



## 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) hydroxocolloids, 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  $O_2$ ,  $H_2S$ ,  $Na^+$ ,  $NH_4^+$ , and  $NO_3^-$  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 m<sup>3</sup>/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 ( $N_2$ ) 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 gamma-spectrometry with HPGe detectors (GEM-60195-P, ORTEC), alpha-spectrometry 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-2-ethylhehyl 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 cm<sup>2</sup> 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  $1 \times 1$  cm<sup>2</sup> filter pieces using the polyethyleneterephthalate (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  $1.1 \cdot 10^{15}$  n/cm<sup>2</sup> 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 depends on pH, Eh, the concentration of major elements and complexing agents. Therefore, both the initial samples and filtrates obtained after micro- and ultrafiltration 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  $\sim 6.6$ –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  $\leq -100$  mV). According to the redox conditions, the samples were divided into *Oxic Zone* and *Anoxic Zone* samples.

**Table 1**  
Sequential extraction protocol used for actinide partitioning in the samples studied [24].

N	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 $CH_3COOH$ 0.5M $Ca(NO_3)_2$	pH = 2.5, V = 50 ml
3	Bound to Fe/Mn oxides	0.01M $NH_2OH \cdot HCl$ in 25% $CH_3COOH$	pH = 2.0, V = 10 ml
4	Bound to organics	0.1M $Na_4P_2O_7$	pH = 10, V = 100 ml
5	Bound to amorphous oxides	0.18M $(NH_4)_2C_2O_4$ 0.1M $H_2C_2O_4$	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

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