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Behaviour of plutonium in the environment

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Plutonium is one of the most toxic components of spent nuclear fuel and of nuclear wastes, which is characterized by very complex chemical behaviour both in engineering processes and under environmental conditions. As a result of the human activities, plutonium is released to the environment and its speciation depends, to a large extent, on the source and release scenario and also on the geochemical conditions. The most recent data about various sources of plutonium in the environment and its speciation are reviewed. The recent trends in the description of one of the most important processes in plutonium migration, *i.e.*, its sorption onto components of soils, rocks, colloidal particles of various origin, natural organic matter, *etc.*, are discussed.
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I. Introduction

Human activity in the field of nuclear weapon development, testing and peaceful uses of nuclear power has led to massive release of man-made radionuclides to the environment.[1] The major source of widespread contamination with radionuclides including actinides were atmospheric and space nuclear weapon tests (so-called global fallout), which reached a maximum in the beginning of the 1960s. The intensity of this fallout began to decrease after the comprehensive prohibition of atmospheric nuclear testing in 1963.[2] Along with nuclear weapons testing, important regional sources of man-made radionuclides in the environment are

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legal and accidental releases from nuclear fuel cycle facilities.

Currently, many countries have adopted programmes for the remediation of previously contaminated sites and the development of engineered barriers preventing further spread of radionuclides from contaminated areas. Engineering principles used for this purpose must be based on the specific behaviour of particular radionuclides and their physicochemical speciation. An example of these engineering principles is the programme of remediation at the Rocky Flats Plant (Colorado, USA).[3] Data on physicochemical speciation of plutonium in contaminated soils was used to develop efficient remediation measures. Based on EXAFS studies of contaminated soils, it was shown that plutonium existed in PuO_2-like particles, which exhibited extremely high kinetic stability. Hence, the only feasible remediation method was the mechanical collection of the upper layer of soils, which involved these particles. Reagent treatment would have failed to provide the necessary clean-up result. Thus, the Rocky Flats Plant was demolished and the contaminated site was remediated within 11 years rather than 70 years as scheduled spending \$7 billion rather than \$37 billion.

Data on physicochemical speciation of radionuclides are necessary not only for the development of methods for remediation of previously contaminated areas, but also for the justification of long-term safety of geological repositories for radioactive wastes (RW) and spent nuclear fuel (SNF). The release of radionuclides to the environment from these repositories will eventually occur if the engineered multi-barrier system (system of engineered and geological barriers) fails. The geologic environment is designed to act as a secondary containment system.

Evidently, the migration behaviour of radionuclides, their bioavailability, and, accordingly, potential hazard for humans are dictated by physicochemical speciation of radionuclides in the environment. Determination of physicochemical speciation of radionuclides in the environment is difficult due to their rather low concentrations, which restricts the use of many instrumental methods for studying their speciation. In Russia, very low permissible concentrations in natural waters are mandated because of the high radiotoxicity of plutonium. Thus, the intervention level for ^{239}Pu, *i.e.*, its maximum permissible concentration in natural waters[4] is $0.55\ Bq\ kg^{-1}$, which corresponds to 1×10^{-12} M.

In contrast to the physicochemical speciation of monomeric plutonium that exists at low concentrations in the environment, plutonium can also exist in so called 'hot' particles, which are formed under high-temperature conditions and exhibit high kinetic stability**.** A specific feature of the behaviour of plutonium is that it can form extremely poorly soluble crystalline oxides (and mixed oxides with other actinides) at high temperatures (see, for example, Ref. 5). Plutonium oxide particles can form different sizes including micrometre and submicrometre particles as a result of nuclear explosions, core disruptive accidents, fires, explosions and other high-temperature impacts. The environmental behaviour of these 'hot' particles is controlled by sources of their origin, *i.e.*, their formation scenarios: temperature conditions, presence of oxygen, presence of other elements, *etc*. Thus, in 'hot' particles, radionuclides occur in extremely kinetically stable physicochemical forms far from thermodynamic equilibrium with the environment. Extremely slow dissolution of these 'hot' particles can proceed on contact with water.[6]

Nuclear physics properties of plutonium isotopes and features of their behaviour in aqueous solutions including possible oxidation states, complexation reactions with different ligands, formation of poorly soluble compounds and intrinsic colloidal particles, *etc*., were described previously in several reviews.[7–9] In this work we restricted ourselves to the systematization of data on the behaviour of plutonium in the environment including general regularities in its release, changes in physicochemical speciation, and behaviour at the mineral–natural water interface.

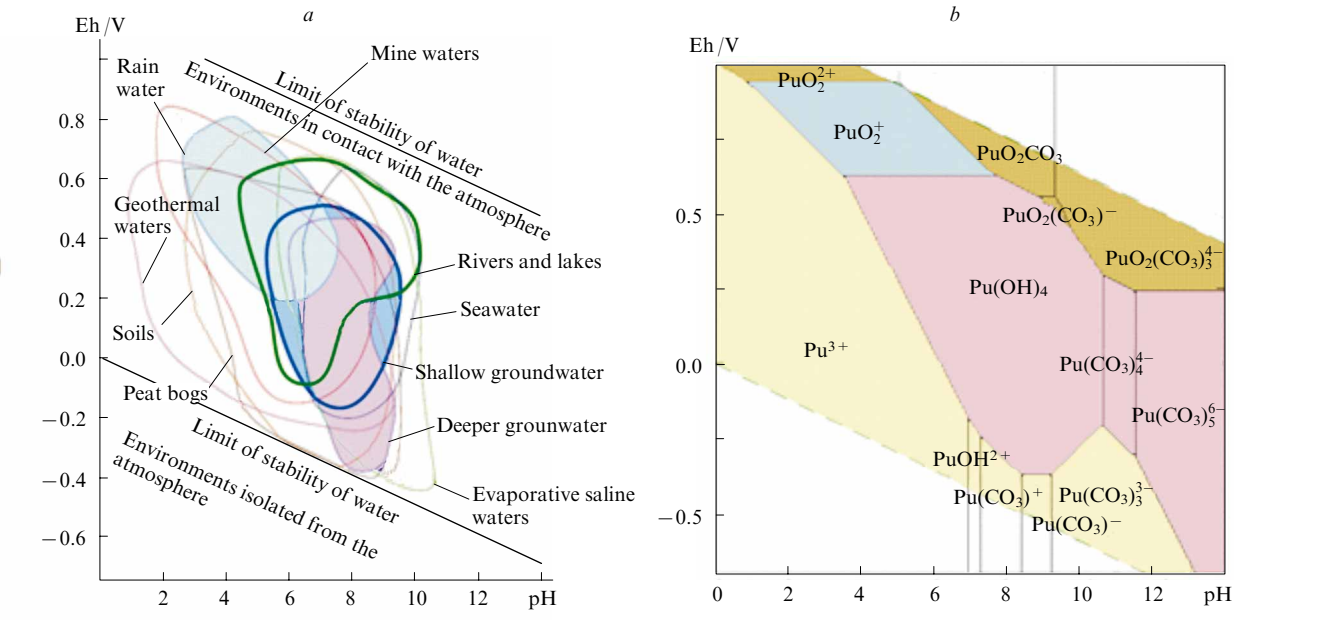


Figure 1. Redox conditions in different environmental materials (*a*)[10] and Pourbaix diagram for plutonium (*b*). (*b*) [Pu] = 10^{-12} mol litre^{-1}, log[p(CO_2)] = −3.5.

Under environmental condition, plutonium can exist in four oxidation states: Pu(III), Pu(IV), Pu(V) and Pu(VI), sometimes simultaneously. Figure 1 shows the different oxidation states of plutonium in water as a function of pH and redox potential (Eh). The oxidation state of plutonium controls its solubility and reactivity, with Pu(VI) and Pu(V) being more soluble in water than Pu(IV) and Pu(III). In addition, plutonium can easily change its oxidation state.

II. Release of plutonium to the environment

As a result of nuclear weapon and nuclear energy production, plutonium has been released into the environment and has contaminated both the global and local (regional) environment. The behaviour of plutonium is initially controlled by both the source composition and surrounding geology and hydrology. In this Section, we will give brief characteristics of several highlighted areas contaminated with plutonium and summarize the data on its physicochemical speciation and migration behaviour.

II.1. Plutonium contamination of the oceans

As a result of human activity, man-made radionuclides including plutonium have got into the oceans, either directly or through river runoff. These radionuclides could have come from global fallout after nuclear weapon tests (both global and regional), discharge of radioactive wastes to the hydrosphere, accidents on ships, aircrafts and satellites with nuclear power units aboard, and accidents at nuclear power plants and nuclear fuel cycle facilities.

A previously common practice, which was in use in the majority of nuclear countries, was to discharge radioactive waste to the seas and rivers. Substantial contamination of the marine environment was caused by the operation of West-European plants reprocessing spent nuclear fuel: Sellafield and Dounreay (UK) and La Hague plant (France). The most significant releases were from the Sellafield plant, which has performed routine discharge of low-level liquid wastes by pipelines to the Irish Sea since 1951.[11] Figure 2 shows the intensity of discharge with time. Most of the discharge occurred from the mid-1960s through the mid-1980s. The further spread of radionuclides from the Irish Sea was determined by currents, resulting in the initial radionuclide discharges to reach the Baltic and the Barents Seas.[12]

A significant number of published works have investigated the concentrations, migration and physicochemical speciation of man-made radionuclides including plutonium isotopes in the Irish Sea as a result of releases from Sellafield. For example, Nelson and Lovett[14] determined the concentration of plutonium and its oxidation states in samples of sea water at the coastal waters and the open part of the Irish Sea. Using micro- and ultramicrofiltration methods, they demonstrated that the major fraction of plutonium is bound to particles larger than 210 nm, in which plutonium occurs in the reduced form, with oxidation numbers +3 or +4. Dissolved plutonium not bound to particles (fraction that passed through filters with pore diameter of 210 and 25 nm), was 'oxidized' plutonium: Pu(V)/Pu(VI).

Analogous results on the partitioning of oxidized and reduced forms of plutonium in sea water were obtained in other works for the Irish and other seas.[11, 15, 16] Irrespective of temperature (0–25 °C), the source, and physicochemical form in which plutonium was released to the marine environment, it was slowly oxidized and stabilized in the dissolved form as Pu(V,VI), whereas plutonium bound to colloidal and suspended particles was in the reduced form, Pu(III,IV). Depending on the original concentration, the distribution of plutonium between the dissolved oxidized and colloidal reduced forms can vary.

The fractionation and speciation of plutonium in bottom sediments from the Ravenglass Estuary in the north-eastern Irish Sea were studied by Lucey *et al.*[17] using sequential extraction method. The vertical distribution profile of plutonium in bottom sediments exhibits an increase in its total concentration with depth, which closely correlates with the intensity of its release in this region (Fig. 3). It was demonstrated that in the deeper sediments, plutonium mostly occurs in the exchangeable/readily-oxidizable and acid-soluble fractions. The authors explain this by the fact that at lower depths, plutonium is mostly bound to readily oxidizable sulfide minerals. In the surface layer, the proportion of plutonium in the exchangeable/oxidizable fraction decreases, which is due to a change in the redox

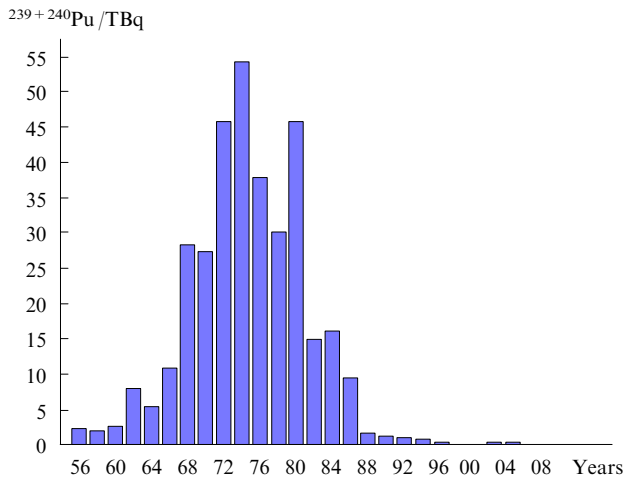


Figure 2. Dynamics of the discharge of plutonium from the Sellafield plant (UK) in 1952–012. [11,13]

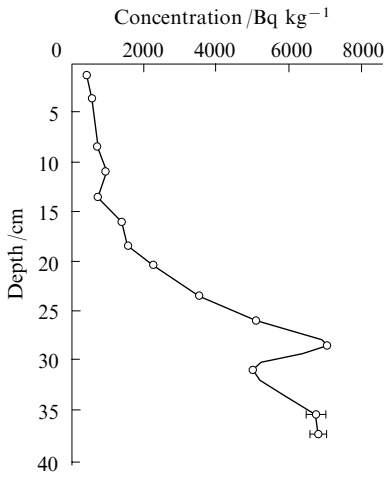


Figure 3. Distribution profile of ^{239,240}Pu in bottom sediments of Ravenglass estuary (Sellafield).[17]

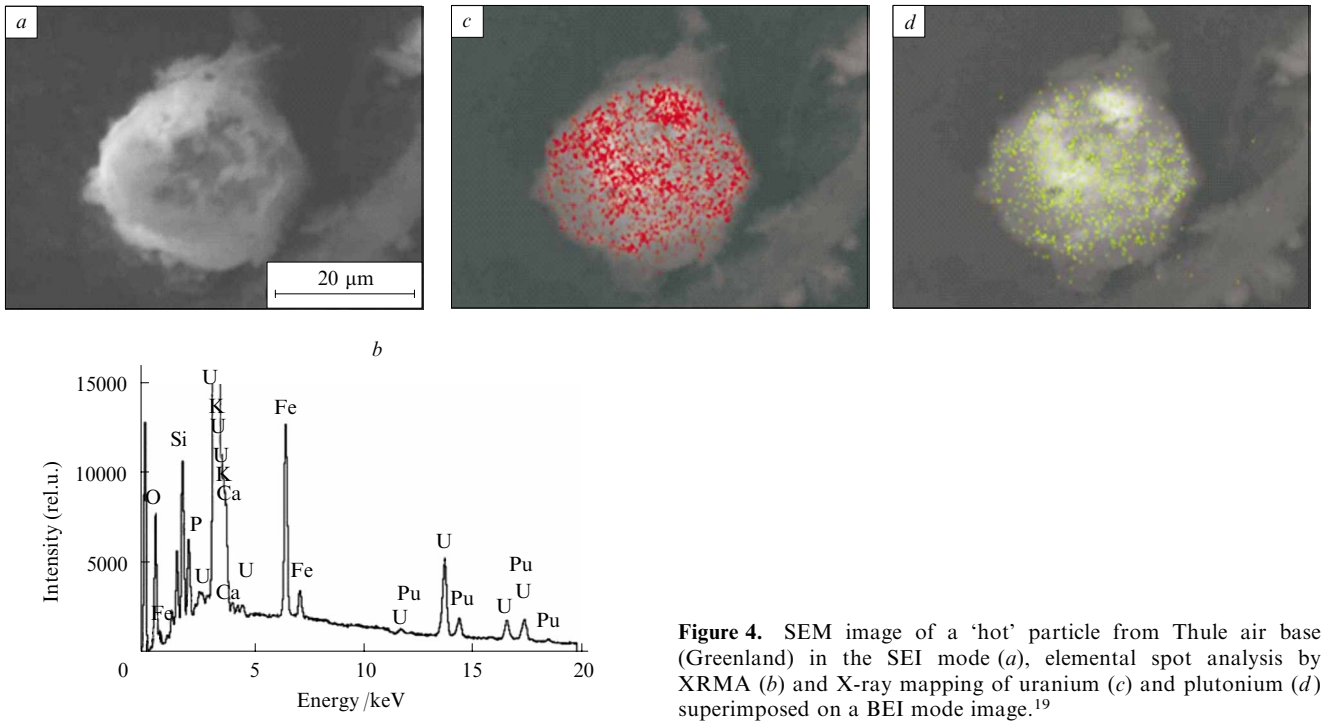


Figure 4. SEM image of a 'hot' particle from Thule air base (Greenland) in the SEI mode (*a*), elemental spot analysis by XRMA (*b*) and X-ray mapping of uranium (*c*) and plutonium (*d*) superimposed on a BEI mode image.[19]

potential, Eh, from 0 to −400 mV with depth. The profile of plutonium occurring in the oxidizable fraction correlated with the concentration of organic substances in the sediment. However, several years later, it was found[18] that addition of citrates, which inhibit possible adsorption of plutonium during sequential extraction, substantially affects the outcome of its fractionation. As a result, the authors assume that in the previous data, the proportion of plutonium occurring in the exchangeable/readily-oxidizable and acid-soluble fractions may have been underestimated.

In 1968, an American aircraft carrying four plutonium-containing bombs crashed near the air base of Thule in Greenland. As a result of the rupture of the weapons, a kilogram quantity of plutonium was dispersed over a distance of several kilometres in the snow pack, ocean water and underlying seabed sediments. Most of the plutonium was removed by mechanical collection of the munitions debris. In several works, both the composition of plutonium-containing particles[19] and the partitioning and speciation of plutonium in seawater[16] were studied. In the region of the accident, Lind *et al.*[19] found plutonium-containing particles with a size of 20–40 μm. XRMA with SEM studies showed that uranium and plutonium were homogeneously distributed throughout the particles, which also contained Si, Fe and Al (Fig. 4). A XANES study showed that plutonium occurred in particles as a mixture of Pu(III) and Pu(IV), whereas plutonium in sea water was dissolved and occurred in the oxidized form Pu(V)/Pu(VI).[16] The distribution of plutonium was non-uniform: its concentration at a depth of 100 to 177 m was higher than in the surface water.

A similar non-uniform depth distribution of plutonium was repeatedly demonstrated for other regions of the Pacific Ocean (Fig. 5). Different hypotheses have been suggested to explain a maximum in the distribution of plutonium at the depth of about 100 m, among which the main explanations are those assuming vertical flows of plutonium-containing particles, which are concentrated in layers according to their mass and density, and plutonium uptake by phytoplankton in this layer.[11,16,20]

In the Soviet Union, the Kara and Barents Seas and Far East seas were used for the disposal of some types of RW from military and civil atomic fleet.[21,22] These were mostly solid RW in steel containers including reactors with SNF dumped into the seas. In addition, significant amounts of RW were dumped in shallow bays of Novaya Zemlya.[23]

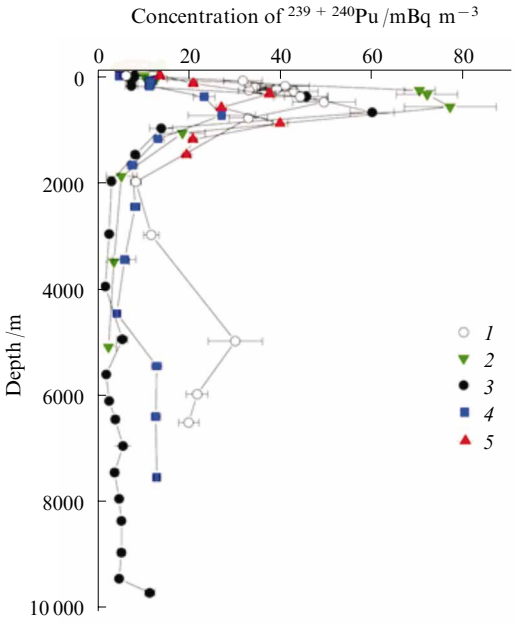


Figure 5. $^{239+240}$Pu depth profiles in seawater from North-east (*1*), Central North (*2*) and North-west (*3*–*5*) Pacific Ocean.[20] (*1*) Aleutian Trench (1981), (*2*) GEOSECS station (1973), (*3*) Bonin Trench (1984), (*4*) Japan Trench (1984), (*5*) Sagami Bay (1992).

Data about release of plutonium as a result of container leaks are quite inconsistent,[24,25] but the amount of Pu contamination in sea water is very low.

II.2. Plutonium contamination on land

As a result of the accident at the Chernobyl nuclear power plant in the Soviet Union in April 1986, large quantities of radionuclides were released to the environment, which was a sub-regional source of radionuclide contamination. A specific feature of this accident was an explosion culminating in the destruction of the reactor core. As a result, a substantial fraction of non-volatile radionuclides were released into the atmosphere as 'hot' particles, which were detected repeatedly.[26–28] The composition of 'hot' particles was determined by the composition of high burnup nuclear fuel, which contained many fission products including ruthenium and caesium.[29] Most of the 'hot' particles were 1–2 μm in size (Fig. 6).

Soils from a 30-km zone surrounding the Chernobyl nuclear power plant were studied over a 10-year period after the accident. Most of plutonium in sandy and podzolic soils was located in the top surface layer, whereas vertical migration of plutonium to a depth of 10–15 cm was observed in peat soils.[30] The results of sequential extraction demonstrated that plutonium was released upon slow dissolution of 'hot' particles predominantly bound to organic substance within the peat soils.

Levchuk *et al.*[31] studied the migration of plutonium from a trench in the Red Forest (5 km from the Chernobyl nuclear power plant) with a depth of 2–3 m and a length of 70 m, in which the mostly contaminated upper layer of soil and residues of trees were placed. Plutonium was found in groundwater at significant distances from the trench; its maximum concentration was observed at a distance of 10 m. By the ultrfiltration method, it was demonstrated that a large part of plutonium in groundwater was bound to low-molecular-mass organic natural compounds (< 1 kDa) such as humic and fulvic acids. A correlation between the plutonium in the solution and the total organic carbon concentration was found.

Low concentrations of plutonium ($\sim 10^{-2}$ Bq litre^{-1}) have also been detected in groundwater collected from wells adjacent to and downgradient from nuclear tests at the Nuclear Nevada Security Site (NNSS, formally the Nevada Test Site), NV, USA.[32,33] The NNSS was the location of over 800 underground nuclear tests between 1956 and 1992 and it is estimated that 3.1×10^{16} Bq of plutonium remains underground.[34] Nuclear tests were detonated in a variety of geologic environments, rhyolitic tuff, alluvium, granite and carbonate, both above and below the groundwater table. Kersting *et al.*[32] measured plutonium isotope ratios in groundwater to identify its source. The plutonium in two different aquifers was shown to originate from a nuclear test located 1.3 km up-gradient.[32] Over 95% of Pu in a groundwater well was associated with the colloidal fraction, which consisted of clays and zeolites (Fig. 7, ER-205 wells). In addition, groundwaters for three additional groundwater wells were analyzed and over 90% of plutonium detected in these samples was also associated with the colloidal fraction (see Fig. 7). In all cases where the plutonium was associated with colloidal fraction of the groundwater, the groundwater had a pH around 8 and low ionic strength.

In contrast to the colloid-associated plutonium observed in many wells of the NNSS, vadose zone water collected in a tunnel system had most of the plutonium in the aqueous fraction rather than in the colloidal fraction (see Fig. 7).[35] Zhao *et al.*[35] showed that over 70% of the plutonium was complexed with high concentrations of dissolved organic matter and not associated with the clays and zeolites in the colloidal fraction of the groundwater. The unusually high organic content in the vadose zone water (15–19 mg C litre^{-1} *versus* 0.2 mg C litre^{-1} from local springs) is caused by anthropogenic mining activity.

One of the largest Russian radiochemical facilities is the 'Mayak' Production Association founded in 1947 for the production of weapon-grade plutonium. The environmental situation at the site of 'Mayak' is complex, because there have been several accidents in the production facilities resulting in the discharge of RW to open reservoirs. The most contaminated reservoirs are V-9 reservoir (Karachay Lake) and V-17 reservoir (Staroe Boloto). According to the results of the inspection in 2002, all components of the open part of V-9 (water, silts and loams from reservoir bed) contain approximately 30 million Ci of β-emitters and 1 million Ci of α-emitters including plutonium.[36,37] Most of radionuclides are found in silts and loams of the reservoir bed. During the operating time, a layer of so-called techno-

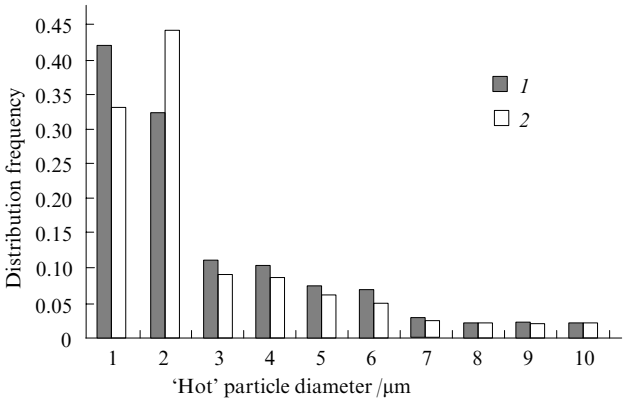


Figure 6. Size distribution of 'hot' particles in the region of the Chernobyl nuclear power plant.[29]
Data of 1987 (*1*) and 1994 (*2*).

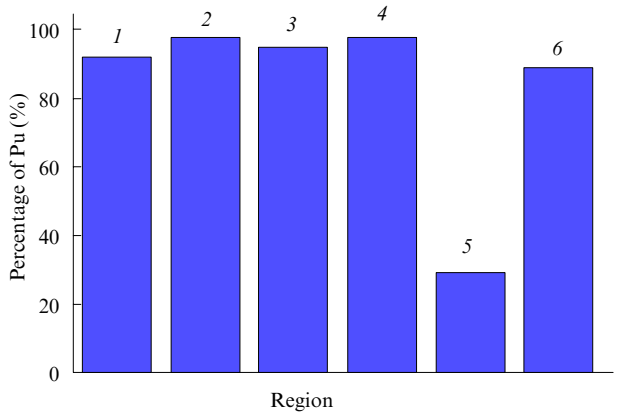


Figure 7. Percentage of plutonium in the colloidal fraction in groundwater samples from different wells at the NNSS.[33]
Reagion: (*1*) ER20-5#1, (*2*) ER20-5#3, (*3*) Cheshire, (*4*) Dalhart, (*5*) Tunnels, (*6*) Chancellor.

genic silts appeared in the reservoir; these are hydroxide and bicarbonate compounds of metals (aluminium, iron and, to a lesser extent, manganese and others) with some fraction of organic substance, primary lake silts and a sand fraction of mostly technogenic nature (perlite pulps). The concentration of ^{239,240}Pu in these silts is about 10^7-10^8 Bq kg^{-1} dry mass. Water in the Karachay Lake has high salt content (16–145 g litre^{-1}) and pH of 7.9 to 9.3.[38] Stukalov *et al.*[39] carried out dynamic experiments on the desorption of radionuclides from technogenic silts into natural groundwater and water enriched with sodium nitrate. It was demonstrated that, irrespective of the desorbing solution, plutonium exhibits extremely low desorption, which is indicative of strong retention of plutonium in silts. However, on washing the silts, radionuclides can be washed out within the colloidal fraction. In particular, plutonium can be washed out within finely dispersed particles of size > 10 nm.

These results were confirmed by Novikov *et al.*[38] It was found that plutonium can migrate over significant distances from the Karachay Lake with ground waters. Thus, plutonium concentration of 0.1 Bq litre^{-1} was found at a distance of 4 km from the source. Groundwaters in this region are characterized by oxidizing values of Eh in the range of 50–480 mV and pH in the range of 6–8. It was found that 70%–90% of plutonium is bound to colloidal particles with a size of < 15 nm. Using a combination of transmission electron microscopy (TEM) and secondary ion mass spectrometry (SIMS), it was found that plutonium is mostly bound to colloidal particles of amorphous ferrihydrite (Fig. 8).

The results of sequential extraction[40] of colloidal particles from groundwaters of the Karachay contaminated area also indicate that plutonium occurs in the poorly soluble form predominantly bound to the fraction of amorphous iron oxides.

The V-17 reservoir was brought into service in 1949.[41] The first liquid radioactive wastes were discharged into a natural ravine at the Karachay Lake, and then, after damming the ravine in 1952 and 1954, a permanent repository was formed. The total β-activity of radionuclides currently stored in the reservoir is ~1.2 million Ci. Like the V-9 reservoir, the V-17 reservoir has a high salt content, which is mostly due to sodium nitrate, and pH of 7.5–9, and radionuclides mostly occur in silts. Experiments on desorption of radionuclides from technogenic silts into natural groundwater and water enriched with sodium nitrate also showed extremely low desorption of plutonium.[42] In spite of the difficulty of determination of physicochemical speciation of plutonium, Vlasova *et al.*[43] found a single plutonium-containing microparticle, which contained, along with Pu and O, impurities of Si, Al, Mg, Fe, P, and Cl (Fig. 9). The complexity of the Pu-laden wastes discharged from V-17 and V-9 reservoirs may imply the existence of multiple plutonium species such as hot

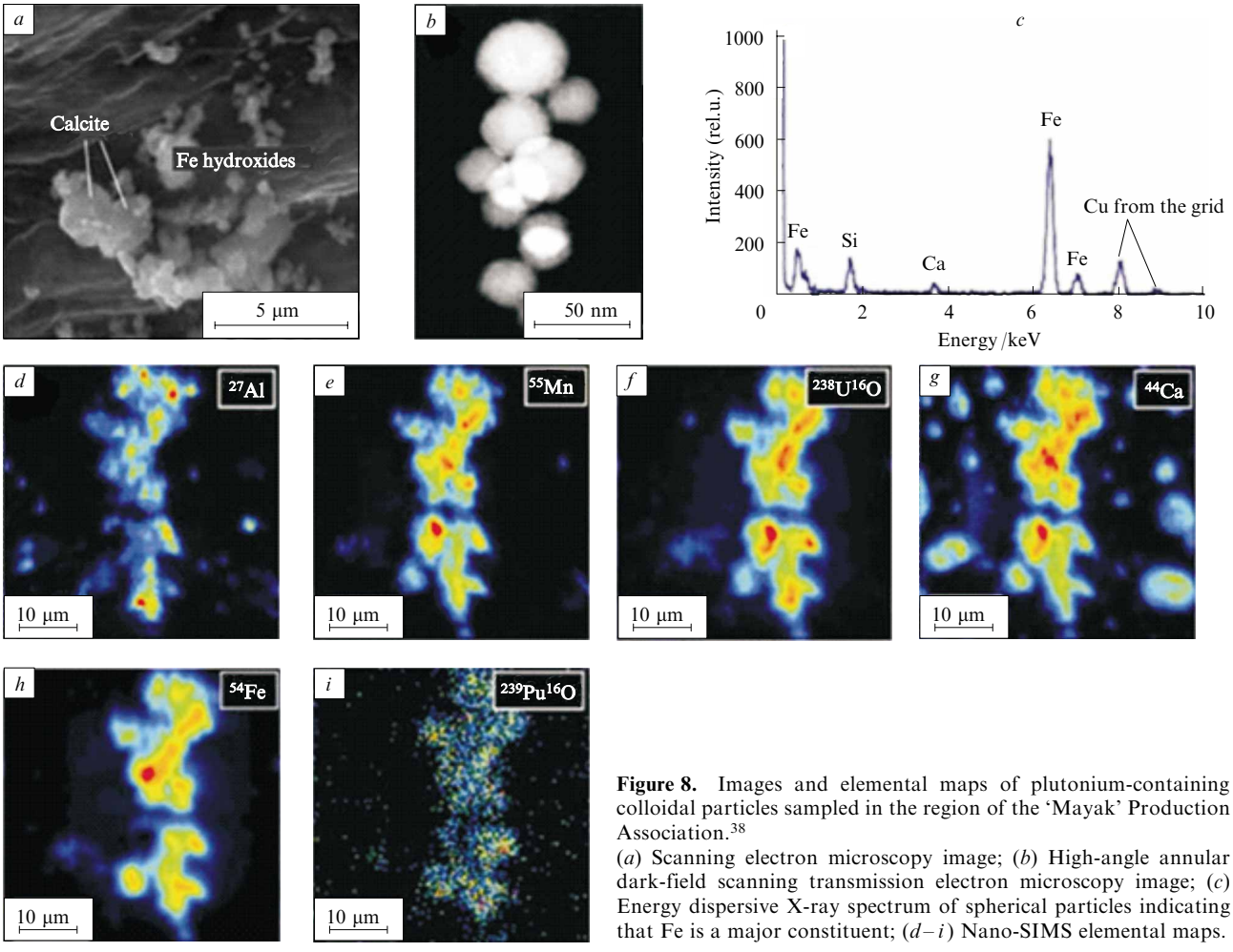


Figure 8. Images and elemental maps of plutonium-containing colloidal particles sampled in the region of the 'Mayak' Production Association.[38]
(*a*) Scanning electron microscopy image; (*b*) High-angle annular dark-field scanning transmission electron microscopy image; (*c*) Energy dispersive X-ray spectrum of spherical particles indicating that Fe is a major constituent; (*d*–*i*) Nano-SIMS elemental maps.

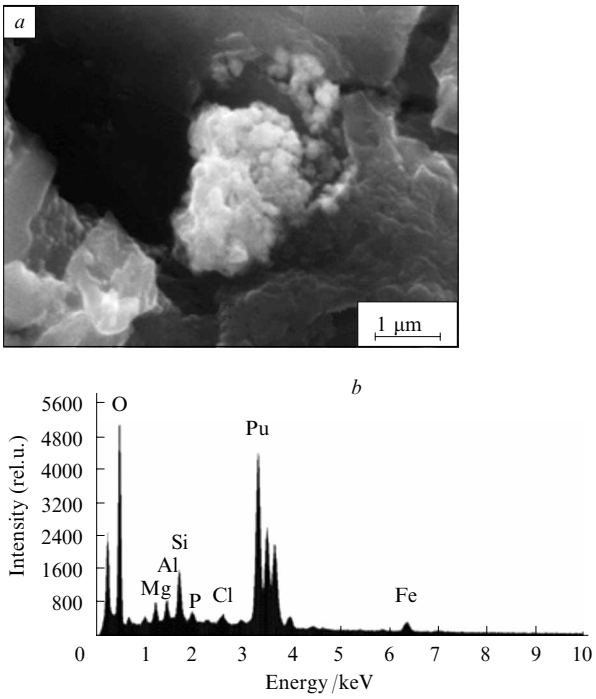


Figure 9. Morphology and composition of a plutonium-containing particle: (*a*) secondary electron SEM image, (*b*) XRMA spectrum.[43]

particles, intrinsic colloids or complexes with the nitrate solutions.

The main source of the radioactive contamination of the Yenisei River (Russia) is the activity of the Krasnoyarsk Mining and Chemical Industrial Complex (MCIC), where so-called direct-flow reactors operated for a long period of time. As a result, radionuclides entered the river ecosystem and were mainly accumulated in bottom sediments and bottomland soils.[44] The vertical distribution of plutonium in bottomland soils is highly non-uniform (Fig. 10), which is possibly caused by either non-uniform delivery of radionuclides and non-constant rate of sediment formation or post-sedimentation processes. The maximum concentration of ^{239,240}Pu in samples studied by Kuznetsov *et al.*[44] was 17.8 Bq kg^{-1}. On moving away from MCIC down the Yenisei River, the concentration of radionuclides in bottomland deposits does not tend to decrease. Using the sequential extraction method, it was demonstrated that most of plutonium exhibits low mobility, *i.e.*, occurs in non-extractable fractions, which may be due to the presence of plutonium-containing 'hot' particles.

In bottom sediments, plutonium occurs at a significantly smaller depth, which commonly does not exceed 10 cm.[45] According to Pavlotskaya *et al.*,[46] plutonium in bottom sediments and bottomland soils mainly occurs in a low-mobility form. However, in comparison with bottomland soils, in bottom sediments, the relative concentration of the water-soluble and poorly soluble fractions decreases and the concentration of the acid-soluble fraction increases. The

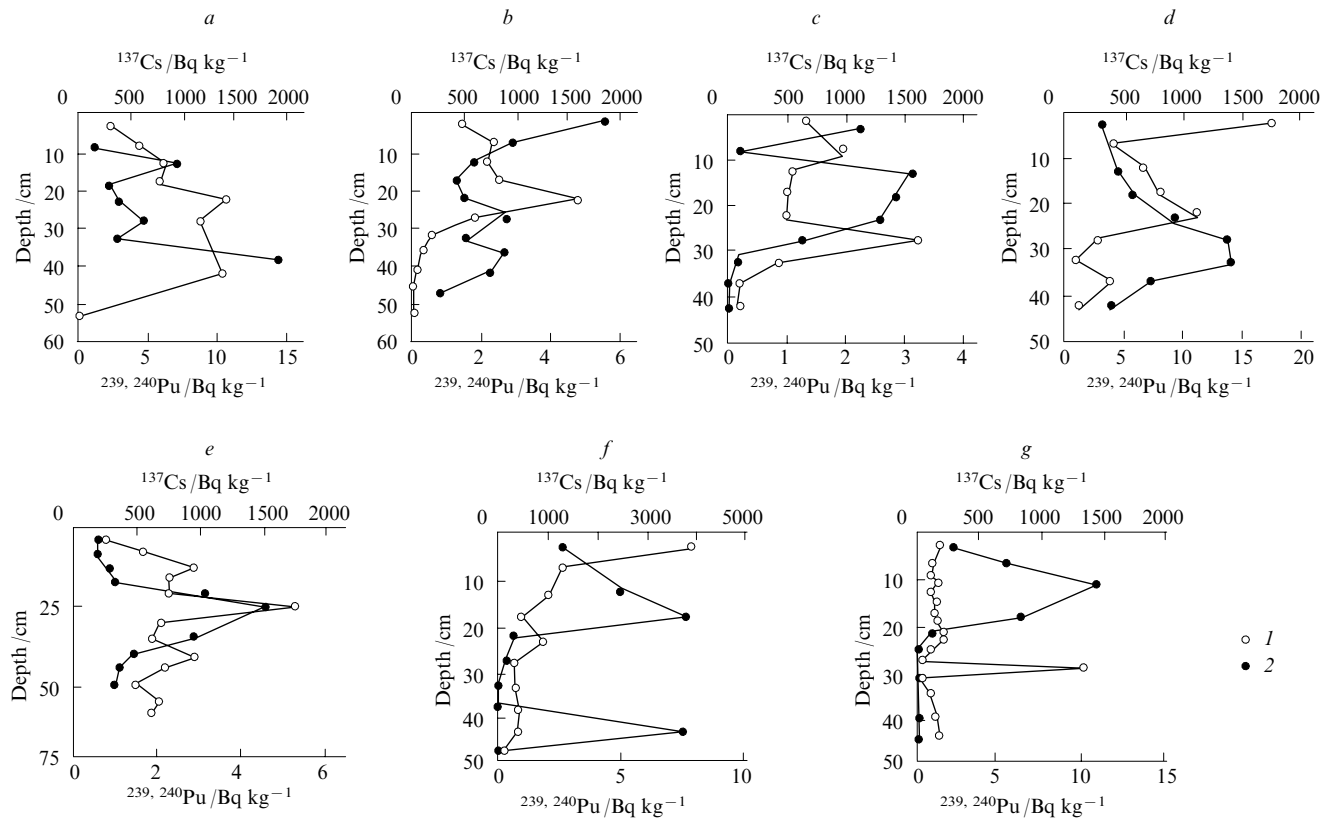


Figure 10. Vertical distributions of ^{239,240}Pu and ^{137}Cs in floodplain sediments of Yenisei river.[37]
Place of sampling, islands: (*a*) Atamanovsky, (*b*) Berezevy, (*c*) Tarygin, (*d*) Predvinsky, (*e*) Cheremuhov, (*f*) Ust-Tungussky and (*g*) Chernyi.
Distances from MCIC /km: (*a*) 2, (*b*) 1.8, (*c*) 24, (*d*) 100, (*e*) 250, (*f*) 255, (*g*) 1236.

decrease in the concentration of the water-soluble fraction is possibly due to its permanent washing out on contact with river water. Treatment with Tamm's solution demonstrated that plutonium is bound to a greater degree to the fraction of amorphous compounds (organometallic complexes and amorphous iron and silicon oxides) rather than to the mineral component, and it is equally distributed between organometallic complexes and amorphous oxides.

In the case of bottomland soils, reducing conditions provided by the life activity of microorganisms in the presence of moisture can be an important factor controlling partitioning of physicochemical forms of plutonium.[47] This leads to the transfer of iron to the Fe(II) form, which is accompanied by the dissolution of hydroxide organometallic films fixed at the surface of clayey soil minerals (gelation). It was demonstrated that simultaneous removal of iron and plutonium is observed in the course of this process. This indicates that plutonium occurs in the form bound to the iron hydroxide and in the form of organometallic complexes. The presence of plutonium in the poorly soluble fraction could be indicative of the presence of 'hot' particles, which were repeatedly found in the Yenisei River sediments.[48,49]

Skipperud *et al.*[50] determined the physicochemical speciation of plutonium in the Yenisei and Ob Rivers. It was found that the major part of plutonium in bottom sediments from the Ob and Yenisei Rivers occurs in fractions soluble in H_2O_2 (mild oxidizing agents) and HNO_3. However, the authors show that plutonium also occurs in the insoluble residue evidently within 'hot' particles. It was found that, both in the case of the Ob River and the Yenisei River, the major part of plutonium can be washed out with H_2O_2. The authors assume that plutonium is predominantly bound to organic substance. In the estuaries of both rivers, the fraction of hardly extractable plutonium increases. The authors explain this effect by washing out plutonium from the organic-bound fraction on interaction with sea water, which exhibits higher salinity and pH, and the subsequent adsorption of plutonium on amorphous Fe/Mn oxyhydroxides yielding hardly extractable species.

The Semipalatinsk Nuclear Test Site was the largest nuclear test site in the USSR. In the period from 1949 to 1989, 456 nuclear weapon tests were carried out in its territory, among them were 116 atmospheric (30 surface and 86 open-air) and 340 underground tests. Napoles *et al.*[51] studied samples of soil collected in three different regions of the Semipalatinsk Test Site: (1) close vicinity of explosion epicentres (ground zero), (2) surrounding dumps of the Lake Balapan and Tel'kem 1 and (3) the central point of the Tel'kem 2 (Fig. 11 *a*). As a result of sequential extraction (Fig. 11 *b*), it was found that in the majority of samples (except for the sample from the region of Tel'kem 2), plutonium occurs in the insoluble residue (*i.e.*, it does not migrate to the solution after boiling in 8 M HNO_3 at a temperature of 90 °C for 2 h), which is indicative of the presence of 'hot' particles. The distribution of plutonium over fractions in different samples can be related to different temperature of the fireball, which envelopes rocks in the moment before and after detonation and to differences in sampling location. The last factor can be especially important in the case of samples from Tel'kem 1 and Tel'kem 2, because conditions of explosions in these regions were similar. However, samples have not been characterized in more detail in this work, precluding futher determination of physicochemical speciation.

Leon Vintro *et al.*[52] determined the concentrations of plutonium and its physicochemical speciation in samples of water (underground water in the region of Sarzhal, rivers and brooks in the area of the test site, and the region of the Tel'kem 1 and Tel'kem 2 craters) collected in the area of the Semipalatinsk Nuclear Test Site. It was demonstrated that the concentration of plutonium in the water samples was rather low and did not exceed the intervention level. The highest concentration of plutonium was found in the region of the Tel'kem 1 crater. Plutonium bound to relatively large particles of > 450 nm was nearly absent in all of the samples (authors extracted only this fraction of particles). The determination of physicochemical speciation of plutonium in the studied water samples demonstrated the predominant presence of reduced species Pu(III)/Pu(IV), which is possibly caused by a high concentration of dissolved

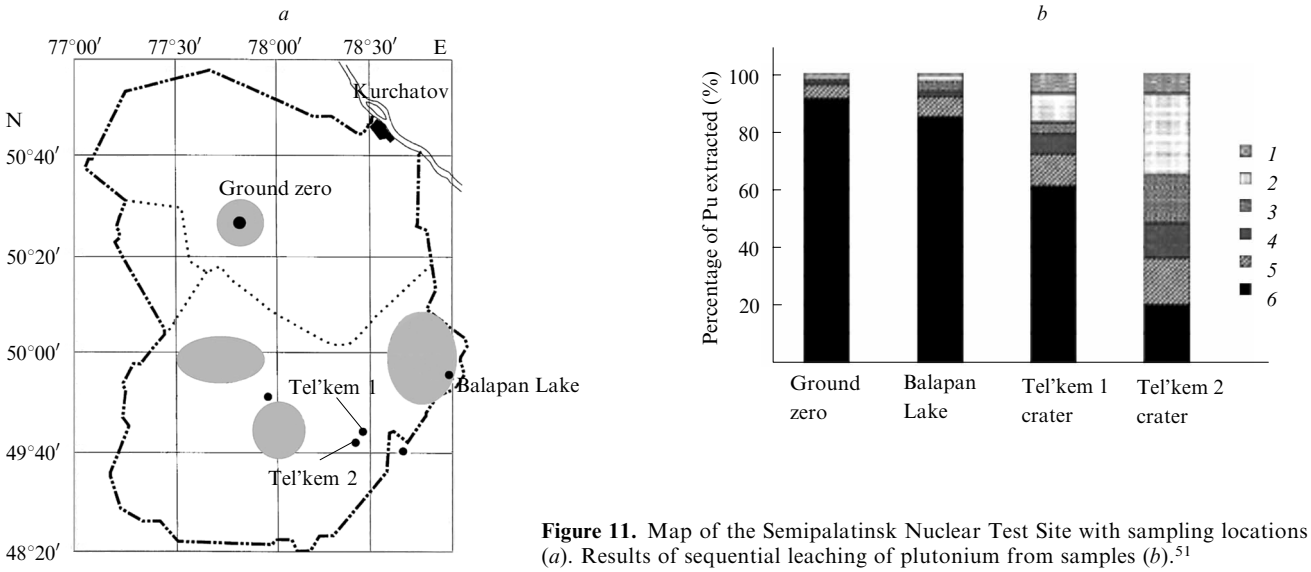


Figure 11. Map of the Semipalatinsk Nuclear Test Site with sampling locations (*a*). Results of sequential leaching of plutonium from samples (*b*).[51]
Fraction: (*1*) exchangeable, (*2*) acid-soluble, (*3*) reducible, (*4*) oxidizable, (*5*) strongly bound, (*6*) residual.

organic substances. It is known that the Tel'kem crater was formed by explosions in rather shallow wells (depth of 31 m) drilled in sandstone, which contained large amounts of organic compounds.

As a result of underground explosions, the major part of high-melting radionuclides was sequestered in vitreous glass. Dubasov *et al.*[53] carried out experiments on leaching of radionuclides from samples collected at the boundary of cavities and from walls of an observation gallery at the Semipalatinsk Nuclear Test Site. Leaching tests were performed by water that was equilibrated with crushed granite at pH 7.55. As a result, it was demonstrated that plutonium exhibits extremely low leaching, and the highest leaching is observed for the first fraction (first 15 minutes). The concentration of plutonium in the first fraction of the solution was nearly the same for different samples (7.8×10^{-3} Bq ml^{-1}). The authors assume that this value corresponds to the concentration of a poorly soluble plutonium compound, which occurs at grain surface. On holding for a longer time, leaching rate significantly decreases. These experiments demonstrate that plutonium is tightly fixed in fused and fritted rocks produced by underground nuclear explosion.

From the survey of available data on physicochemical speciation of plutonium in the environment, the following conclusions can be drawn:

— four most widespread forms of plutonium occurring in different materials can be distinguished: plutonium occurring as 'hot' particles PuO_2, plutonium bound to natural organic substances, plutonium bound to the inorganic fraction (Fe and Mn oxides/hydroxides, clays, zeolites, *etc.*) and dissolved plutonium species [Pu(V) or Pu(VI)];

— extremely poorly soluble 'hot' particles, mostly of PuO_2 composition, are produced as a result of explosions and fires;

— plutonium exhibits extremely high stability with respect to washing out from soils and bottom sediments;

— plutonium can migrate over long distances as a part of colloidal particles of different nature (both organic and mineral);

— the presence of organic substances significantly affects the behaviour of plutonium. Plutonium forms complexes with organic substances, which improves both the potential mobility and elevated concentration of plutonium compared to colloidal concentrations found in the environment;

— under oxidizing conditions, plutonium can migrate to a solution in the oxidized form [Pu(V) or Pu(VI)]. However, plutonium bound to particles occurs as Pu(IV) even under oxidizing conditions.

III. Plutonium behaviour at a mineral–water interface

The above data on the physicochemical speciation of plutonium in different environmental materials demonstrated that sorption on solid phases (soils, rocks, engineered-barrier corrosion products, *etc.*) is among the processes that control the behaviour of this element. Plutonium is remarkable among other chemical elements for its very complex physical and chemical properties.[54] Its chemical behaviour both in the environment and in industrial processes is determined by a large number of oxidation states, which can coexist and be interconverted (as discussed earlier). Sorption processes can be accompanied by redox reactions. Changes in the oxidation state of plutonium in the course of sorption on both redox-active and redox-inactive minerals were repeatedly demonstrated in the literature.

Among the first studies demonstrating a change in the plutonium oxidation state at the water–mineral interface are the works by Sanchez *et al.*[55] and Keeney-Kennicutt *et al.*[56] In both studies, it was shown that the sorption of Pu(V) at the surface of goethite (α-FeOOH) is a fairly fast process, which results in stabilization of Pu(IV) at the surface under dynamic equilibrium conditions. Later it was repeatedly demonstrated that redox reactions accompanying sorption occur most often upon plutonium interaction with redox-active minerals.

The reduction of Pu(V) upon sorption on magnetite (Fe_3O_4) was demonstrated by Powell *et al.*[57] At pH 5–8, reduction occurred in the near-surface layer of magnetite, where sorption is a rate-limiting step, and plutonium does not change its oxidation state in the solution. The authors attributed the fast reduction of Pu(V) at the surface to its interaction with ferrous ions present in magnetite. The authors carried out experiments at different concentrations of plutonium (6×10^{-11} and 1.5×10^{-8} mol litre^{-1}) and obtained similar results, which indicated that the rates and paths of redox reactions in the system under study exhibit no concentration dependence for the concentration range investigated.

It was also found that redox reactions take place on sorption at the surface of Mn-containing minerals. Manganese dioxide, unlike magnetite, exhibits oxidizing properties. Keeney-Kennicutt *et al.*[56] demonstrated that, after the sorption of Pu(IV) trace on δ-MnO_2, plutonium was oxidized to Pu(V) and Pu(VI). Similar results were obtained by Morgenstern and Choppin,[58] who studied Pu(IV) oxidation kinetics on sorption on pyrolusite (β-MnO_2) using solvent extraction. It was found that Pu(IV) is oxidized to Pu(V,VI) at pH 2–3.5. At pH 8.1, a significantly lower Pu(V) concentration was found in the system over time compared with that observed at lower pH. The authors attributed this to retardation of the oxidation caused by the stabilization of Pu(IV) on the surface at high pH.

In some works,[59,60] the sorption of Pu(V) on volcanic tuff containing iron oxides and impurities of manganese oxide was studied. Micro-X-ray fluorescence (μ-XRF) analysis showed that Pu(V) is predominately associated with manganese oxides [rancieite, $(Ca,Mn)OMn^{IV}O_2 \cdot 3H_2O$] and smectites rather than with iron oxides and zeolites (Figs 12 *a–d*).[59] XANES spectra of adsorbed plutonium obtained within 1 day of phase contact indicated that plutonium either retains its oxidation state Pu(V) or is oxidized to Pu(VI). The determination of the oxidation state after long-term phase interaction demonstrated the presence of redox reactions in the system. Thus, Pu(VI) was present in a sample within 6 months, whereas Pu(IV) was found within 2 years (Fig. 12 *e*). Accordingly, sorption of Pu(V) was initially accompanied by oxidation to Pu(VI); however, subsequent slow reduction to Pu(IV) was observed later (within 2 years).

To determine the detailed mechanisms of this behaviour, Powell *et al.*[60] studied the sorption of Pu(IV) on synthesized pyrolusite. It was found that initially Pu(IV) is rapidly adsorbed. Next it is oxidized to Pu(V,VI), which is accompanied by partial desorption. At high pH, the oxidation step is followed by the reduction and sorption of plutonium,

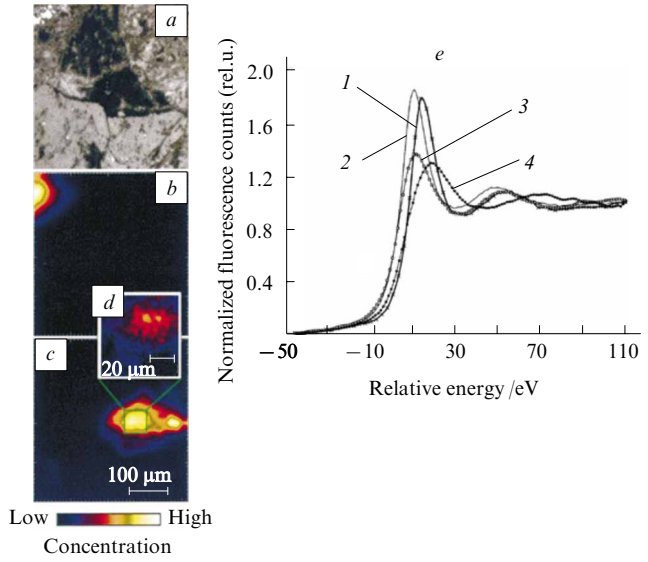


Figure 12. Photomicrograph (*a*), elemental maps (*b*–*d*) and XANES spectra (*e*) of a test sample of volcanic tuff.[52,60]
The silvery particles in the upper-left corner are hematite; manganese oxide is located at the central part and surrounded by zeolite. The μ-XRF elemental maps show the distribution of Fe (*b*), Mn (*c*) and Pu (*d*); (*e*) XANES spectra for Pu(V) adsorbed on a test sample: (*1*) sample after 6 months, (*2*) sample after 2 years, (*3*) Pu^{IV} standard, (*4*) Pu^{V} standard.

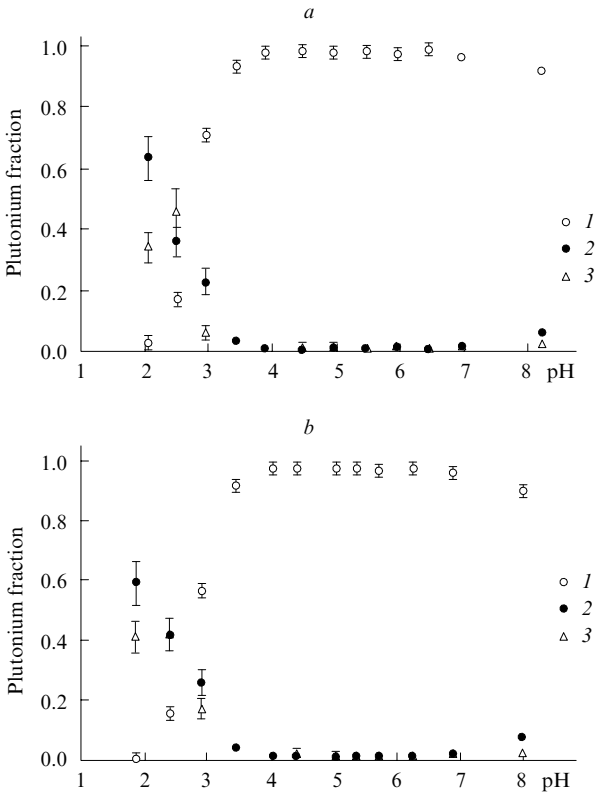


Figure 13. Ratio of different plutonium oxidation states in a water + solid phase suspension.[60]
Solid phase: (*a*) initial Pu^{IV} + pyrolusite, (*b*) initial Pu^{V} + pyrolusite after 30 days of interaction. (*1*) Pu^{IV}, (*2*) Pu^{V}, (*3*) Pu^{VI}.

now in the tetravalent form. As a result of determination of the oxidation number of plutonium in a pyrolusite-containing suspension at different pH (Fig. 13), it was found that, irrespective of the initial oxidation state, plutonium is predominantly stabilized in the solution in the oxidized form Pu(V,VI) at pH < 3, whereas at pH > 3 its sorption in the tetravalent form is observed. The authors note that the O : Mn ratio in pyrolusite is 1.95 ± 0.03; this is indicative of the presence of Mn(II) or Mn(III), which are evidently responsible for its reducing properties. Once again, this work demonstrates that the reaction of plutonium with manganese dioxide passes through the steps of oxidation and, next, reduction. The pH of the suspension significantly affects the kinetics of these processes. Upon increasing pH, redox reactions at the water–mineral interface proceed more rapidly, which can be attributed to the fact that these reactions accompany sorption, which increases with pH.

A XANES study of the sorption of Pu(VI) on manganite (MnOOH) and hausmannite (Mn_3O_4)[61] in the pH range of 5–10 also demonstrated the reduction of hexavalent plutonium at the surface of adsorbents to the tetravalent state, whereas Pu(V) was present in the solution. Like in the above-mentioned study,[60] the authors of this work also assume that the reduction of Pu(VI) at the surface became possible because of the presence of Mn(II) in the solid phase. Analogous results were obtained by Kersting *et al.*,[62] who employed the XANES and EXAFS methods and found that sorption of Pu(V) on colloidal particles of birnessite and pyrolusite is accompanied by its gradual reduction to Pu(IV).

Hu *et al.*[63] demonstrated the reduction of Pu(VI) upon sorption at the surface of Mn(III)-substituted goethite. On the interaction of Pu(VI) with these colloidal particles, plutonium occurred on the particle surface as Pu(IV) (from 35% to75%) and Pu(V) (from 25% to 65%).

Thus, when Pu(IV,V,VI) is adsorbed on different Mn-containing minerals, stabilization of Pu(IV) at the surface of particles and Pu(V) in the solution occurs at different rates under dynamic equilibrium conditions.

Powell *et al.*[64] studied the sorption of Pu(V) on synthesized hematite and goethite and found that at pH ± 4.5 the reduction to Pu(IV) takes place at the surface of both minerals, whereas in the solution, reduction was absent and Pu remained pentavalent. The analysis of kinetic data demonstrated that, in the case of hematite, sorption is the rate-limiting step of the overall process. In the case of interaction of Pu(V) with goethite, sorption proceeds more rapidly than reduction.

Romanchuk *et al.*[65] also demonstrated the reduction of Pu(V,VI) to Pu(IV) on the sorption on hematite, and, as in the above-mentioned work, Pu(V) was found to remain stable in the solution. In all these studies, both Fe-bearing and Mn-bearing minerals were shown to reduce plutonium to Pu(IV) on the surface, while Pu(V,VI) remained in the solution.

The cases most complicated for description and explanation are those when redox reactions occur upon sorption of plutonium at the surface of redox-inactive minerals (containing no reducing agents). The determination of the mechanism of Pu(V,VI) reduction upon sorption under oxidizing conditions (with the access of oxygen) on a redox-inactive mineral is a difficult problem. Different mechanisms of processes resulting in the formation of Pu(IV) at the surface of hematite were proposed:

— disproportionation of Pu(V) in an electric double layer upon accumulation in the surface layer upon sorption,

— autoreduction of Pu(V,VI) by radiolysis products,

— reduction of Pu(V,VI) by trace amounts of Fe(II) occurring in hematite,

— reduction of Pu(V,VI) due to photocatalytic properties of hematite.

Romanchuk *et al.*[65] also demonstrated reduction of Pu(V,VI) upon sorption on hematite at very low plutonium concentrations ($\sim 10^{-14}$ mol litre^{-1}). These results eliminated some possible causes of the reduction of plutonium to Pu(IV) at the surface of hematite. First, the effect of plutonium radiolysis products was rejected: experiments with femtomolar concentrations were performed with the use of the short-lived radionuclide ^{237}Pu, which decays by the K-capture rather than α-decay mechanism. Second, disproportionation reactions are impossible at so low concentrations. Thus, the reduction of plutonium is related exclusively to its interaction at the surface of hematite.

The possibilities of determining trace concentrations of Fe(II) in the studied minerals are rather limited, because methods such as Mössbauer spectrometry, XRF analysis and EPR are insufficiently sensitive for solving this problem.

Hematite and goethite are typical semiconductors with band gaps of 2.2 and 2.06 eV, respectively,[66] which correspond to light with wavelength of 550–600 nm. This indicates that visible light can cause electron transfer from the valence band to the conduction band in hematite and goethite, which can be further utilized for reduction. Indeed, an effect of daylight on the Pu(V) reduction kinetics on sorption at the hematite and goethite surface was detected by Powell *et al.*,[64] Keeney-Kennicutt *et al.*[56] and McCubbin *et al.*,[67] who attributed the occurence of redox reactions to the semiconductor properties of these iron oxides.

The reduction of Pu(V) to Pu(IV) was also found for sorption at the surface of other minerals that are not semiconductors and do not exhibit redox properties.

For example, Kersting *et al.*[62] studied sorption of Pu(V) at the surface of birnessite, $Na_{0.3}Ca_{0.1}K_{0.1}Mn^{4+}Mn^{3+}O_4 \cdot 1.5\,H_2O$; calcite, $CaCO_3$; montmorillonite, $(Ca,Na...)(Mg,Al,Fe)_2[(Si,Al)_4O_{10}](OH)_2 \cdot H_2O$; clinoptilolite, $(Na,K,Ca)_{2\text{-}3}Al_3(Al,Si)_2Si_{13}O_{36} \cdot 12H_2O$; goethite; and silicon dioxide. XANES spectra of plutonium adsorbed at the surface of these minerals indicate that tetravalent plutonium is stable (Fig. 14) under dynamic equilibrium conditions. In the case of redox-inactive minerals that are not semiconductors, such as silicon dioxide and clinoptilolite, the authors noted extremely slow reduction and sorption kinetics. In the case of clinoptilolite, dynamic sorption equilibrium is not attained even within 77 days of phase contact. In addition, Zavarin *et al.*[68] also confirmed slow reduction of Pu(V) on its sorption on calcite, $CaCO_3$. Thus, in the case of minerals that do not exhibit reducing and semiconducting properties, sorption and reduction also proceed, although much more slowly.

A detailed study of the interaction of Pu(V) with high-purity quartz free from impurities of other phases was carried out by Hixon *et al.*[69] It was also demonstrated that Pu(V) is reduced to Pu(IV) at the surface with time. Dynamic equilibrium in the suspension is attained within more than 1 year of phase contact. The authors used different plutonium isotopes (^{238}Pu and ^{242}Pu) and demonstrated only insignificant effect of α-radiolysis; this provided the conclusion that, evidently, radiolysis products cannot be the major cause of the reduction of Pu(V) upon sorption on quartz. It was demonstrated that plutonium disproportionation reactions are not responsible for Pu(V) reduction on sorption, which is in agreement with the results obtained by other authors. The main driving force for the reduction of Pu(V) on sorption on quartz is the energetic favourability of the formation of chemisorbed Pu(IV) compounds at the surface of the solid phase.

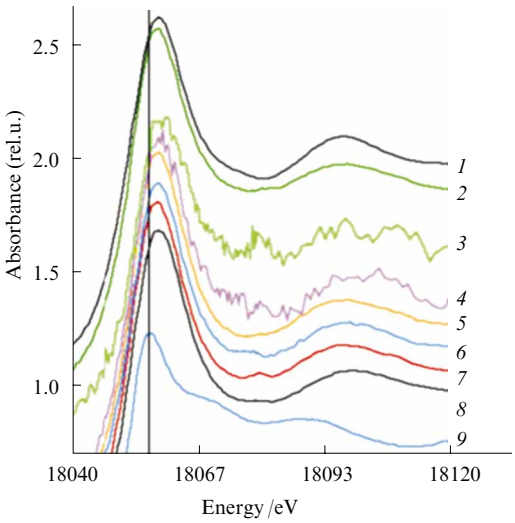


Figure 14. XANES spectra of plutonium sorbed on different minerals at pH 8.4 (the initial oxidation state is Pu^V).[62]
(*1*) PuO_2 (Pu^{IV}), (*2*) birnessite, (*3*) calcite, (*4*) clinoptilolite, (*5*) goethite, (*6*) montmorillonite, (*7*) pyrolusite, (*8*) silica, (*9*) PuO_2^+ (Pu^V).

Many scientific groups studied the interactions of plutonium with clay minerals. Slow (for more than 2 months) reduction of plutonium on interaction of Pu(V) with montmorillonite was demonstrated.[70] In the absence of a solid phase, high kinetic stability of Pu(V) in a solution was found. The authors believe that the major cause of the reduction of Pu(V) on interaction with montmorillonite is high thermodynamic stability of Pu(IV). The authors studied sorption kinetics in detail and, as a result, found that sorption slows down upon increasing pH, which is at variance with previous works on Pu(V) sorption on iron oxides (magnetite, hematite, and goethite), where the sorption rate increased with pH.[57,64] At pH < 5, the sorption rate strongly depends on ionic strength, namely, the sorption rate decreases with increasing ionic strength. All of this allows the following conclusion for montmorillonite: at pH < 5 sorption occurs by a mechanism of ion exchange with cations in interlayer positions, whereas at higher pH, sorption occurs by the mechanism of complexation with aluminol and silanol sorption sites at the surface. Like in the works considered above, plutonium remaining in the solution was in the Pu(V) form. However, it cannot be ruled out that a trace amount of Fe(II) participates in Pu(V) reduction.

Kirsch *et al.*[71] studied the interaction of Pu(V) and Pu(III) with magnetite (Fe_3O_4), chukanovite [$Fe_2(CO_3)(OH)_2$] and mackinawite (FeS) under reducing anoxic conditions (−0.50 mV < Eh < 0.25 mV). The state of plutonium was determined using XAFS analysis. Relatively high total concentrations of plutonium

(10^{-5} mol litre^{-1}) were used because of a relatively low sensitivity of this method. In the case of magnetite, Pu(III) is stabilized at the surface irrespective of the initial oxidation state of plutonium. In the case of chukanovite and mackinawite, the major form of plutonium is PuO_2 with possible Pu(III) impurity. In the case of chukanovite, the fraction of Pu(III) can amount to 30%. Thus, the reduction of plutonium to Pu(III) is possible under reducing conditions.

Some works published in recent years give evidence of the formation of hydrated plutonium oxide sediments at the surface of minerals. This is possibly due to a low solubility of oxygen compounds of Pu(IV), which are stabilized at the surface of minerals as a result of redox reaction accompanying sorption. This effect was assumed in some works described above. Romanchuk *et al.*[65] assumed the formation of Pu(IV) polynuclear species at the surface of hematite on sorption of Pu(IV,V,VI) even at its relatively low concentration ($\sim 10^{-10}$ mol litre^{-1}). Kumar *et al.*[72] found a decrease in Pu(IV) sorption rate at the surface of smectite and also explained it by slow formation of polynuclear plutonium complexes.

Powell *et al.*[73] demonstrated the formation of 2- to 5-nm plutonium-containing particles on addition of a Pu(IV) solution to suspensions of goethite (Fig. 15) and quartz. It was demonstrated that Pu_4O_7 nanoparticles are formed at the surface of goethite, whereas PuO_2 nanoparticles are formed at the surface of quartz. The authors explain the formation of Pu_4O_7 particles by the epitaxial growth of the corresponding plutonium oxide at the surface of goethite, which is caused by similarity of the lattice parameters. Later it was demonstrated that the resulting Pu_4O_7 particles are stable for several months temperatures of both 25 °C and 80 °C and their transformation to PuO_2 does not occur.[74] It is important to note that the experiments described above consisted in the addition of Pu(IV) solutions with relatively high concentrations ($\sim 10^{-6}$ mol litre^{-1}) at pH 8. In this case, insoluble hydrated plutonium oxides are formed even in the absence of mineral colloidal particles.

Slow formation of aggregates of $PuO_{2+x}\cdot nH_2O$ crystalline nanoparticles upon interaction of Pu(V,VI) with hematite at neutral pH was demonstrated with the use of spectral and electron-microscopy methods.[75] It is important that, in the absence of a solid phase under analogous conditions, Pu(V) remained stable in a solution for a long time (up to 3 years of observation). Paths of variation of the physicochemical speciation of plutonium at the water–hematite interface at different total plutonium concentrations were proposed (Fig. 16).

An important result of this work was a detailed study of the kinetics of leaching of the resulting particles in solutions with pH 1.3. It was demonstrated that the resulting Pu_4O_7 nanoparticles are highly kinetically stable and are dissolved very slowly in spite of low pH.

Schmidt *et al.*[76] ascertained the formation of plutonium oxide nanoparticles at the surface of muscovite. Even though plutonium was initially in the trivalent state, it was oxidized on the interaction with the muscovite surface, and oxide particles were formed (Fig. 17). It was found that, in the absence of a solid phase, Pu(III) remains the stable form of plutonium. However, in this work, as well as in the previous one, plutonium concentrations used in experiments were rather high ($\sim 10^{-3}$ mol litre^{-1}).

Similar particles were found at the surface of quartz:[69] a sample containing a rather high concentration of Pu(V) (1.76×10^{-5} mol litre^{-1} of ^{242}Pu) was obtained at pH 6 and quartz concentration of 2.5 g litre^{-1}. This sample was studied using XAFS and HRTEM. The XAFS study indicated that, after as early as 10 days of interaction, the sample contained about 66 % Pu(IV). HRTEM showed the

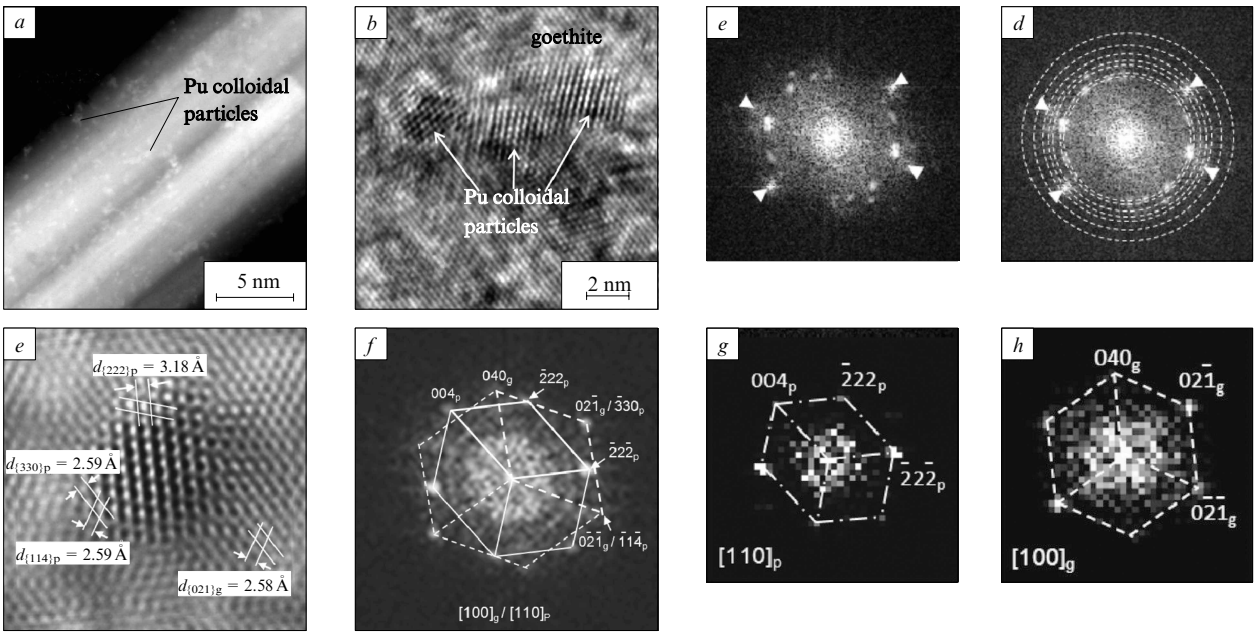


Figure 15. Images of Pu_4O_7 nanoparticles at the surface of goethite.[73]
(*a*) STEM image where colloidal plutonium particles at the surface of goethite particles can be seen, (*b*) HRTEM image of Pu_4O_7 nanoparticles at the surface of goethite, (*c*, *d*) Fourier transform of image (*b*) arrows show goethite reflections and circles show reflections corresponding to the Pu_4O_7 structure, (*e*) HRTEM image of a single Pu_4O_7 particle, (*f*) Fourier transform of image *e* and separate parts corresponding to Pu_4O_7 (*g*) and goethite (*h*).

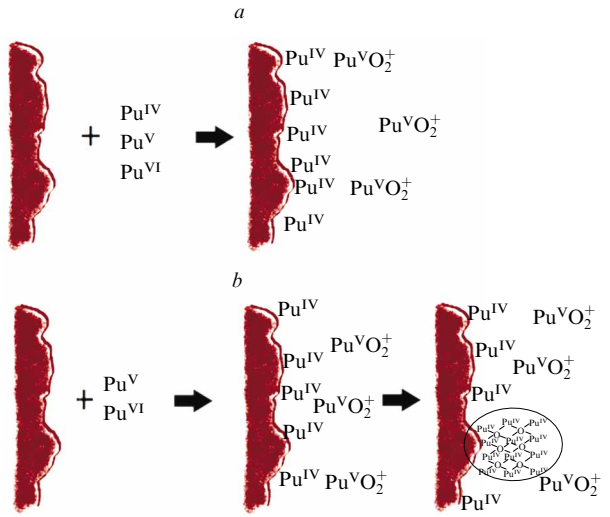


Figure 16. General scheme for the interaction of Pu with hematite colloids for various Pu redox states and total Pu concentrations of $\sim 10^{-14}$ (*a*) and $> 10^{-9}$ mol litre^{-1} (*b*).[75]

presence of plutonium-containing sediments at the surface of quartz (Fig. 18).

This means that the total concentration of plutonium in the experiment is an important factor. In the majority of works described above, the concentration of plutonium in the experiment was above 10^{-10} mol litre^{-1}. Spectral methods providing direct information on the physicochemical speciation of plutonium can be used only at concentrations of $> 10^{-6}$ mol litre^{-1}. These are the plutonium concentrations that often occur in contaminated areas and are higher than the global fallout level ([Pu] $< 10^{-12}$ mol litre^{-1}). Therefore, it is important to find out whether the results of the experiments can be extrapolated to lower concentrations.

To reveal the effect of plutonium concentration on the mechanism of the process, Begg *et al.*[77] studied the sorption of Pu(IV) and Pu(V) on montmorillonite in a wide range of plutonium concentration (10^{-6} to 10^{-16} mol litre^{-1}). Linear sorption isotherms were obtained, which, in the opinion

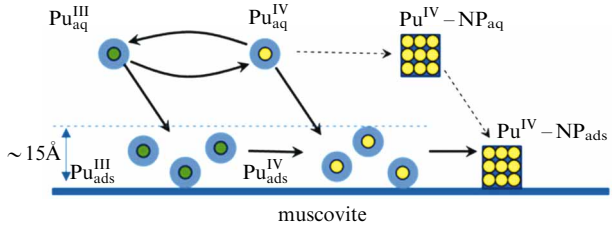


Figure 17. Schematic diagram of the mechanism of formation of plutonium-containing nanoparticles at the surface of muscovite. Solid arrows show the expected main reaction path; dashed arrows denote a possible alternative reaction path.[76]

of the authors, demonstrates similar behaviour of plutonium in a wide concentration range.

However, Romanchuk *et al.*[65] noted a difference in the behaviour of plutonium at concentrations of $\sim 10^{-14}$ mol litre^{-1} and $\geqslant 10^{-10}$ mol litre^{-1}. Different sorption kinetics makes it possible to reject the formation of $PuO_{2+x}\cdot n\,H_2O$ particles at femtomolar concentrations of plutonium. Different reaction mechanisms at different concentrations of plutonium were also proved by Hixon and Powell.[78]

Thus, there are many lines of evidence to suggest that sorption reactions of plutonium are accompanied by redox processes: Pu(IV) is stabilized at the surface of the solid phase, while insignificant concentrations of plutonium in the solution are due to Pu(III) or Pu(V) depending on redox conditions. At [Pu] $\geqslant 10^{-10}$ mol litre^{-1}, the formation of plutonium oxide nanoparticles was demonstrated.

Since redox reactions involving plutonium at the water–mineral interface occur, in particular, on redox-inactive minerals and it was assumed that the driving force for these reactions is high thermodynamic stability of Pu(IV) compounds chemisorbed at the surface, the most important problem is thermodynamic description of the sorption interaction of plutonium with minerals. For this purpose, Kalmykov *et al.*[79] proposed a method for the description of plutonium sorption with the use of equilibrium constants of sorption reactions obtained from linear relationships of free energies of sorption and hydrolysis reactions.

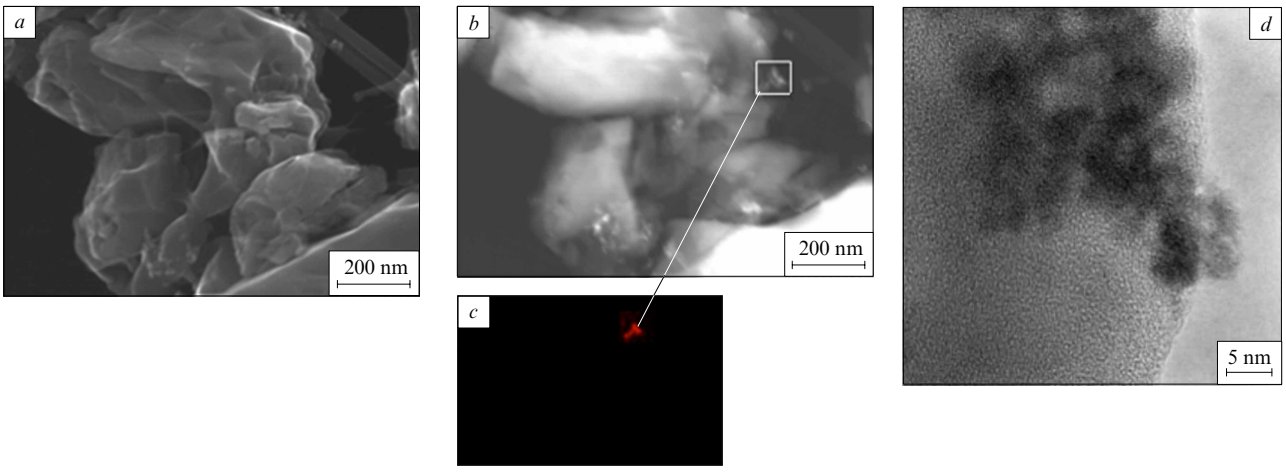


Figure 18. Images of plutonium-containing sediments at the surface of quartz in SEM (*a*) and z-contrast mode (*b*), plutonium distribution map (*c*) and (*d*) HRTEM image for the selected region.[69]

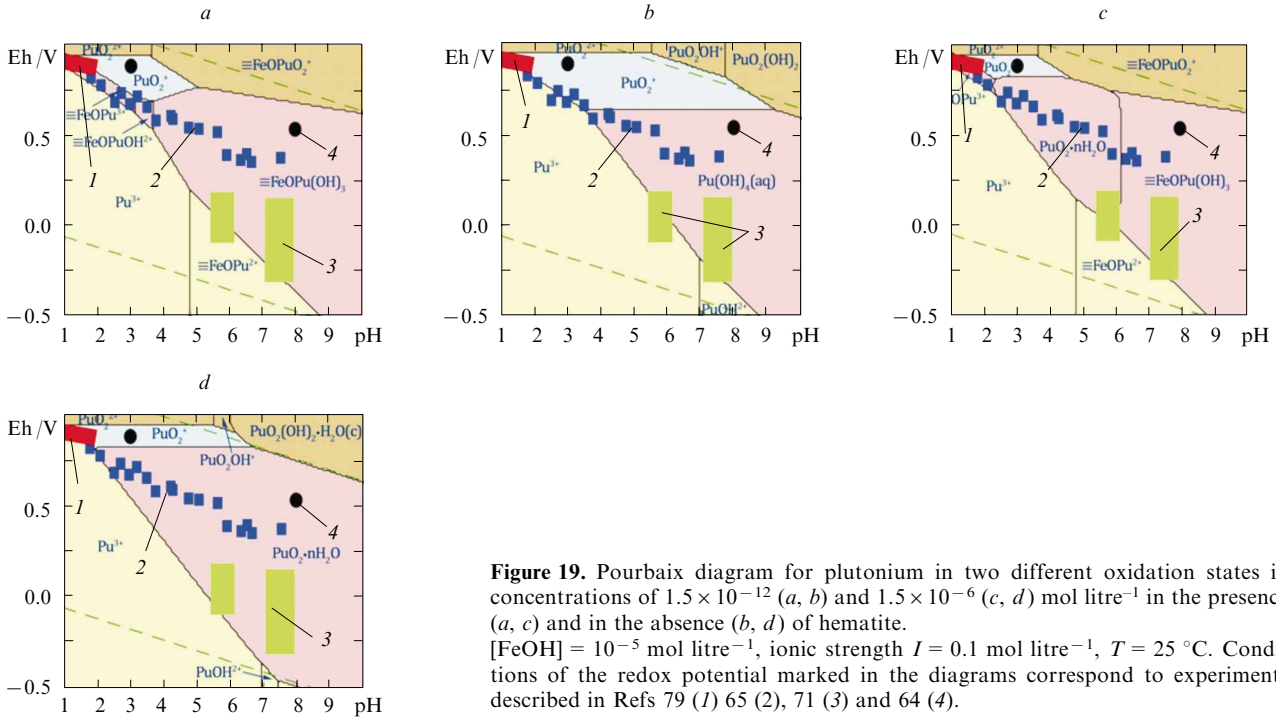


Figure 19. Pourbaix diagram for plutonium in two different oxidation states in concentrations of 1.5×10^{-12} (*a*, *b*) and 1.5×10^{-6} (*c*, *d*) mol litre^{-1} in the presence (*a*, *c*) and in the absence (*b*, *d*) of hematite.
[FeOH] = 10^{-5} mol litre^{-1}, ionic strength $I = 0.1$ mol litre^{-1}, $T = 25$ °C. Conditions of the redox potential marked in the diagrams correspond to experiments described in Refs 79 (*1*) 65 (2), 71 (*3*) and 64 (*4*).

In addition to inorganic surfaces, natural organic matter (NOM) is ubiquitous in shallow groundwaters and has been shown to have an important role for the geochemical behaviour of radionuclides.[80–82] Natural organic matter is a complex mixture of organic molecules ranging from simple organic acids to complex microbial exudates such as extracellular polymeric substances and siderophores as well as larger macromolecules such as humic and fulvic acids. Humic acid can agglomerate smaller particles forming nanocolloids ranging from 60 to 500 nm.[83] The composition and structure of NOM is variable and can be hard to characterize. It can range in size from low-molecular-weight dissolved species of < 1 nm in size to 100 nm.[81] As a result of high variability of NOM size and complex structure, it can behave both as a dissolved species or as a colloid. For instance, a Pu organic complex can exist as a dissolved species in solution or be sorbed by colloids and be transported. Humic substances have been shown to bind plutonium and uranium and enhance transport (see, *e.g.*, Refs 82, 84 and 85). In addition, waters may also contain an appreciable amount of man-made organic substances, as it was found in the area of the Karachay Lake.[86] In this case, such organics may play similar role as the NOM.

In general, plutonium is mainly sorbed by humic acids and fulvic acids in the pH region below pH of its sorption by mineral particles.[87] Yang *et al.*[85] used NMR and STXM to show that uranium binds to the hydrophobic organic matter resulting from decomposition of microbes. Buda *et al.*[88] showed that plutonium is complexed with humic acid, which enhances its transport in groundwater as both a dissolved species or larger nanocolloid. In addition, humic substances have been shown to rapidly reduce plutonium (V) and (VI) to plutonium (III) and (IV).[89]

Microorganisms are known to be associated with a range of radioactive elements at contaminated sites (see, *e.g.*, Refs 90 and 91), yet their role in controlling the behaviour of plutonium in the subsurface is largely unknown and is an ongoing topic of current research. Many microbes can release organic matter such as extracellular polymer substances contributing to the complexity of their interactions with actinides. Recent work has shown that microorganisms can affect the speciation and solubility of plutonium.[92–96] Ohnuki *et al.*[97] showed that *Bacillus subtilis* reduces Pu(VI) to Pt(IV) with simultaneous reduction of Pu(VI) to Pu(V) in solution. It was found that *Bacillus* sp. can solubilize solid $PuO_{2(s)}$ by reducing it to Pu(III) under anoxic conditions.[98] The sorption of Pu to microorganisms may have several mechanisms, including redox transformations. Currently, the specific mechanism controlling these redox transformations in the presence of microbes needs additional research. Microbes should be considered on a continuum with natural organic matter for understanding of how humic substances and microbes control the behaviour of plutonium and other contaminants in groundwater.

IV. Conclusion

Although plutonium is one of the most toxic chemical elements with a number of long-lived isotopes that is present in SNF and RW, its behaviour in the environment is still unclear. The behaviour of plutonium in the environment is complex and depends on the initial depositional history and the surrounding geochemistry. 'Hot' particles formed during the nuclear explosions, fires and reactor core melt-down accidents are accumulated in the environment where they could remain stable during long-term periods. However, till now it is unclear how the release scenario is linked with the structure and composition of these particles and what is their solubility.

Plutonium is redox-sensitive and can interact with inorganic, organic and microbial material in the subsurface. At high concentrations, plutonium can be hydrolyzed to form PuO_2 particles. At lower concentrations, plutonium, like other radionuclides, takes part in the number of chemical reactions including sorption on the components of soil,

rocks, bottom sediments, colloids of various origin including microorganisms; complexation with various ligands including humic and fulvic acids and products of microorganism life activity. Many of these reactions are accompanied by changes of plutonium redox state. The development of a universal (not a site-specific) model of plutonium behaviour that would take into account the diversity of chemical reactions remains an important task.

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