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Colloid Transport of Plutonium in the Far-Field of the Mayak Production Association, Russia

Alexander P. Novikov, Stepan N. Kalmykov, Satoshi Utsunomiya, Rodney C. Ewing, François Horreard, Alex Merkulov, Sue B. Clark, Vladimir V. Tkachev, Boris F. Myasoedov

Sorption of actinides, particularly plutonium, onto submicrometer-sized colloids increases their mobility, but these plutonium colloids are difficult to detect in the far-field. We identified actinides on colloids in the groundwater from the Mayak Production Association, Urals, Russia; at the source, the plutonium activity is ~1000 becquerels per liter. Plutonium activities are still 0.16 becquerels per liter at a distance of 3 kilometers, where 70 to 90 mole percent of the plutonium is sorbed onto colloids, confirming that colloids are responsible for the long-distance transport of plutonium. Nano-secondary ion mass spectrometry elemental maps reveal that amorphous iron oxide colloids adsorb Pu(IV) hydroxides or carbonates along with uranium carbonates.

Submicrometer-sized colloids, consisting of inorganic and/or organic compounds, occur at up to 10^17 particles per liter in groundwater and provide an important means of transporting elements with low solubilities, including the actinides (1–3). The stability of these colloids is a function of the composition of groundwater and the hydrologic conditions (4).

The formation of actinide pseudo-colloids, in which the actinide sorbs onto aquatic colloids, can stabilize actinides in natural waters and increase their concentrations by many orders of magnitude over the values expected from solubility calculations (2, 5). The association of Pu with colloids 25 to 450 nm in size has been observed 3.4 km from a source at Los Alamos National Laboratory (6). This migration distance is greater than modeled estimates (7). Similar transport has also been seen at the Savannah River Site (8). At Nevada Test Site, Pu has migrated 1.3 km in 30 years in groundwater by means of colloids with sizes of 7 nm to 1 μm (9). Model results imply that colloid-facilitated transport of actinides at Yucca Mountain could lead to as much as a 60-fold increase in the total effective dose equivalent to an exposed population (10).

Colloid-facilitated transport is likely the means for actinides’ long-distance transport in groundwater. Many previous studies have experimentally demonstrated adsorption of Pu onto a variety of minerals and mineral assemblage (11–13). However, little is known of the speciation of the actinides or the type of colloids with which they are associated, particularly during the transport in the far-field where there are many competing processes, such as desorption from the colloids and resorption onto minerals.

To understand the colloid-associated actinides and their long-distance transport in groundwater, we investigated Pu migration in the natural groundwater system at one of the most contaminated nuclear sites in the world: Mayak, Russia. Mayak is a nuclear waste reprocessing plant near Kyshtym, in the Southern Urals, Russia (14) (Fig. 1). Waste effluents containing Sr, Cs, Am, and Pu were discharged into Lake Karachai (15, 16); these were weakly alkaline NaNO₃ brine solutions with a pH of 7.9 to 9.3 and a salt concentration of 16 to 145 g/liter. The major dissolved ionic species were NO₃⁻ (11 to 78 g/liter), CH₃COO⁻ (0.6 to 20 g/liter), CO₃²⁻ (0.9 to 14 g/liter), SO₄²⁻ (0.12 to 1.3 g/liter), Na⁺ (6 to 32 g/liter), Cl⁻ (20 to 350 mg/liter), U(VI) (13 to 196 mg/liter), Cs⁺ (8 to 80 mg/liter), and
Mg\(^{2+}\) (8 to 69 mg/liter) (17). Lake Karachai is connected to the 55- to 100-m-thick groundwater zone, in which fluids flow through fractured Silurian and Devonian metavolcanic rocks with andesitic and basaltic composition (17). We completed systematic analyses of the composition and redox state of groundwaters and filtered samples, and we characterized the actinides associated with the colloids (18).

Because of the high concentration of NO\(_3^-\) in waste effluents, we used the presence of NO\(_3^-\) as a measure of the extent to which the contaminant plume had penetrated the groundwater system. The Pu radioactivity was ~4.8 becquerels (Bq/liter) at 0.05 km from the source, whereas it was ~0.029 Bq/liter at 4.0 km (Table 1), which is approximately equivalent to ~2.1 parts per trillion (ppt) and ~0.013 ppt, respectively, versus ~1000 Bq/liter (19) in the waste effluent. The redox potential, \(E_h\), of the groundwater was +50 to ~+480 mV, and the pH was ~6 to 8. Nitrate concentrations decreased as distance from the source increased, although at greater depths (~100 m) original waste effluents with relatively high concentration of Pu (0.16 Bq/liter) were present even 3.9 km from the source.

To understand stable chemical species of the actinides under the groundwater conditions, we constructed predominance diagrams for U and Pu species using thermodynamic calculation (20) with updated solubility data (21), based on the total concentrations of the groundwaters from the wells nearest to the source (Fig. 2, A and B) and from a well located 3.2 km away [well number 1, drilled in 1969 (1/69)] (Fig. 2, C and D). This analysis implies that \(\text{UO}_2\text{(CO}_3\text{)}_2^{2-}\) is the dominant species near the source, whereas \(\text{UO}_2\text{(CO}_3\text{)}_3^{3+}\) is present at well 1/69. However, the data (circles in Fig. 2, A and C) are close to the equilibrium boundary between these two U carbonate species. Thus, it is likely that both of these U(VI) carbonate species are dominant in the groundwater of Mayak, which is consistent with the oxidation state analysis (table S1). In addition, the U distribution on the colloidal matter for fractions of different sizes also indicates that 80 to 90\% of the U is present as a soluble species (Fig. 2E). Similarly, most of the Np (70 to 80\%) is present as a soluble Np(V) phase (Fig. 2E and table S1), most likely as NpO\(_2^{2+}\), as anticipated from the stability diagram (fig. S1).

The stability diagrams (Fig. 2, B and D) show that the total groundwater compositions near the source (solid square) and at the well 1/69 (open square) are in the region of solid PuO\(_2\) and the Pu distribution on the colloidal matter for fractions of different sizes also indicates that 80 to 90\% of the Pu is present as a soluble species (Fig. 2E) shows that ~30 and ~10\% of Pu is present as a soluble species in well 63/68 (near the source) and 1/69, respectively, which indicates that the actual Pu concentration in the “solution” was lower than the total Pu concentration in the groundwater. Because particles smaller than ~1 nm (the size of the 3-kD filter) were counted as a soluble species, a part of the Pu associated with the colloids, which are <1 nm, may have been counted as part of the soluble fraction. The

**Table 1.** Concentration of actinides in the groundwaters from the Mayak region, Russia. The well index represents the well number followed by the depth (m) labeled with the numbers in (km).

<table>
<thead>
<tr>
<th>Well index</th>
<th>Distance (km)</th>
<th>Depth (m)</th>
<th>(E_h) (mV)</th>
<th>pH</th>
<th>I.C. (ppm)</th>
<th>NO(_3^-) (ppm)</th>
<th>(\text{Pu}^{239,240}) (Bq/liter)</th>
<th>(\text{Am}^{244}) (Bq/liter)</th>
<th>(\text{Np}^{237}) (Bq/liter)</th>
<th>(\text{U}^{238}) (Bq/liter)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Source</td>
<td>0.0</td>
<td></td>
<td></td>
<td>5.9</td>
<td>4,760</td>
<td>45,000</td>
<td>1,000</td>
<td>420</td>
<td>41</td>
<td>25</td>
</tr>
<tr>
<td>41/77</td>
<td>0.05</td>
<td>20</td>
<td>+480</td>
<td>6.0</td>
<td>1,220</td>
<td>45,000</td>
<td>4.8</td>
<td>0.91</td>
<td>0.14</td>
<td>n.d.</td>
</tr>
<tr>
<td>3/68</td>
<td>0.95</td>
<td>45</td>
<td>+50</td>
<td>6.0</td>
<td>1,220</td>
<td>45,000</td>
<td>2.8</td>
<td>0.34</td>
<td>0.12</td>
<td>n.d.</td>
</tr>
<tr>
<td>10/68</td>
<td>1.5</td>
<td>60</td>
<td>+390</td>
<td>6.6</td>
<td>1,830</td>
<td>52,000</td>
<td>0.86</td>
<td>4.75</td>
<td>9.1</td>
<td>24</td>
</tr>
<tr>
<td>65/68</td>
<td>1.75</td>
<td>60</td>
<td>+300</td>
<td>7.5</td>
<td>28,000</td>
<td>52,000</td>
<td>0.46</td>
<td>0.72</td>
<td>2.8</td>
<td>0.3</td>
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<tr>
<td>3/68</td>
<td>1.9</td>
<td>60</td>
<td>+350</td>
<td>7.1</td>
<td>1,160</td>
<td>32,000</td>
<td>1.62</td>
<td>0.29</td>
<td>10.4</td>
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<tr>
<td>9/68</td>
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<td>60</td>
<td>+310</td>
<td>7.6</td>
<td>952</td>
<td>27,100</td>
<td>0.036</td>
<td>1.10</td>
<td>5.8</td>
<td>26</td>
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<tr>
<td>176/94</td>
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<td>27</td>
<td>+90</td>
<td>7.3</td>
<td>251</td>
<td>3,910</td>
<td>0.8</td>
<td>0.11</td>
<td>0.78</td>
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</tr>
<tr>
<td>1/69</td>
<td>3.2</td>
<td>44</td>
<td>+100</td>
<td>7.9</td>
<td>159</td>
<td>21</td>
<td>0.089</td>
<td>0.15</td>
<td>2.1</td>
<td>0.26</td>
</tr>
<tr>
<td>14/68</td>
<td>3.9</td>
<td>100</td>
<td>+100</td>
<td>7.9</td>
<td>200</td>
<td>498</td>
<td>0.16</td>
<td>0.087</td>
<td>2.5</td>
<td>19</td>
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<tr>
<td>209/70</td>
<td>4.0</td>
<td>40</td>
<td>+50</td>
<td>8.12</td>
<td>136</td>
<td>6.5</td>
<td>0.029</td>
<td>0.08</td>
<td>0.03</td>
<td>0.02</td>
</tr>
</tbody>
</table>

**Fig. 1.** Map of the study area. The locality map and stratigraphy are modifications of those in (17). The Mayak site covers ~160 km\(^2\) (17). Red points labeled with the numbers are wells. The numbered basins are natural or man-made reservoirs for nuclear waste fluids.
actual Pu concentration in the groundwater could have been even lower than the percentage shown in Fig. 2E. Thus, the data points for the actual soluble Pu concentrations should be plotted at lower values in the diagram of Fig. 2, B and D, as indicated by the arrows. In the event that an intrinsic Pu(IV) phase precipitates from solution, the Pu concentrations in solution (data points in Fig. 2, B and D) will also be shifted downward to the stability field of aqueous plutonium hydroxide Pu(OH)₄(aq) (the dashed arrows).

A dominant fraction of Pu(OH)₄(aq) is not inconsistent with the oxidation state analysis that reveals a predominance of Pu(IV), although it is also possible that different chemical Pu(IV) species are incorporated into aquatic colloids. In addition, 70 to 90% of Pu was associated with the colloidal fraction on 3- and 10-kD filters (the size range of 1 to 15 nm). The ratio of Pu associated with colloids to soluble species (Fig. 2F) was nearly constant (~2.2) within 2.15 km of the source, regardless of the Pu concentration, and the values became higher (>5) at distances of >2.5 km (Fig. 2F) as well as U partitioning (Fig. 2G). This result suggests that Pu was partitioned between colloids and soluble species within 2.5 km, whereas at >2.5 km, the excess fraction of Pu-bearing colloids is transported in the groundwater system, ascribed to a disequilibrium derived from the slow desorption of Pu from the colloids or to the irreversible incorporation of trace Pu into aquatic colloids.

Electron microscopy analysis of the colloid fraction from well 1/69 revealed a variety of phases (Fig. 3A). Spherical Fe oxide and Fe hydroxide are the most abundant phases, and they are associated with minor Si and Ca that range in size from a few nanometers to 100 nm across, forming aggregates up to several micrometers in size (Fig. 3, B and C). Based on the electron diffraction pattern, the Fe oxide/Fe hydroxide is characterized to be an amorphous Fe hydroxide (HFO). Amorphous HFO commonly occurs in soils and is known to be an efficient adsorbent of toxic metals (23). The other identified phases include clays and calcite; rutile, hematite, barite, and rancieite; and monazite, in decreasing order of abundance. Nano–secondary ion mass spectrometry (SIMS) elemental maps for the colloids from well 1/69 reveal that some Al and Mn are also associated with the Fe (Fig. 3D). The approximate atomic ratios of Al to Fe and Mn to Fe are ~0.003 and ~0.004, respectively. The amount of associated Ca is not less than the amount of Al and Mn but is at the same level as in the mixture of HFO (Fig. 3C). Thus, this aggregate of colloids can be characterized as amorphous HFO adsorbing less than 1 atomic % of Al and Mn.

The Pu map (Fig. 3D) is nearly the same as that of the U, which is associated with the Fe oxide. Semiquantitatively, the atomic ratio of U to Fe is ~0.0004, and the ratio of Pu to U is ~0.03, indicating that amorphous HFO is a pseudo-colloid sorbing both the Pu and U. Based on the thermodynamic calculations for the expected, dominant Pu and U species, Pu(OH)₄(aq) occurs with UO₂(CO₃)₃⁻ and to a lesser extent with UO₂(CO₃)₂⁻, subsequently sorbing onto the amorphous HFO. Because the SIMS analysis causes the destruction of the sample, there are no crystallographic data available for the same HFO grain for which Pu was detected by nano-SIMS and examined by electron microscopy. Elemental mapping of the other colloidal material showed that U is predominantly adsorbed onto amorphous HFO and to a lesser extent onto rancieite [(Ca,Mn)Mn₄O₉·3H₂O] and hematite (Fe₂O₃) (fig. S2). We did not find any intrinsic Pu(IV) colloids nor any actinide adsorption onto the other colloidal phases, including clays, calcite, rutile, barite, and monazite in the sample from well 1/69. These results are consistent with experiments that have reported a higher adsorption coefficient for Pu onto Fe oxide colloids than onto montmorillonite and silica (24). Additionally, the high ionic strength of this system may inhibit adsorption onto inorganic colloids, with the exception of Fe oxide (24). At distances greater than 2.5 km, the desorption process is anticipated to occur slowly, because the previous experiments revealed that the Pu desorption process from a hematite surface is considerably slower than the adsorption rate (24). Based on the Pu adsorption onto amorphous HFO in this system, most Pu(IV) in our oxidation analysis (table S1) may be the result of reduction of Pu(V) to Pu(IV) after adsorption.

![Fig. 2. Stable species of actinides and evidence of actinides bound to colloids.](image-url)

**Fig. 2.** Stable species of actinides and evidence of actinides bound to colloids. (A and B) Thermodynamic stability diagrams of U and Pu species under the conditions near Karachi Lake (well 41/77). (C and D) Thermodynamic stability diagram of U and Pu species under the conditions at well 1/69 located 3.9 km from the source at a depth of 44 m. Total concentrations in the groundwater are plotted as circles (U) and squares (Pu). Solid symbols show data near the source [(A) and (B)], and open symbols show the data at well 1/69 [(C) and (D)]. Roman and italic fonts represent solid and aqueous species, respectively. The arrows indicate the transition of solution composition that occurs when Pu precipitates as intrinsic or aquatic colloids or is sorbed onto pseudo-colloids. For these
onto Fe oxide (11, 12). In addition, the high concentration of dissolved organic carbon (<20 g/liter of CH₃COO⁻) near the source may result in the reduction of Pu(V) into Pu(IV) in solution, as reported in (12, 22). Even inorganic colloids can be coated by humic acid, forming pseudo-colloids, which can sorb the hydrolyzed species more strongly than simple inorganic colloids (22).

As compared with other minerals that may sorb actinides, the Fe oxides have a high zero point of charge (ZPC): 6.5 for Fe₂O₃ and 7.8 for α-FeOOH versus 4.6 for kaolinite, 2.5 for montmorillonite, 2 to 2.4 for feldspars, and 2.0 for SiO₂ (25). In particular, the ZPC for amorphous Fe(OH)₃ is 8.5 (25), and the value should be the most appropriate for the HFO we found because of the amorphous structure of the Fe oxide/hydroxide. The high ZPC must result in the positive charge on the surface of HFO under the conditions in the Mayak system, the negatively charged Pu species can be sorbed by HFO, as could the U carbonate species. Ultimately, the polymerization of carbonate species might result in Pu association with U. Although further analysis is required, we conclude that both Pu and U species are adsorbed similarly onto the HFO surface.

The subsurface migration of Pu from Lake Karachai over more than 4 km within ~55 years after discharge is comparable to the transport rate seen at the Nevada Test Site (1.3 km/30 years minimum) (9). Up until now, there has been an argument over which colloidal phase carries Pu and how they associate. Our evidence of Pu sorption onto the specific colloidal phase is applicable to systems that are dominated by U under oxidizing conditions, such as the proposed repository at Yucca Mountain in Nevada. Because of differences in physicochemical conditions, site-specific investigations of actinide colloids in the far-field are necessary at each potential nuclear waste repository site.

References and Notes
14. Mayak produced Pu for nuclear weapons by reprocessing spent nuclear fuel. After more than 50 years, there have been major episodes of contamination of the surrounding area—Chelyabinsk, Kurgan, and Sverdlovsk (25, 26).
18. Materials and methods are available as supporting material on Science Online.
20. The Geochemist’s Workbench, Release 3.1; RockWare.
29. The work was supported by The Office of Basic Energy Sciences of the U.S. Department of Energy (DE-FG02-04ER15582 and DE-FG03-01ER15168), Russian Academy of Sciences (RDO-20003-SC14 and RGO-20012-RR04), and by Russian Basic Research Foundation (05-03-33028). We thank W. Halsey (Lawrence Livermore National Laboratory) for useful discussion.

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Materials and Methods
Fig. S1 to S3
Table S1
References
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Fig. 3. Direct evidence of Pu adsorption onto amorphous Fe hydroxide. (A) Scanning electron micrograph of typical colloids from well 1/69. Many spherical particles were observed with a size of <1 μm. (B) High-angle annular dark-field scanning transmission electron microscopy image of the spherical colloids. Electron diffraction patterns from these particles indicate that they are amorphous. (C) Energy-dispersive x-ray spectrum from the spherical particles shows that Fe is a major constituent associated with trace amounts of Si and Ca, a.u., arbitrary units. (D) Nano-SIMS maps. Because the contrast of these maps has been enhanced to show the distribution clearly, the intensity of the color in the chemical maps corresponds to the relative concentration for each element but cannot be used to compare one element to another.

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