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Speciation of actinides in groundwater samples collected near deep nuclear waste repositories



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ABSTRACT

Actinide binding to colloidal particles of different nature was studied under oxic and anoxic conditions of an underground nuclear waste disposal site using successive micro- and ultrafiltration techniques. According to the actinide redox speciation, under oxic conditions they were present in high oxidation states except for plutonium, for which a significant part was found in the tetravalent state. In case of the anoxic conditions, the share of An (IV) was proportional to the total U(IV) concentration. This indicated formation of intrinsic U(IV) hydro-xocolloids, which bound other actinides. Formation of the intrinsic actinide colloids was proven by the secondary ion mass spectrometry (SIMS) with the submicron resolution. In contrast, under the oxic conditions uranium and plutonium were sorbed by natural colloids (amorphous hydrous ferric oxide and Mn oxides).

1. Introduction

In recent decades, development of the nuclear energy applications has resulted in a significant environmental contamination because of both the regulated discharges and several accidents. In addition, disposal of the man-made radionuclides from the nuclear waste or spent nuclear fuel in geological media, as adopted in several countries, is a potential source of the environmental contamination.

There are three sites in Russia where disposal of the nuclear waste is under way, namely, the Production Association "Mayak" (PAM), Krasnoyarsk Mining and Chemical Combine (MCC), and Siberian Chemical Combine (SCC). To date liquid nuclear waste injection in deep geological formations is considered in Russia as the safest way of its management (Rybaltchenko et al., 1994), in contrast to the historical open surface repositories at "Mayak" that led to the severe environmental pollution with radionuclides (Novikov et al., 2009).

The main parameters that were taken into account in safety forecasting for existing and planned radioactive waste (RW) storage facilities were the following: geological and hydrogeological characteristics of the environment, the mineral composition and sorption characteristics of the host rocks, and physicochemical parameters of the formation water, such as redox conditions, pH, the concentration of complexing agents, etc. The presence of colloids was not usually considered, because its part was difficult to account for in reactive contaminant transport calculations, and bench-scale experiments may result in major underestimation of colloid constituent. On the other hand, enhanced migration of radionuclides bound to colloid particles was observed in many studies (Kersting et al., 1999; Degueldre et al., 2000; Flury et al., 2002; Geckeis et al., 2003; Novikov et al., 2006).

Three types of colloids were recognized in (Sen and Khilar, 2006; Kim, 1991,. Kim et al., 1991; Flury and Qiu, 2008; Walther et al., 2009; Neck and Kim, 2001) as follows: aquatic colloids, real or intrinsic colloids, and carrier colloids. Aquatic colloids were represented by mineral particles, hydrolyzed metal ion precipitates, high-molecular weight organic substances, microorganisms, etc. Real colloids were typical for some low-soluble radionuclides, e.g. tetravalent actinides or Tc(IV), which produced aggregates of hydrolyzed species through oxo- or hydroxyl bridge formation. When radionuclides were sorbed by aquatic colloids, the so-called "carrier colloids" were generated. Several studies dealt with formation of An (IV) hydroxocolloids (Neck et al., 1989; Knopp et al., 1999; McCarthy and McKay, 2004; Gadd, 1996; Batuk et al., 2015); there was some information about the bacterial impact on actinide mobilization and immobilization in the colloidal form in subsurface environments (Francis and Dodge, 2015; Ohnuki et al., 2010).

This paper describes experimental results of the radionuclide behavior studies in a permeable sandy penetrable horizon environment affected by nuclear waste effluents. Our work was aimed to investigate the colloidal actinide speciation depending on the geochemical

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conditions. Therefore, the groundwater samples chosen for the experiments were taken at the depth of 80–100 m in the Karachay pollution zone adjacent to the PAM nuclear facility and at the depth of 350–400 m near the SCC liquid RW repository in Tomsk region.

2. Materials and methods

Field studies included groundwater sampling in oxic and anoxic condition areas. Maps of the sites examined were given in refs (Rybaltchenko et al., 1994) (SCC) and (Novikov et al., 2006) (PAM). On SCC site the water samples were taken at the depth of 350–400 m from monitoring wells located on the deep liquid radioactive waste injection site. The distance to the injection wells was a few tens of meters. The Eh value of water was – 200 mV (anoxic conditions). On the PAM site, the samples were taken in the near-field Karachay zone of 1–2 km from the depth of 80–100 m. The Eh of water was 100–300 mV (oxic conditions). The *in-situ* measurements were performed with a multi-channel hydrogeochemical probe developed at the Institute of Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry of the Russian Academy of Sciences, the readings of pH, Eh, temperature, concentrations of dissolved O₂, H₂S, Na⁺, NH₄⁺, and NO₃⁻ being recorded simultaneously (Solodov et al., 1998).

Groundwater samples were pumped out of the well by an *in-situ* pump at the flow rate of 2–2.5 m³/hour and collected into glass bottles first cleaned by nitric acid (reagent grade) and deionized water. Before sampling, the equipment was purged with nitrogen. A 5 L container with the samples taken was placed into the nitrogen atmosphere. The conductivity, pH, and Eh were measured in the course of sampling; samples were taken after the readings became steady. Immediately after sampling, samples of 1 L volume were subjected to successive micro-and ultrafiltration using 200 nm and 50 nm nucleopore filters, Dubna and 5 nm filters by Vladipor, Russia. We used standard filtration modules at the constant pressure (N₂) of about 300 kPa. Filtration was performed in the nitrogen atmosphere. Aliquots taken from each filtrate were analyzed to determine the concentrations of major and trace elements and radionuclides.

The cation and anion composition of the initial samples and filtrates was determined using ICP-MS ("Element 3, Finnegan"), atomic absorption spectrometry (Quantum-AFA), and ion chromatography (Zvet-4).

The radionuclide concentration was determined using gammaspectrometry with HPGe detectors (GEM-60195-P, ORTEC), alphaspectrometry with PIPS detectors ("Alpha-Analyst", Canberra), and liquid scintillation spectrometry (TriCarb-2700 TR, Canberra) after the appropriate chemical separation procedures described earlier (Myasoedov et al., 1998).

For some samples, speciation of the radionuclides was studied using the sequential extraction procedure developed by Miller (Miller et al., 1986) as shown in Table 1.

For the actinide redox speciation at the tracer-level concentration, solvent extraction using tenoyl-trifluoroacetone (TTA) described by Choppin (1999) and supported liquid membrane extraction with di-2ethylhehyl phosphoric acid (HDEHP) as described by Myasoedov and Novikov (Novikov and Myasoedov, 2003; Myasoedov and Novikov, 1999) were used. Membrane extraction was advantageous for the anoxic conditions, as no adjustment of the pH value was needed, and the liquid-to-organic phase ratio was 10^3 .

The colloidal matter collected was characterized by SEM (Hitachi S-3200N) and TEM (JEOL JEM 2010F). SEM was performed with 1 cm² filter pieces coated with gold-palladium alloy to minimize charging effects. To prepare samples for TEM, the pieces of filters were immersed in deionized water and ultrasonicated for few minutes at 2.64 MHz. Then the colloid suspension was deposited on holey-carbon films supported by copper grids. The TEM measurements were conducted using JEM 2010F field emission TEM gun. Bright-field (BF), dark-field (DF), high resolution (HR) TEM, selected area electron diffraction (SAED), and nano-beam energy dispersive X-ray spectroscopy (EDX) analysis were conducted using 200 keV electron beam to characterize the sample.

To study the spatial distribution of actinides, fission track analysis (FTA) was performed with about $1 \times 1 \text{ cm}^2$ filter pieces using the polyethyleneterphtalate (Lavsan) solid-state nuclear track detector (SSNTD). The sample – SSNTD sandwich was irradiated in the research reactor at the Moscow Engineering Physical Institute at the thermal neutron flux of $1.1 \cdot 10^{15} \text{ n/cm}^2$ for about 100 min. Etching procedure comprised treatment by 6M NaOH solution at 60 °C for one hour.

The spatial distribution of long-lived radionuclides on colloids was studied by SIMS with the submicron resolution (nanoSIMS-50, Cameca). For SIMS measurements an aliquot of the suspension containing colloidal particles was deposited on silicon chips and air-dried. All analyses were performed using 16 keV O⁻ primary ions and detecting positive secondary ions. Mass resolution was set at M/ dM = 2000 for all data. The spatial distribution was traced for major elements (Fe, Mn, Ti, Ca, Al) and actinides.

3. Results and discussion

3.1. Chemical composition of groundwater samples

Samples from 14 wells for both sites were collected (Fig. 1). The distribution coefficient of radionuclide adsorption by surrounding rocks, colloidal primary and secondary minerals dependes on pH, Eh, the concentration of major elements and complexing agents. Therefore, both the initial samples and filtrates obtained after micro- and ultra-filtration were analyzed for their chemical composition and redox potential.

The Eh value of water ranged from -200 mV (anoxic conditions) to 100–300 mV (oxic conditions). In both zones, the groundwater was low acidic (pH~6.6–7.4). The samples differed in the major element composition and salt background. In some samples, a high concentration of nitrate-ions, alkaline and alkaline earth element was found, whereas some samples had the composition typical of the natural groundwater (Fig. 1). The redox potential was affected by the sampling location and depth and varied from slightly oxic conditions (Eh = 300 mV) to anoxic conditions (Eh ≤ -100 mV). According to the redox conditions, the samples were divided into *Oxic Zone* and *Anoxic Zone* samples.

Table 1

Ν	Fraction	Reagent	Conditions (pH, solution volume)
1	Exchangeable	0.5M Ca(NO ₃) ₂	pH = 5.5, V = 100 ml
2	Acid soluble	0.44M CH ₃ COOH 0.5M Ca(NO ₃) ₂	pH = 2.5, V = 50 ml
3	Bound to Fe/Mn oxides	0.01M NH ₂ OH·HCl in 25% CH ₃ COOH	pH = 2.0, V = 10 ml
4	Bound to organics	0.1M Na ₄ P ₂ O ₇	pH = 10, V = 100 ml
5	Bound to amorphous oxides	0.18M (NH ₄) ₂ C ₂ O ₄ 0.1M H ₂ C ₂ O ₄	pH = 3.5, V = 50 ml
6	Bound to crystalline oxides	0.15M Na Citrate 0.75 g Na ditionite	pH = 5.5, V = 10 ml
7	Residual	$HF + H_2SO_4$	pH = 0



Fig. 1. Piper diagram of groundwater samples studied.





Fig. 2. Association of actinides with colloid particles of different size in groundwater samples collected in Oxic Zone. Average values and uncertainties.

Fig. 3. Association of actinides with colloid particles of different size in groundwater samples collected in Anoxic Zone. Average values.



Fig. 4. The share of different redox plutonium species in the groundwater samples from Oxic Zone and the total uranium concentration.



Fig. 5. The share of different redox actinide species in the samples collected from Anoxic Zone and the total uranium concentration.



Fig. 6. The backscattered electron image (a) and EDX of the colloid particle containing Sm and Ti (a) (collected in Oxic Zone).





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Fig. 7. FTA images corresponding to the fissile actinide distribution. A- Oxic Zone sample, B and C- Anoxic Zone sample.

For both *Oxic Zone* and *Anoxic Zone* samples, the carbonate concentration was high and varied from 140 to 1800 mg/kg. The presence of low molecular weight organic substances was detected, such as acetate, oxalate and sulfate. The content of nitrite differed from 0.05 to 1.5 mg/L.

3.2. Distribution of actinides among different particle sizes

In order to compare results of micro- and ultrafiltration, filtering was performed under the same conditions. The pumping rate was rather high to minimize possible changes in the chemical composition (e.g. oxidation of Fe(II) to Fe(III)), but the pressure was to be minimal to prevent disturbing the morphology of colloids. The quantity of colloidal matter on the filter was sufficient for further analysis, but formation of a "cake" on the filter surface altered the filtration properties. In this study, we managed to attain the constant filtering conditions. The major K and Na components were scarcely retained by filters, thus proving the absence of an additional hydraulic resistance.

For groundwater samples from *Oxic Zone*, Pu and Am were preferentially bound to nanocolloids, while U and Np were found in the filtrate. (Fig. 2). The fraction of actinides and other elements bound to colloids decreased in the following sequence: Pu > Zr \geq Am \geq Eu » Np > U. The share of U and Pu bound to nanocolloids increased upon dilution of waste with groundwater.

In contrast to *Oxic Zone* samples, under anoxic conditions of *Anoxic Zone*, U and other actinides were bound to relatively larger colloidal particles (Fig. 3). For groundwater samples from *Anoxic Zone*, the following sequence of radionuclide inclusion into colloidal particles was observed: $U > Np > Pu \ge Am \ge Zr \ge Zn \ge Eu$.

3.3. Actinide redox speciation

According to membrane extraction, U and Np in *Oxic Zone* were present in higher oxidation states, i.e. U(VI) and Np(V). However, in case of Pu, both Pu(IV) and Pu(V) were found as presented in Fig. 4, and, despite the oxic conditions, only in few cases a small fraction of Pu (VI) was detected.

The presence of Pu(V) in groundwater samples was considered as one of the factor enhancing Pu migration. According to Choppin (Choppin and Wong, 1998), the effective charge at the central actinide atom of AnO_2^+ unit is +2.2; hence, it has a low tendency towards complexation and sorption. Among different oxidation states, AnO_2^+ was found in the true soluble fraction. However, for samples from *Oxic Zone* the share of Pu in this fraction was low and preferentially it was bound to nanocolloids as shown in Fig. 2. The Pu redox speciation found in 5 nm filtrate indicated that despite the share of Pu(V) was higher (5–12%) than in 200 nm filtrate, it was not the dominant redox form of this species were bound to colloidal matter.

In groundwater samples collected in *Anoxic Zone*, actinides in lower oxidation state (tetravalent) were dominating (Fig. 5). Despite the anoxic conditions of *Anoxic Zone*, natural U in the wells outside the contamination plume was found in hexavalent state. Interaction of groundwater with waste effluents has led to stabilization of actinides in low oxidation states. This could be either due to the presence of actinides in low oxidation states in waste effluents or due to their reduction upon interaction with the geological media. In the studied systems, the nuclear waste contained nitric acid solutions originated from the PUREX process, where U was present in the hexavalent state. Other factors that might govern the redox equilibrium between different redox forms in the samples were the presence of complexing substances and radiolytic effects that produced high nitrite concentrations (Solodov et al., 1998). High concentrations of colloids and the strong tendency of actinides to sorb might also shift the redox equilibrium.

In view of the redox speciation, the way of actinide inclusion into colloidal particles for *Oxic Zone* samples was reasonable. For ground-water samples from *Anoxic Zone*, one would expect another way of the actinide distribution. However, as they were present in low oxidation states, this sequence was defined by their total concentration that changed as follows: $U \gg Np \gg Pu > Am$. It was established for *Anoxic Zone* samples that the share of U(IV) and Np(IV) (Pu was present in tetravalent state only) increased with the increase in the total U concentration (Fig. 5). This was an indirect indication that U(IV) formed intrinsic hydroxocolloids under anoxic conditions of *Anoxic Zone*, and these colloids were responsible for binding other actinides. When



Fig. 8. The typical distribution of major elements (e.g. Fe) and ²³⁸U for Anoxic Zone samples.

Table 2

Partitioning of actinides bound to colloids of different size.

Fraction	200 nm				50 nm	50 nm			5 nm	5 nm			
	Oxic Zone		Anoxic Zone		Oxic Zon	Oxic Zone		Anoxic Zone		Oxic Zone		Anoxic Zone	
	Pu	Am	U	Pu	Pu	Am	U	Pu	Pu	Am	U	Pu	
Exchangeable	4.2	5.4	4.5	3.2	a	a	2.0	1.5	1.7	2.3	1.0	0.9	
Acid soluble	17.9	19.2	16.7	15.9	2.9	2.7	13.3	10.9	a	-	-	-	
Fe/Mn oxide bound	30.9	30.9	16.9	17.9	11.2	14.2	6.8	7.2	-	-	-	-	
Organically bound	22.6	15.4	5.8	9.0	27.9	29.9	1.6	0.8	8.2	12.3	0.6	0.2	
Amorphous oxides	16.9	17.9	6.5	2.2	11.6	10.9	0.9	1.1	14.2	5.6	0.8	1.1	
Crystalline oxides	2.2	5.5	18.0	14.6	11.1	12.4	18.0	14.6	31.6	22.2	39.2	45.9	
Residual	5.3	5.7	31.6	37.2	1.9	1.6	57.4	63.9	44.3	57.6	58.4	51.9	

^a treatment by the acidic solution was skipped because of the partial dissolution of the filter material.

natural groundwater was mixed with a technological solution, the equilibrium was not attained for a long period of time, and uranium species existing in the form of true colloids and $UO_{2(s)}$ were gradually

precipitated on the confining rocks. That is why the lateral migration extent did not exceed a several meter distance (A.A. Zubkov et al., 2008).



Fig. 9. General scheme of actinide particles in oxic and anoxic zone.

3.4. The nature and composition of actinide bearing colloidal particles

The origin and chemical composition of colloids played dominating roles in actinide binding and speciation. In samples collected from *Oxic Zone*, the colloidal matter distribution was quite heterogeneous with a predominance of the amorphous hydrous ferric oxide (HFO), which also contained Si and Ca admixtures. The concentration of other colloidal particles identified by SEM and TEM decreased as follows: clays \approx calcite (CaCO₃) > rutile (TiO₂) \approx hematite (Fe₂O₃) \approx barite (BaSO₄) \approx rancieite (CaMn₅O₉) \approx plagioclase (NaCaAlSi₂O₈) > monazite (REE phosphate) \approx quartz (SiO₂).

Among the colloidal particles, a single suspended particle of about $2 \,\mu m$ size found by SEM using backscattering electron image, contained high concentrations of Ti and Sm (Fig. 6). Most probably, despite the Ti concentration in bedrock samples of Oxic Zone averages 0.84%, that particle was of an artificial origin, since it did not contain other rare earth elements (REE) except for Sm.

For the samples collected in *Anoxic Zone*, relatively large particles of a few μ m size prevailed, being probably formed by coagulation of the smaller submicron size particles. These phases were mostly typical to the anoxic environments such as pyrite (FeS₂), chalcopyrite (CuFeS₂), galena (PbS), and to clays in a less extent. Few particles of barite (BaSO₄) were found, as well as hematite (Fe₂O₃) and monazite (REE phosphate).

If U(IV) formed intrinsic hydroxocolloids under the anoxic conditions of *Anoxic Zone*, its spatial distribution should differ from *Oxic Zone* where the oxic conditions prevailed. To prove this, we used FTA as shown in Fig. 7. The star-like distribution of actinides in the colloid sample collected in *Anoxic Zone* corresponded to their inhomogeneous distribution, in contrast to the sample collected in *Oxic Zone*, where actinides were rather homogeneously distributed.

SIMS study was performed to obtain elemental mapping with the submicron resolution. Presented elemental maps of 238 U, 239 Pu, Fe, Ca, Al, and Mn for Oxic Zone samples were published earlier (Novikov et al., 2006). The distribution of 238 U and 239 Pu followed the distribution of major elements, i.e. Fe, Al, Mn, Ca, Si that corresponded to formation of actinide "pseudo-colloids" (actinides adsorbed by other colloid particles).

In *Anoxic Zone* samples, U was present in tetravalent state, and formation of the intrinsic hydroxocolloids was possible. In contrast to *Oxic Zone*, the elemental distribution for *Anoxic Zone* indicated that ²³⁸U was anti-correlated with major elements (Fe, Mn, Ti, Ca, Si, Al). As an example, the typical distribution of ²³⁸U and Fe was presented in Fig. 8.

3.5. Sequential extraction of actinides bound to colloids

Sequential extraction was performed for colloids collected on different filters from *Oxic* and *Anoxic Zones* as presented in Table 2. The strength of actinide binding to colloids collected from *Anoxic Zone* was higher than for colloids collected from *Oxic Zone*. This corresponded to a relatively higher concentration of actinides in the *Residual fraction* of Anoxic Zone samples. The relative actinide content in the *Exchangeable fraction* was only few percent and decreased with the colloid size, thus characterizing the relative immobility of actinides. In samples collected from *Anoxic Zone*, partitioning of Pu did not differ from partitioning of U; that was an indication that it was either co-precipitated or sorbed by U(IV) hydroxocolloids under the anoxic conditions. According to the SIMS data, for the samples collected from *Oxic Zone*, the major part of actinides was bound to Fe and Mn oxides. (see Fig. 9).

4. Conclusions

Actinide binding to colloidal particles of different nature under oxic and anoxic conditions of an underground nuclear waste disposal site was different. According to the actinide redox speciation, under the oxic conditions they were present in high oxidation states except for plutonium, for which a significant part was found in the tetravalent state. In case of the anoxic conditions, the share of An (IV) was proportional to the total U(IV) concentration. This indicated formation of the U(IV) intrinsic hydroxocolloids, which bound other actinides. Formation of the intrinsic actinide colloids was proven by secondary ion mass spectrometry (SIMS) with the submicron resolution. In contrast, under oxic conditions uranium and plutonium were sorbed by natural colloids, such as amorphous hydrous ferric oxide and Mn oxides.

The strength of actinide binding to colloids collected from Anoxic Zone was higher than for those collected from Oxic Zone. This corresponded to a relatively higher concentration of actinides in the Residual fraction of the Anoxic Zone samples.

The results obtained could be useful for prediction of the actinide behavior both in freshwater ecosystems and in the area contaminated by the Fukushima accident (Sasaki et al., 2016).

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References

- Batuk, O.N., et al., 2015. Multiscale Speciation of U and Pu at Chernobyl, Hanford, Los Alamos, McGuire, AFB, Mayak, and Rocky Flats. Environ. Sci. Technol. 49 (11), 6474–6484.
- Choppin, G.R., Wong, P.J., 1998. The chemistry of actinide behavior in marine systems. Aquat. Geochem. 4, 77–101.
- Choppin, G.R., 1999. Role of humics in actinide behavior in ecosystems. Chemical Separation Technologies and Related Methods of Nuclear Waste Managements 247–260.
- Degueldre, C., Triay, I., et al., 2000. Groundwater colloid properties: a global approach. Appl. Geochem. 15 (7), 1043–1051.
- Flury, M., Mathison, J.B., Harsh, J.B., 2002. In situ mobilization of colloids and transport of cesium in Hanford sediments. Env.Sci. & Tech 36 (24), 5335–5341 Myasoedov, B. F. 1997. Radioactive pollution of some regions of Russia. Geoecology 4, 3-18.
- Flury, M., Qiu, H., 2008. Modeling colloid-facilitated contaminant transport in the vadose zone. Vadose Zone J. 7 (2), 682–697.
- Francis, A.J., Dodge, C.J., 2015. Microbial mobilization of plutonium and other actinides from contaminated soil. J. Environ. Radioact. 150, 277–285.
- Gadd, G.M., 1996. Influence of microorganisms on the environmental fate of radionuclides. Endeavour 20 (4), 150–156.
- Geckeis, H., Manh, T.N., Bouby, M., Kim, J.I., 2003. Aquatic colloids relevant to radionuclide migration: characterization by size fractionation and ICP-mass spectrometric detection. Colloids and Surfaces a Physicochemical and Engineering Aspects 217 (1–3), 101–108.
- Kersting, A.B., Efurd, D.W., Finnegan, D.L., et al., 1999. Migration of plutonium in ground water at the Nevada Test Site. Nature 397, 56–59.
- Kim, J.I., 1991. Actinide colloid generation in groundwater. Radiochim. Acta 52 (3), 71–81.
- Kim, J.I., Rhee, D.S., Buckau, G., 1991. Complexation of Am(III) with humic acids of different origin. Radiochim. Acta 52 (3), 49–55.
- Knopp, R., Neck, V., Kim, J.I., 1999. Solubility, hydrolysis and colloid formation of plutonium (IV). Radiochim. Acta 86 (3–4), 101–108.
- McCarthy, J.F., McKay, L.D., 2004. Colloid transport in the subsurface. Vadose Zone J. 3 (2), 326–337.
- Miller, W.P., Martens, D.C., Zelazny, L.W., 1986. Effect of sequence in extraction of trace metals from soils. Soil Sci. Soc. Am. J. 50 (3), 598–601.
- Myasoedov, B.F., et al., 1998. Complex geochemical studies of radionuclide behavior in

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aquatic and surface ecosystems. Methodology, investigation objects and procedures. Radiochemistry 40 (5), 461–467.

- Myasoedov, B.F., Novikov, A.P., 1999. Radiochemical procedures for speciation of actinides in the environment: methodology and data obtained in contaminated regions of Russia by radionuclides. In: Evaluation of Speciation Technology, Workshop Proceedings Tokai-mura, Ibaraki, Japan 26-28 October 1999, pp. 25–37.
- Neck, V., Kim, J.I., 2001. Solubility and hydrolysis of tetravalent actinides. Radiochim. Acta 89 (1), 1–16.
- Neck, V., Kim, J.I., Seidel, B.S., et al., 1989. A spectroscopic study of the hydrolysis, colloid formation and solubility of Np(IV). Radiochim. Acta 439–446.
- Novikov, A.P., et al., 2009. Speciation of radionuclides in colloidal matter of underground waters taken from observation wells in the zone of impact of Lake Karachai. Radiochemistry 51 (6), 649–653.
- Novikov, A.P., et al., 2006. Colloid transport of plutonium in the far-field of the Mayak production association, Russia. Science 314 (5799), 638–641.
- Novikov, A.P., Myasoedov, B.F., 2003. Radiochemical procedures for speciation of actinides in the Environment. Environment Protection against Radioactive pollution 147–154.
- Ohnuki, T., Kozai, N., Sakamoto, F., et al., 2010. Association of actinides with

microorganisms and clay: implications for radionuclide migration from waste-repository sites. Geomicrobiol. J. 27, 225–230.

- Rybaltchenko, A.I., Pimenov, M.K., Kostin, P.P., et al., 1994. The Deep Injection of LNW. Moscow IzdAT 256 p.
- Sasaki, T., Takeno, Yu, Kobayashi, T., Kirishima, A., Sato, N., 2016. Leaching behavior of gamma-emitting fission products and Np from neutron-irradiated UO2–ZrO2 solid solutions in non-filtered surface seawater. J. Nucl. Sci. Technol. 53, 303–311.
- Sen, T.K., Khilar, K.C., 2006. Review on subsurface colloids and colloid-associated contaminant transport in saturated porous media. Adv. Colloid Interface Sci. 119 (2), 71–96.
- Solodov, I.N., Zotov, A.V., Khoteev, A.D., 1998. Geochemistry of natural and contaminated subsurface waters in fissured bed rocks of the Lake Karachai area, Southern Urals, Russia. Appl. Geochem. 13 (8), 921–939.
- Walther, C., et al., 2009. New insights in the formation processes of Pu (IV) colloids. Radiochim. Acta 97, 4–5.
- Zubkov, A.A., et al., 2008. Predictive Modelling of the Distribution of the Filtrate of Liquid Radioactive Waste in Reservoirs Landfill Deep Burial of Siberian Chemical Plant. Vestnik of Tomsk state University 306, pp. 161–167.