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Sorption of radionuclides on the rocks of the exocontact zone of Nizhnekansky granitoid massif

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ABSTRACT

Study of sorption behavior of radionuclides toward five rock samples drilled in the deep-well R12 in the exocontact zone of Nizhnekansky granitoid massif ("Eniseysky" area) in the range of depth 166 m – 476 m was carried out. The sorption kinetics and Kd values of the long-lived radionuclides of different chemical behavior ^{137}Cs, ^{226}Ra, ^{79}Se, $^{237+239}$Np, ^{239,240}Pu, ^{241,243}Am were determined. Experiments were performed under the conditions that are relevant for the future high level waste disposal (atmosphere; composition, pH and Eh of the solutions). Digital radiography demonstrated heterogeneous sorption of all the investigated radionuclides and revealed phases with higher sorption ability. It was established that sorption of metal cations is fast and reaches steady state in a few hours while Se in the form of selenate-ion sorbs insignificantly.

INTRODUCTION

The principal concept of the high level wastes (HLW) disposal into the deep crystalline rock formations is accepted in Russia [1]. Several perspective sites of Nizhnekansky granitoid massif (Itatsky, Kamenny areas) have been thoroughly studied [2-4]. Recently Eniseysky area is chosen as a site of an underground research laboratory for final isolation of HLW and some geological and geophysical researches have been performed in the area. In 2016 the building of Underground Research Lab (URL) at the Eniseysky area will begin. According to Safety standards of IAEA and the idea of multibarrier systems the crystalline rocks are the last barrier to prevent radionuclides release from the repository to the environment [5]. The backfilling of the canisters with the vitrified HLW by bentonites (Khakassiya) is accepted in Russia. Thus, determination of sorption properties of the host rocks in the presence of the simulated ground water, pre-equilibrated with bentonites, towards long-lived radionuclide is essential for safety assessment of future HLW repository.

Time dependence of sorption of cesium (I), plutonium (IV), americium (III) and neptunium (V) onto samples of leucogranite, tonalite and granodiorite from Nizhnekansky massive (Itatsky and Kamenny areas) was studied earlier [3, 4]. The distribution coefficients for Cs, Pu and Am were found to be $n \cdot 10^2$ - $n \cdot 10^3$ mL/g and only up to 2 mL/g for Np. These previous studies were performed in aerobic conditions that are not relevant for the deep geological media with low oxygen content. The presence of oxygen and other redox active substances (Fe^{2+}, H_2, O_2^{2-} etc.) is controlling the Eh values of the aqueous solutions. The redox conditions are strongly affecting the speciation of elements such as plutonium, neptunium, uranium, selenium and some others that are relevant for high level wastes. Thus, the Eh value has to be controlled carefully during sorption experiments.

Sorption of cesium, europium and uranium was studied for rock samples from Äspö site, Sweden. In [6] two types of diorites were used for experiments: «oxidized» diorite contacted for few years with air and «unoxidized» diorite that was freshly extracted from underground in Ar atmosphere. It was shown with X-ray photoelectron analysis that ca. half of the uranium, that was initially added as U(VI) was located in the form of U(IV) on the surface of «unoxidized» diorite after one month of experiment. This indicates that even under weakly reducing conditions (Eh ca. 0 V) uranium can present in lower oxidation state. Authors described this process as sorptive reduction of uranium. The main reducing agent proposed to be structural Fe(II) e.g. in biotite or magnetite.

Recently [7, 8] sorption of cesium was studied for rock samples from two areas of Nizhnekansky massif: "Kamenny" and "Itatsky". The linear growth of the distribution coefficient of Cs with increasing biotite content in rock samples is visible in Fig. 1. Biotite is a common phyllosilicate mineral that can control the distribution and mobility of different radionuclides (see for instance [9, 10]). The predominant sorption of cesium on biotite can be explained by cation exchange mechanism and that is the case for radium as well [11]. On the other hand, the main mechanism for multivalent ions sorption is accepted to be complex formation with surface hydroxo-groups of different nature (e.g. ≡Al-OH, ≡Si-OH, ≡Fe-OH) [12, 13]. Recently another, «Eniseysky», area was selected as a final site for URL construction. The aim of the present study is to analyze the sorption behavior of radionuclides with different chemical properties towards rock samples from "Eniseysky" area in the exocontact zone of Nizhnekansky granitoid massif under controlled pH and Eh conditions and with thorough analysis of the rock samples.

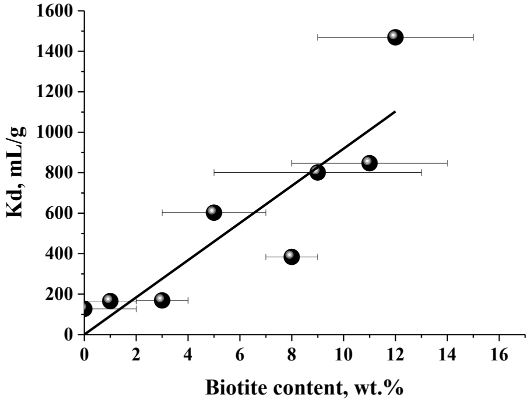

Figure 1. Dependence of Kd of cesium sorption on biotite content in granites (from [8]).

MATERIALS AND METHODS

Five rock samples from different depths (166 m, 417 m, 443 m, 459 m, 476 m) were used in our experiments and can be divided into three types: 1 – sillimanite-containing plagiogneisses (#166 and #417); 2 – migmatized granitogneisses and plagiogneisses (#459 and #476); 3 – intensively metamorphized gabbro-diabase (443). The significant difference in petrochemical properties and specific surface area (table I) is accompanied by variations of metosomatic and hydrothermal alterations of the studied samples [14].

Table I. Characterization of the rock samples

Sample number	**166**	**417**	**443**	**459**	**476**
Specific surface area, m^2/g	0.17	0.53	0.46	2.6	1.3
SiO_2, %	62.1	57.3	45.4	66.4	67.5
$FeO+Fe_2O_3+MgO+TiO_2$, %	10.7	17.3	31.5	10.2	10.2
$Al_2O_3/(FeO+Fe_2O_3+MgO)$	1.62	1.03	0.36	1.38	1.42
Na_2O/K_2O	0.47	0.25	1.38	0.25	0.81
Na_2O+K_2O/Al_2O_3	0.50	0.35	0.13	0.33	0.38

Rock samples were prepared for two types of sorption experiments: set #1 – determination of distribution coefficients and time-dependencies of sorption; set #2 – determination of spatial distribution of sorbed radionuclides depending on mineral composition, structure and/or degree of metasomatic and deformation transformations. Rock samples were crushed to grain size of 1-2 mm for experimental set #1. Solid to liquid ratio was 1 g : 4 mL in these experiments. Thick plain slices of rock samples with polished sides and size of 8x12x30 mm were used for experimental set #2.

All sorption experiments were performed in glove-box with inert atmosphere (N_2) at room temperature. The total mineralization of simulated ground water (SGW) was 200 mg/L, main cation – Ca^{2+}, main anion – HCO_3^{2-}. SGW solution was pre-equilibrated with bentonite (Khakassiya, Russia) for 3 weeks and further filtrated with 50 nm filter. Absence of bentonite colloids in final SGW solution was determined by scanning electron microscopy with X-ray energy dispersive microanalysis. The Eh value was ca. -200 mV, pH = 7.6.

The following radionuclides were used for the subsequent radiometric counting Cs-137 (β^-, $T_{1/2}$ = 30.07 a), Ra-226 (α, $T_{1/2}$ = 1600 a), Se-79 (β^-, $T_{1/2} = 1.13\cdot10^6$ a), Np-237 (α, $T_{1/2} = 2.14\cdot10^6$ a) + Np-239 as a tracer (β^-, $T_{1/2}$ = 2.36 d), commercial mixture of Pu-239 (α, $T_{1/2}$ = 24110 a) + Pu-240 (α, $T_{1/2}$ = 6563 a), commercial mixture of Am-241 (α, $T_{1/2}$ = 432.2 a) + Am-243 (α, $T_{1/2}$ = 7370 a). Initial concentration of all radionuclides was 10^{-9} mol/L. In experimental set #1 suspensions of crushed granites and SGW solutions of individual radionuclides were permanently shaking and aliqots of solutions were taken after 30 minutes, 1 hour, 4 hours, 8-10 hours, 1 day, 2 days, 4 days, 1 week and 2 weeks of experiment. Specific activity of radionuclide in solution after centrifugation was analyzed by liquid-scintillation counting. The sorption efficiency (%) was calculated as a ratio of specific activity of radionuclide in solution after experiment to its initial specific activity: $\Gamma = \frac{I_0 - I}{I_0} \cdot 100\%$,

where I – count rate of the solution after sorption (cpm), I_0 – initial count rate (cpm). The distribution coefficient, Kd, was calculated as specific activity of radionuclide sorbed on solid phase (Bq/g) divided by its specific activity in solution (Bq/mL). Spatial distribution of the sorbed radionuclides within the surface of rock slices was analyzed by digital radiography with Cyclone Storage System (Perkin-Elmer) after their careful washing with deionized water and drying.

RESULTS AND DISCUSSION

Experimental set #1. Time-dependency and distribution coefficients

Aliquots of suspensions were taken periodically, centrifuged and measured for radionuclide content. The dependence of radionuclide sorption (%) with time is shown in Fig. 2

for all the investigated rock samples. Sorption of metal ions is fast, quantitative and almost independent on rock sample. It reaches 95% within 1 hour for americium, 4 hours – for plutonium and cesium. Fast and quantitative sorption of actinides can be explained by fast surface complex formation with different hydroxo-groups on the surface of minerals. The aqueous speciation of radionuclides has been calculated by thermodynamic simulations using the HYDRA-MEDUSA software [15] with the equilibrium constants from NEA thermodynamic database only [16]. According to performed calculations americium is present mainly as the positively charged $AmCO_3^+$ under conditions of the experiment. It was found with solvent-solvent extraction technique that plutonium is presented in tetravalent state under our experimental conditions while neptunium is in pentavalent state. Results of thermodynamic calculations indicated that neptunium is present mainly as positively charged NpO_2^+ species and plutonium is present as noncharged $Pu(OH)_4$ species in solution. Cesium and radium behavior is typical for non-complexing cations and they are present in solution as positively charged Cs^+ and Ra^{2+} species. Sorption of radium reaches steady-state only after 7 days. Kinetically hindered cation exchange mechanism was proposed to explain this behavior. Selenium is characterized by low sorption values under experimental conditions. The initial form of selenium was selenite-ion SeO_3^{2-}. But thermodynamic calculations show that under reducing conditions the more stable form becomes selenide-ion, Se^{2-}, that has low tendency to sorb.

The results obtained in experimental set #1 with crushed rock samples demonstrate that sorption of cesium, radium, neptunium, plutonium and americium is quantitative onto investigated rock samples from exocontact of Nizhnekansky massif. The obtained values of distribution coefficients are shown in Fig. 3. Values of the distribution coefficients obtained in the present work are conformed to the data reported in [4-8, 11]. Actinides tend to form strong complexes with ligands binding through oxygen atom, such as hydroxo-groups onto mineral surfaces [12, 13]. That results in strong sorption of actinides, that is the case for Pu and Am in our experiments. That is not the case for sorption of Np onto rock samples #417, #443 and #476.

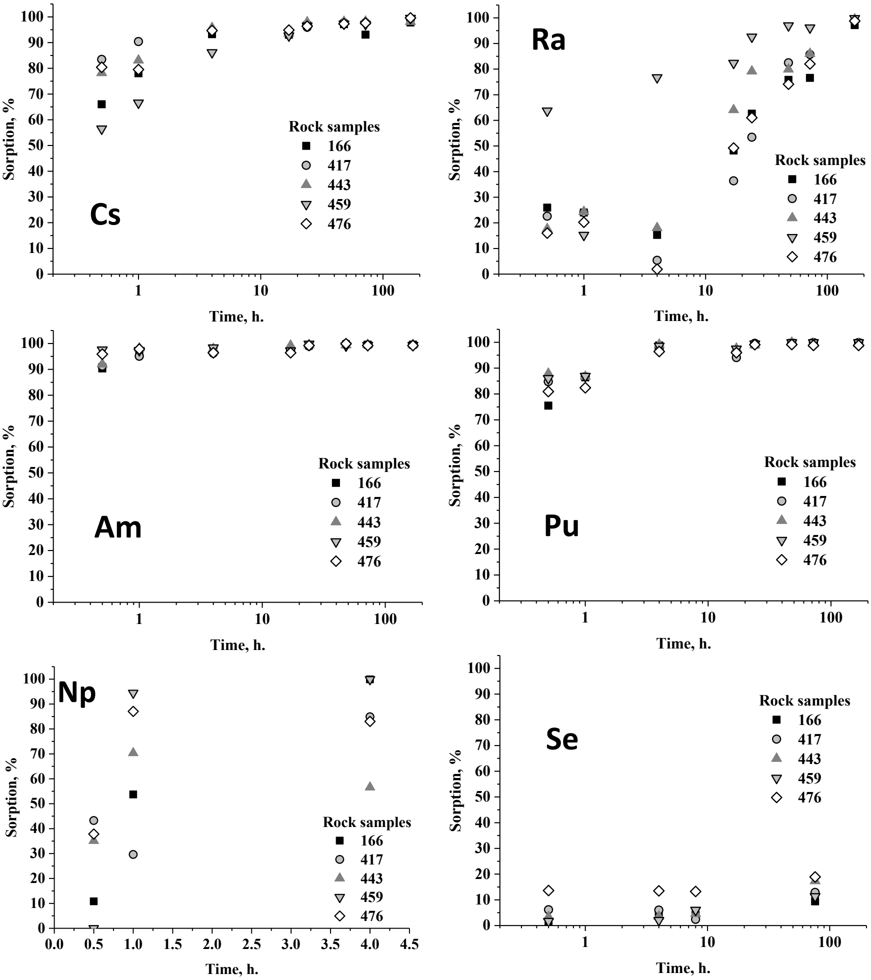

Figure 2. Time - dependency of radionuclide sorption onto rock samples.

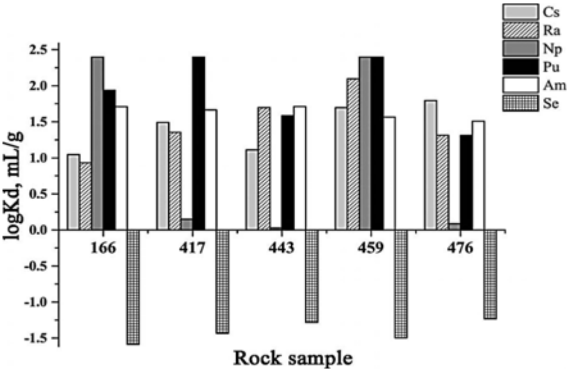

Figure 3. The obtained values of log Kd (mL/g) for the investigated rock samples.

Experimental set #2. Spatial microdistribution of radionuclides onto rock slices surface

Distribution of sorbed radionuclides onto polished rock surfaces was investigated by digital radiography with Cyclone Storage System (Perkin Elmer). Typical view of radiograms is presented in Fig. 4. The radiography analysis shows that sorption of the radionuclides is heterogeneous. Quartz and unaltered feldspars (plagioclase and K-feldspar) showed very low sorption activity (white areas on radiograms). Some of the mafic minerals and phyllosilicates group minerals (biotite, muscovite, sericite, magnetite, zeolites) have very high sorption activity (black areas on radiograms). Cesium and radium demonstrate preferable tendency to sorb on phyllosilicates. These results are comparable with our previous data on Cs sorption onto rock samples from “Kamenny” and “Itatsky” area [7, 8] and with other published data [9, 10, 17, 18].

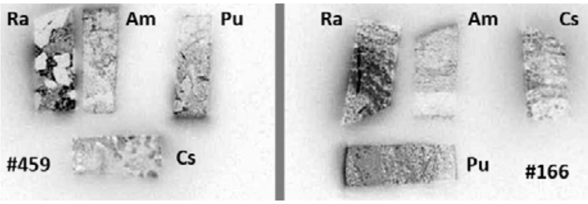

Figure 4. Examples of digital radiography images of rock slices of granitogneiss (#459) and plagiogneiss (#166) with sorbed radionuclides after 22 hours of exposure.

CONCLUSIONS

Preliminary results on sorption properties of the rock samples from the “Eniseysky” area in the exocontact of Nizhnekansky massif have been obtained. The fast and quantitative sorption of mono- and multivalent metal cations in nanomolar concentrations was observed under conditions relevant to HLW repository (reducing media, pH 7-8).The only exception is selenium that has low sorption tendency towards investigated rock samples. Despite of the considerable diversity in the petrochemical and structural properties of the rock samples, the sorption behavior of the studied radionuclides towards them have no substantial difference. The possible explanation of this discrepancy is the low concentration of all the radionuclides. Analysis with the digital radiography technique revealed the heterogeneous distribution of radionuclides onto rock samples surface with predominant sorption on the phyllosilicate minerals and zones of microbrecciation, chloritization and sericitization.

REFERENCES

1. Kudrjavtsev E.G., Gusakov-Stanjukovich I.V., Kamnev E.N. et al. Creation of the object of the final isolation HLW in the deep geological formations. (Nizhnekansky massif, Krasnoyarsky region) // Seminar «Final burial of HLW and SNF – experience and plans», Sweden, Bommersweek, 22-24 February 2009.
2. Anderson E.B., Savonenkov V.G., Lubtceva E.F. et al. The results of searching and scientific researches on the choice of the site for underground isolation HLW and SNF at Nizhnekansky granitoid massif (South-Eniseysky Ridge) // Radium Institute Bulletin, v. XI, 2006, 1-19.
3. Anderson E.B., Rogozin Yu.M., Bryzgalova R.V. et al. Experimental investigation of sorption-barrier properties of granitoids of the Nizhnekanskiy Massif // International Conference on Material Research Society (MRS'2000), Sydney, Australia, 2000.
4. Anderson E.B., Rimski-Korsakov A.A., Savonenkov V.G. et al. Status of the Nizhnekanskiy Granitoid Massif as a Candidate for HLW Deep Geological Repository in Russia // Symposium on HLW, LLW, Mixed Wastes and Environmental Restoration (WM'02), Tucson, USA, 2002, Abstr. 77.
5. IAEA Safety Standards series. Geological Disposal Facilities for Radioactive Waste. Specific Safety Guide No. SSG-14. Vienna, 2011.
6. Stage E., Huber F., Heck S., Schäfer Th. Sorption/desorption of ^{137}Cs(I), ^{152}Eu(III) and ^{233}U(VI) onto new crock derived Äspö diorite – a batch type study // 1st Workshop Proceedings of the Collaborative Project „Crystalline Rock Retention Processes“ (7th EC FP CP CROCK). Vol. 7629 of KIT SCIENTIFIC REPORTS. Karlsruhe Institute of Technology Karlsruhe, Germany, 2012, P. 51–62.
7. Petrov V.G., Vlasova I.E., Kuzmenkova N.V. et al. Characterization of rock samples from areas of the proposed HLW and SNF repository in Russia (Nizhnekansky Massive) and first sorption studies // 1st Workshop Proceedings of the Collaborative Project „Crystalline Rock Retention Processes“ (7th EC FP CP CROCK). Vol. 7629 of KIT SCIENTIFIC REPORTS. Karlsruhe Institute of Technology Karlsruhe, Germany, 2012, P. 37–42.
8. Petrov V., Kuzmenkova N., Petrov V. et al. Sorption of Cs, Eu and U(VI) onto rock samples from Nizhnekansky Massive // International Conference on Radioecology and Environmental Radioactivity 2014 (ICRER'14), Barcelona, Spain, 2014.
9. Kónya J., Noémi M. Nagy N.M. & Nemes Z. The effect of mineral composition on the sorption of cesium ions on geological formations // Journal of Colloid and Interface Science, 2005, Vol. 290, P. 350-356.
10. Vandergraaf T.T., Abry D.R.M. & Davis C.E. The use of autoradiography in determing the distribution of radionuclides sorbed on thin sections of plutonic rocks from the Canadian shield // Chemical Geology, 1982, Vol. 36 , P. 139-154.
11. Huitti T., Hakanen M., Lindberg A. Sorption of cesium, radium, protactinium, uranium, neptunium and plutonium on Rapakivi granite // Report Posiva-96-23, Helsinki, Finland, 1996, 57 P.
12. Goldberg S., Criscenti L.J., Turner D.R., Davis J.A. & Cantrell K.J. Adsorption–Desorption Processes in Subsurface Reactive Transport Modeling. // Vadose Zone J., 2007, Vol. 6, P. 407–435.
13. Wang P. & Anderko A. Thermodynamic Modeling of the Adsorption of Radionuclides on Selected Minerals. I: Cations // Ind. Eng. Chem. Res., 2001, Vol. 40, P. 4428-4443.
14. Petrov V.A., Poluektov V.V., Hammer J. R., Zulauf G. Analysis of mineralogical and deformation-induced transformations of Nizhnekansky Massif rocks to estimate their retention capacity in geological disposal and isolation of radioactive waste // Gorny Zhurnal – Mining Journal. 2015. № 10. pp. 67–74.
15. HYDRA : Hydrochemical Equilibrium-Constant Database. MEDUSA : Make Equilibrium Diagrams Using Sophisticated Algorothms. Royal Institute of Technology, Stockholm, Sweden. http://www.kth.se/che/medusa/ (accessed on 01/02/2017)
16. Guillaumont R., Fanghänel Th., Fuger J., Grenthe I., Neck V., Palmer D.A., Rand M. Update on the chemical thermodynamics of uranium, neptunium, plutonium, americium and technetium. 2003, Elsevier B.V., Amsterdam, The Netherlands.
17. Torstenfelt B., Andersson K., Allard B. Sorption of Strontium and Cesium on rocks and minerals // Chemical Geology, 1982, Vol. 36, P. 123-137.
18. Qin H., Yokoyama Y., Fan Q., Iwataki H. et al. Investigation of cesium adsorption on soil and sediment samples from Fukushima Prefecture by sequential extraction and EXAFS technique // Geochemical Journal, 2012, Vol. 46, P. 297-302.