge, mylonite, cataclasite, which sometimes exhibit cohesionless properties), occupying the central part of this tectonic structure, referred to as the core having increased fracture porosity, and surrounding rock damage area (zone) in the periphery. Each part of fractured rock massif has unique features which control the retardation of migrating radionuclides: porosity, the proportion of the central (core) part of the shear zone to the surrounding damage area, the bulk density, sorption capacity, the specific flow-wetted area (area in contact with flowing water).

Such concept yields the expression for the total porosity (n^T) of the fractured rock massif:

$$n^T = (1 - \xi)[n_l + (1 - n_l) \cdot n_o] + \xi \cdot n_2 \quad (3)$$

where n_o , n_l are porosities of intact rock and linear shear zones, ξ is a partitioning parameter reflecting the relative width of the core material in the total width of the shear zone.

The partial retardation factors representing the fracture domain, filling materials inside, and pore matrix (R_l , R_2 , R_o) related to the studied gneiss formation are:

$$R_l = 1 + a_R \cdot K_a / n_l \quad (4)$$

$$R_2 = 1 + \rho_{bi} \cdot K_{d2} / n_2 \quad (5)$$

$$R_o = 1 + \rho_{bo} \cdot K_{do} / n_o \quad (6)$$

Where K_{di} and K_a are the bulk and surface sorption distribution coefficients; ρ_{bi} is the bulk density; a_R is the specific flow-wetted area.

The influence of the content of dispersion fraction (ξ) on the effective retardation coefficient (Fig. 2) demonstrated that calculated values are comparable with those obtained from observations of water-bearing channels in tunnels and drifts in western Sweden [6].

Fig. 2. The influence of ξ on retardation factors for the shear zone (R_{SZ}) of (a) Cs, Eu, Pu and (b) Sr, Se, Tc. $a_R(SZ) = 0.05 \text{ m}^2/\text{m}^3$. For a comparison purpose, data on sorption retardation in host rock domain (R_{HR}), are also represented in plots [$a_R(HR) = 0.005 \text{ m}^2/\text{m}^3$] (dashed lines).

4 Conclusion

The study showed that fractured zones in host rocks most often correspond to the contact of intrusions of dolerites into surrounding gneiss/plagiogneiss formations. These fractured

rock zones were typically located on the upper boundary of dolerites on the contact with gneiss. Calcite (or carbonate as defined in stripe logs) was the predominant mineral of the interspace of fractures. Sorption tests on disintegrated rocks showed the correlation of sorption distribution coefficients of ^{239}Pu and ^{137}Cs . Similar behavior was observed for pairs $^{152(154)}\text{Eu}$ - ^{90}Sr . The degree of sorption has decreased in the series: rocks from shear zones $\rightarrow$ brecciated rocks $\rightarrow$ fractured and altered dolerites. Radionuclides sorption onto the surfaces of fractures was generally uniform in monolithic fragments, i.e. radionuclides did not form pairs “plutonium – cesium”, europium – strontium” as in the case of disintegrated rocks. There was a tendency that the most efficient sorbents of plutonium are fracture surfaces (i.e., clay minerals) in plagiogneiss rocks from shear zones, while europium was sorbed mostly onto carbonate-containing fracture surfaces in dolerites. Comparison with previous literature data showed that fractured gneiss has better retardation properties than granitic rocks.

Two elementary structural units were distinguished: host rock blocks and large linear shear zones. They have different effects on the transport of radionuclides at different locations of the rock massif. The presence of dispersed fractions in the tectonic deformation zones and their increased specific surface can increase effective retardation factors of radionuclides dramatically. Thus, the firm conclusion on the preferential radionuclide transport through a linear deformation zone of tectonic origin may not always be true, and in many cases, it appears dubious.

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