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Speciation methods of actinides in trace concentrations

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Abstract

The development of actinide speciation methods in the environment is discussed. The results on speciation and migration of radionuclides in near-surface and deep conditions at the Krasnoyarsk mining and chemical plant and at the Production Association 'Mayak' (southern Ural) are reported. For surface conditions, the mobile plutonium fraction is mostly associated with inorganic complexes (carbonate) of the higher plutonium oxidation state, while less mobile fraction is associated with low-soluble Pu(IV) complexes with humic acids. The mobile fraction of americium consists of complexes with low molecular weight fulvic acids of non-specific nature with molecular weights lower than 10 kDa. Plutonium and americium behaviour in deep conditions is governed by colloid migration. **To cite this article:** *A.P. Novikov et al., C. R. Chimie 7 (2004)*. © 2004 Académie des sciences. Published by Elsevier SAS. All rights reserved.

Résumé

Méthodes de spéciation des actinides en traces. Le développement de méthodes pour la spéciation des actinides dans l'environnement est discuté. Nous présentons des résultats concernant la spéciation et la migration des radionucléides dans des conditions de sub-surface et en milieux géologiques profonds à la mine de Krasnoyarsk et à l'usine chimique de Mayak (Oural du Sud). En conditions de sub-surface, la fraction mobile contient essentiellement des complexes inorganiques (carbonates) de Pu dans ses degrés d'oxydation élevés, tandis que la fraction moins mobile contient des complexes insolubles du Pu(IV), avec des acides humiques. La fraction mobile de Am comporte des complexes d'acides fulviques de nature non précisée, mais d'une masse molaire inférieure à 10 kDa. En conditions de milieu profond, le comportement de Am et de Pu est influencé par la migration des colloïdes. **Pour citer cet article :** *A.P. Novikov et al., C. R. Chimie 7 (2004)*. © 2004 Académie des sciences. Published by Elsevier SAS. All rights reserved.

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1. Introduction

In the Russian Federation, the radiochemical plant activities are the main sources for man-made radionuclides in the environment. Several radiochemical plants are responsible for spent nuclear fuel and high-level radioactive wastes treatment, including those located at the Southern Ural, Production Association ‘Mayak’ (‘PA Mayak’) and in western Siberia – Krasnoyarsk Mine chemical plant (MCP) and Tomsk Siberian chemical plant (SCP). The radiological effects of these plants are different and result from technical and equipment conditions. ‘PA Mayak’, the first Soviet enterprise on weapon plutonium production, has the most polluted territories due to the erroneous concept of waste storage to the occurrence of some accidents (in 1957 and 1967).

The environmental monitoring in the territories affected by the radiochemical plants activities is one component of the closed nuclear-fuel cycle programme that is under the development in Russia. Nuclear power plants have their own monitoring capabilities, including network of dosimetry laboratories and automated control systems inside a 30-km zone. According to the experts of the Russian Committee for Hydrometeorology (Rosgidromet), the radiological conditions stay stable in Russia during the last years, except in the territories near ‘PA Mayak’. The data on radionuclide contamination in different regions of Russia are given in the Rosgidromet annual report [1]. However, less data on radionuclide speciation and migration in the environment could be found, despite the fact that speciation governs directions, rates and mechanisms of radionuclide migration. The correct estimation of radiological situation as well as its evaluation is impossible without knowledge on the distribution and migration abilities of radionuclides in the environment.

Some data on actinide speciation and migration ability in highly contaminated areas as well as in the territories with contamination slightly higher than the global fallout level are given in this paper.

2. Results and discussion

The redistribution of radionuclides in the landscape environment after the contamination is a major diffi-

culty during radiochemical monitoring. In order to minimize the influence of natural factors affecting radionuclide distribution (landscape, soil and vegetation types) and to compare results from different laboratories, the sampling should be based on comparative geographical methods used in landscape-geochemical research [2]. Despite this approach, which is widely used nowadays, it does not provide reliable data on radionuclide distribution. This is due to the presence of ‘hot’ particles classified by researchers of the Radium Institute (Saint Petersburg) as belonging to two types [3].

The differences between the first- and second-type ‘hot’ particles are as follows.

- *Prevalence.* The prevalence of the second-type particles is in the order of 10^9 – 10^{10} particles/km² and ~100 particles/km² for the first-type particles;
- *Radionuclide composition.* ¹³⁷Cs is the predominant radionuclide in the first-type particles, while the second-type particles have more various radionuclide compositions. There are particles enriched in an only nuclide (e.g., ¹³⁷Cs, ²⁴¹Am, ⁶⁰Co or ¹⁵²Eu, etc.) and polynuclide particles, enriched by radionuclide combination (e.g., ¹³⁷Cs + ²⁴¹Am or ²⁴¹Am + ¹⁵²Eu, or ⁶⁰Co + ¹⁵²Eu, etc.);
- *Specific activity.* The specific activity of the ‘hot’ second-type particles is 4–6 orders of magnitude higher than the average specific activity of the soil, the specific activity of the first-type particles being 2–3 orders of magnitude higher than the specific activity of the second-type ‘hot’ particles;
- *Contribution to the total specific activity of the tidal soil.* The radionuclides included in ‘hot’ second-type particles contribute to more than 50% and even about 100% for some radionuclides (e.g., ²⁴¹Am);
- *Distribution in the vertical profiles of the tidal soils.* The ‘hot’ first-type particles are found in the surface horizons of the tidal soils, while second-type particles are present in all horizons of the studied profiles.

The ‘hot’ first-type particles are frequently found in the territories affected by the nuclear tests and the Chernobyl accident and are studied extensively. Experts of Krasnoyarsk Institute of Biophysics and GEOKHI found such ‘hot’ particles in 1994 in the floodplain of the Enysey River [4]. Their specific activities were of millions Bq per particle. Such particles were found in

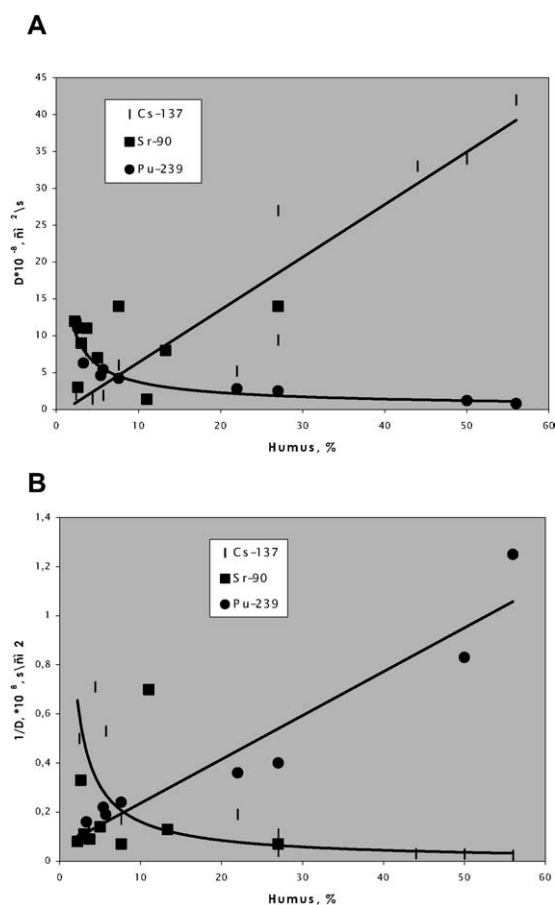


Fig. 1. Diffusion coefficients of radionuclides in upper horizons of EURT soils (A) and diffusional resistance (B) of these soils.

tidal soils of the Gorodskoy Island (340 km away from the KMCP). These particles were 10–200 μm in size. The ‘hot’ second-type particles were detected in highly contaminated soil samples collected in the frontal and rear parts of the Atamanovsky Island (2–7 km downstream from MCP) [3]. All data presented below were obtained after the careful analysis of samples in the presence of ‘hot’ particles. Circuits of used methods of selective partitioning and organic matter fractionation are given in [5].

The organic matter of soils and bottom sediments plays the major role in the migration ability of many radionuclides, particularly plutonium and americium [6–9], while the migration of radiocaesium and radiostromium is not dependent on the organic content. Data in Fig. 1 shows that the higher organic content, the lower migration ability of plutonium and higher migra-

tion ability of caesium are observed (since its migration is governed by clay minerals). No clear correlation for strontium is observed. This figure deals with diffusion coefficients versus organic content in the case of an ecosystem with rather simple hydrochemical regime, e.g., vertical migration in the Eastern Ural Radioactive Trace (EURT) zone (Fig. 1). The diffusion coefficients are calculated using the Fick equation for diffusion from flat surface to quasi-infinity. Fig. 2 shows a similar case of stationary conditions in reservoirs at PA ‘Mayak’. Plutonium and americium distribution in floodplain soils of the Yenisei River is governed by more complicated mechanisms, as illustrated in Fig. 3. Such distributions cannot be described by models that do not consider different sources of radionuclides and species distribution.

The fractionation of organic and inorganic matter in floodplain soils of the Yenisei River indicates that plutonium is mostly associated with low mobile organic

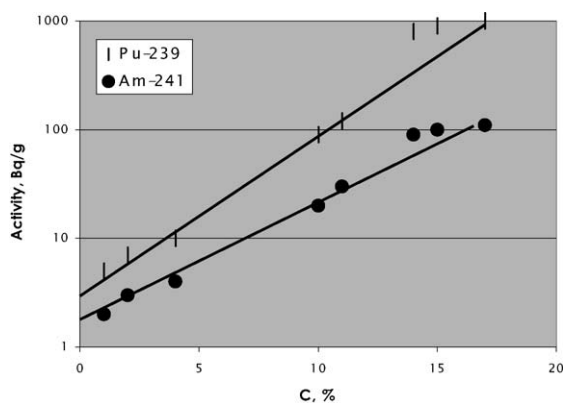


Fig. 2. Accumulation of ^{239}Pu and ^{239}Am by bottom sediments of basin-10 (PA Mayak) vs. the content of organic matter.

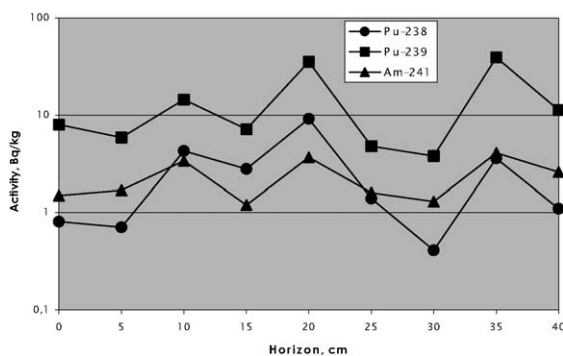


Fig. 3. Vertical distribution of Pu and Am in the floodplain soil of the Yenisei River.

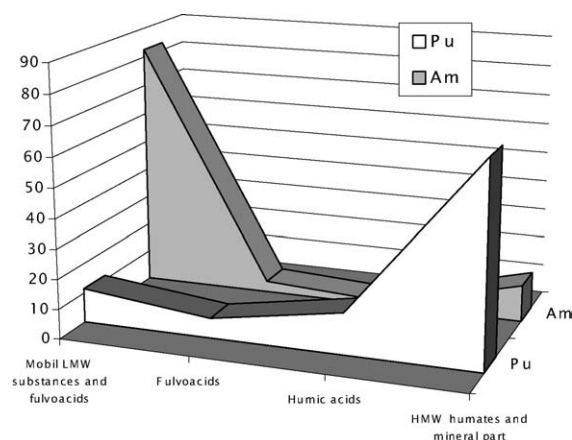


Fig. 4. Percentage of Pu and Am in various groups of organic matter of the flood-land soils of the Yenisey River.

group, in contrast to americium (Fig. 4). This could explain that the concentration of plutonium decreases greatly with distance from MCP if compared to americium (Fig. 5).

The redox state of elements appears to be a key factor for the actinide behaviour in the environment. This factor determines kinetics and thermodynamics of co-precipitation, sorption on active minerals, complex, and colloid formation. The data on plutonium oxidation state determination in environmental samples is rather limited. Several methods could be used, including those proposed by G. Choppin, based on TTA extraction [10]. However, this method has two potential disadvantages: need of pH adjustment to 4.0–5.0 and TTA reducing properties. We proposed a

Table 1

Speciation of plutonium in various soil leaches

| Fraction | Water leach | | | | | |
|--------------------------------|---|--------------|----------|---------------------|--------------|----------|
| | After 0.2- μ m filter | | | After 10-kDa filter | | |
| Oxidation state | IV | V | III + VI | IV | V | III + VI |
| Pu (% of total in fraction) | 14 | 79 | 7 | 12 | 82 | 6 |
| Pu (% of total in soil sample) | 0.23 | 1.3 | 0.12 | 0.08 | 0.6 | 0.04 |
| Fraction | 1 M CH ₃ COO leach | | | | | |
| | After 0.2- μ m filter | | | After 10-kDa filter | | |
| Oxidation state | IV | V | III + VI | IV | V | III + VI |
| Pu (% of total in fraction) | 39 | 55 | 6 | 30 | 61 | 9 |
| Pu (% of total in soil sample) | 2.4 | 3.4 | 0.4 | 1.3 | 2.6 | 0.4 |
| Fraction | 1 M HCl leach after 0.2- μ m filter | | | | | |
| | Pu | | | Am | | |
| Oxidation state | IV | III + V + VI | | IV | III + V + VI | |
| Ac (% of total in fraction) | 73 | 27 | | — | 100 | |
| Ac (% of total in soil sample) | 25.0 | 9.3 | | — | 49.4 | |

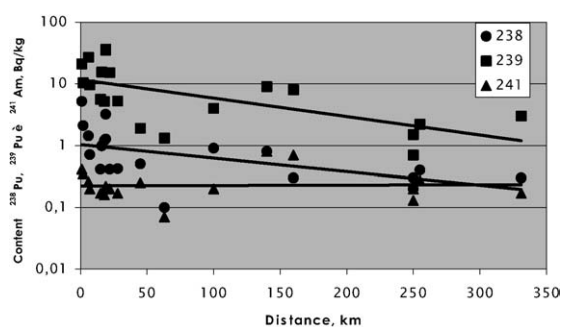


Fig. 5. Content of radionuclides in bottom sediments of the Yenisey River vs the distance from the discharge location (MCP).

membrane extraction method for plutonium redox speciation [11], which seems to provide reliable quantitative separation, with minimal effect on the original oxidation state distribution.

The pentavalent plutonium compounds are the most soluble among other oxidation forms, which is demonstrated by data presented in Table 1 for the Yenisey River floodplain soils. Only about 1% of total plutonium is leached by water, but 80% of it is found in the Pu(V) form. The share of Pu(V) in exchangeable fraction (extracted by acetate) reaches 55%. However, according to our data and those published earlier, if plutonium is found in pentavalent form, it is easily reduced upon sorption to minerals (see Fig. 6). As it is shown in [12], fast plutonium-sorption kinetics on the goethite (α -FeOOH) surface is due to reduction on the mineral surface, which contains Fe²⁺.

Influence of natural-water composition on the actinide oxidation state can be shown by the example of

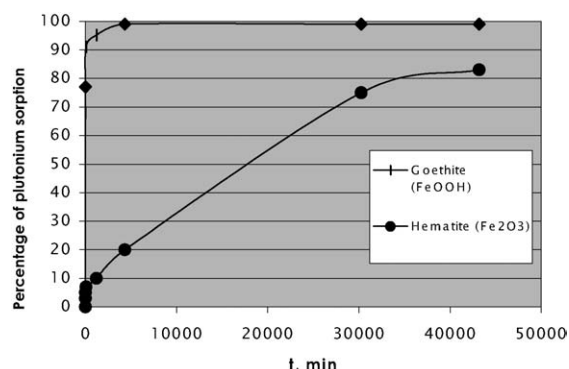


Fig. 6. Kinetics of plutonium (V) sorption on goethite and hematite.

groundwaters of ‘PA Mayak’ and strata waters of SCP. These selected under-investigation zones are characterized by different actinide migration conditions. The ground waters within the Karachai (Mayak) zone are weakly oxidizing, with appreciable carbonation not far from the source [13]. The stratum waters of the SCC radioactive waste pump-in site are determined by reducing conditions and rather low carbonation.

The results obtained are displayed in Tables 2 and 3. The data in these tables are averaged according to the results of three series of membrane-extraction experiments.

Obviously, uranium and neptunium have no alternative U(VI) and Np(V) form in the ‘PA Mayak’ groundwaters. Plutonium takes the same way as the sum of

Pu(IV) and Pu(V) does. The main difference from the literature data with respect to surface waters consists in the absence of reliably identified Pu(VI) [14].

The actinide distribution on oxidizing forms in the SCC stratum waters (Table 3) is more complicated than for the Mayak groundwaters (Table 2). The prevalence of lower oxidizing states of the actinides is appreciable. However, only Pu(IV) appears to be the dominant form of plutonium. For uranium and neptunium, a share of forms whose behaviour is similar to U(VI) and Np(V) makes from 20 up to 40%.

Colloid transport is considered as one of the effective mechanisms of actinide migration in underground systems, especially in reducing conditions and when significant amounts of complexing substances are absent [15]. However, the nature of the colloids at the under-investigation depth condition remains unknown so far.

The data on the actinide distribution on the size of particles for the Mayak groundwaters are presented in Fig. 7 (by the example of well #176). The analysis of speciation data (10 wells) allows us to draw the following conclusions.

- (i) The actinide (even plutonium) content in 450-nm particles is abnormally low (in comparison with the surface waters) [9], and the distribution in various fractions is obviously of a casual nature. It can be explained by the low content of high-molecular

Table 2

Oxidizing forms of the actinides found in the Mayak ground waters, percentage of the total content of an element in a sample

| Number of samples | U(IV) | U(VI) | Np(IV) | Np(V) | Pu(III) | Pu(IV) | Pu(V) | Pu(VI) | Am(III) ^a |
|-------------------|-------|-------|--------|-------|---------|--------|-------|--------|----------------------|
| 1 | – | 100 | – | 100 | – | 54 | 37 | 9 | 100 |
| 2 | – | 100 | – | 100 | – | 49 | 44 | 7 | 100 |
| 3 | – | 100 | – | 100 | – | 60 | 40 | – | 100 |
| 4 | – | 100 | – | 100 | – | 67 | 33 | – | 100 |

^a Determined to control correctness of liquid membranes functioning.

Table 3

Oxidizing forms of the actinides found in the SCP stratum waters, percentage of the total content of an element in a sample

| N | U(IV) | U(VI) | Np(IV) | Np(V) | Pu(III) | Pu(IV) | Pu(V) | Pu(VI) | Am(III) ^a |
|---|-------|-------|--------|-------|---------|--------|-------|--------|----------------------|
| 1 | 53 | 47 | 59 | 41 | 5 | 85 | 10 | – | 100 |
| 2 | 64 | 36 | 76 | 24 | – | 100 | – | – | 100 |
| 3 | 57 | 43 | 72 | 28 | 4 | 96 | – | – | 100 |
| 4 | 39 | 61 | 55 | 45 | 9 | 91 | – | – | 100 |

^a Determined to control correctness of liquid membranes functioning.

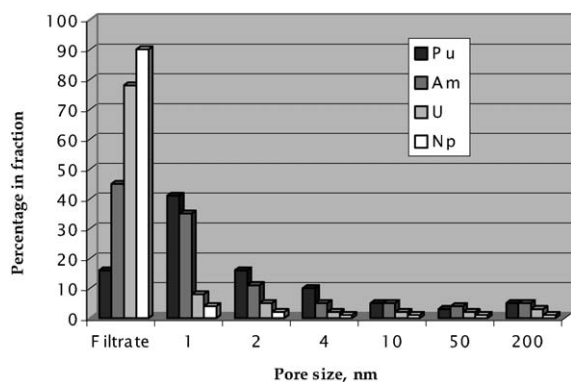


Fig. 7. Membrane fractionation of particles of the groundwaters near Karachay.

humic substances in rather large-depth groundwaters (80–100 m).

- The relative actinide content in 3000 up to 30 000 molecular-weight particles increases in the following succession: $U < Np < Am + Cm < Pu$. Besides, uranium and plutonium shares in a filtrate (a solution with the content of particles of less than 3000) decrease from 93 up to 83% and from 29 up to 9%, respectively, with a distance from the pollution source. For americium and neptunium, such tendency is not found. The intensification of the colloid formation for uranium and plutonium may qualitatively be explained by the total carbonate content decrease. In fact, for neptunium and transplutonium trivalent elements, this factor plays a smaller role, especially in the presence of organic substances. However, the strict correlation between the carbonate content and the actinide retention degree by the filters is not found.
- The effect of the phosphate content on retention degree of the actinides is not found, possibly because the increased content of the former is observed in some wells only.

The electrophoresis research carried out to measure the charge of colloid particles after a 450-nm filter for the water samples from wells 14 and 176 shows that the share of anionic forms of plutonium in the second well is much more than 61%, and is only 35% in well 14. The remainder belongs to neutral forms. The share of cationic forms does not exceed several percents. As a comparison, the share of anionic forms of plutonium lies in surface waters within the same range, but the share of cationic forms is considerably higher [9]. This fact is of importance, since the sorption degree of basic

natural minerals for the anionic and the neutral forms is lower than for the cationic ones.

3. Conclusions

Thus, it is possible to assume that the most mobile actinide forms in the under-investigation system appear to be negatively charged carbonate complexes having the following composition: $Ac(VI)O_2(CO_3)_3^{4-}$ and $Ac(V)O_2(CO_3)_2^{3-}$.

Detection of Pu(V) forms modifies substantially the initial ideas about the primary colloid transport of this element. In spite of the fact that only 10 to 30% of plutonium is found in a true solution, these forms certainly are considerably more mobile and the colloid-facilitated transfer becomes dominant, obviously only in strong reducing conditions.

Ac(V) may partly be of cationic forms [16] and be sorbed on the enclosing rocks, though having not high sorption factors (in comparison with the lower oxidizing states). However, the processes of precipitation and sorption for Ac(VI) play a prior part. The last statement proves to be true that the ratio of $^{234}U/^{237}Np$ technogenic isotopes decreases in 50 times with 15-km distance from the source in the under-investigation groundwaters at the 'PA Mayak' site.

The dissolved organic substance has a certain effect on Am(III) and Cm(III) migration intensity in the under-investigation conditions. The metal-fulvic complexes including appreciable amounts of americium are mobile enough, though the last factor depends essentially on the environmental concentration conditions. Therefore, for Ac(III), it is necessary to take into account the transport of both carbonate and organic complexes in these ecosystems.

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