Environmental Actinide Science

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This article is a short qualitative summary of a chapter in the forthcoming book Advances in Plutonium Chemistry: 1967–2000, *edited by Darleane Hoffman for the Amarillo National Research Center. Readers are referred to the chapter for more technical details.*

Introduction

Considerable progress has been made in the study of environmental plutonium science in the last 30-plus years, driven to a large extent by concerns about the release and migration of large amounts of plutonium into the accessible geosphere. Plutonium has been introduced into the environment through several pathways. Environmental contamination has been caused by nuclear-weapons production and testing, nuclear-reactor accidents, and accidents during the transport of nuclear weapons. Above-ground testing of more than 420 nuclear weapons has produced large amounts of radionuclides through fission and neutron activation products. More than three metric tons of plutonium have been distributed on the earth's surface by global fallout.[1] For example, the MAYAK plutonium production complex in the former Soviet Union is located in the southern Urals, about 70 km north of Chelyabinsk and 15 km east of Kyshtym. Between 1949 and 1951, about 76 million m^3 of liquid radioactive waste with a total activity of 100 PBq (2.7 MCi) were discharged into the Techa River.[2,3]

The reactor explosions in 1986 in Chernobyl[2] released 23 kg of plutonium isotopes totaling 6.5 PBq (0.18 MCi). Within a 30-mi radius, the concentration of $^{239,240}Pu$ is between 3.7 GBq/km^2 and 185 GBq/km^2 (0.1–5 Ci/km^2). Large areas in Belorussia and Ukraine were contaminated also.

Severe contaminations occurred in the United States at sites within the nuclear-weapons complex. The Hanford Site in southeastern Washington State was the first industrial-scale plutonium production site. Between 1944 and 1981, approximately 220,000 m^3 of liquid reprocessing waste, totaling 11.8 EBq (320 MCi), were produced and are stored in 149 single-shell and 28 double-shell steel tanks.[4,5] As much as 3800 m^3 of radioactive contaminated liquid were released into the environment. During the earlier times of operation, some high-level wastes (HLW) and other contaminated liquids were discharged directly into the ground through trenches and shallow subsurface drainage systems, so-called cribs. The released volume of more than one billion m^3 contaminated around 500 km^2 with radionuclides and toxic chemicals. At Oak Ridge National Laboratory (ORNL), 160,000 m^3 of liquid waste containing fission products and transuranium elements were directly discharged into the ground, thus creating a radioactive burden of about 44.4 TBq (1.2 kCi). In the whole U.S. weapons complex, 5700 contaminated groundwater plumes exist, and estimates for the volume of contaminated soil range from 73 million to 200 million m^3.

At Sellafield, the British nuclear-fuel reprocessing plant, between 1950 and 1992, discharges were made into the Irish Sea of 120 TBq (3.2 kCi) of ^{238}Pu and 600 TBq (16.2 kCi) of $^{239,240}Pu$. As of 1977, 280 TBq (7.6 kCi) of $^{239,240}Pu$ were strongly sorbed to the seabed sediments.[6,7]

Proposed disposal of radioactive HLW and direct disposal of spent fuel in deep underground geologic repositories, as well as the storage and disposal of plutonium from nuclear-weapons dismantlement (it has been estimated that in excess of 250 metric tons of plutonium, primarily ^{239}Pu, is stored as nuclear weapons[8]), are further potential sources for plutonium releases into the environment. Although much of the radioactivity of the waste is caused by the relatively short-lived isotopes ^{90}Sr (29 yr), ^{137}Cs (30.2 yr), and other fission products, a potential long-term hazard comes from the following long-lived plutonium isotopes: ^{238}Pu (87.7 yr), ^{239}Pu (2.4×10^4 yr), ^{240}Pu (6.4×10^3 yr), and ^{241}Pu (14.4 yr).

It is essential to understand the behavior of plutonium in the environment in order to (1) develop efficient methods for the remediation and cleanup of contaminated sites, (2) predict the transport behavior, (3) carry out performance-assessment studies to determine if the repositories can safely contain HLW, and (4) engineer methods to retard their release and migration rates. To make this task even more challenging, predictive modeling has to cover time frames of up to 10,000 years, according to regulatory requirements in certain countries.

Plutonium can migrate in the environment via aqueous media, such as groundwater and surface, river, lake, and seawater, and then become fixed as a precipitate, colloid, or mineral-adsorbed species. Models predicting the hydrological transport through the environment require as input a plutonium concentration, the true amount that is actually available for transport. It is defined as the plutonium source term and not as true solubility, because it may be a combination of dissolved and colloidal material.

Plutonium can undergo a variety of complex chemical reactions in the environment. In addition to the formation of solid precipitates, colloids, and dissolved solution species common to aqueous systems, Pu ions can interact with the surrounding geomedia to change oxidation states or sorb on surfaces and colloids. Four important processes that can control the amounts and forms of the plutonium in solution are (1) precipitation, (2) complexation, (3) sorption, and (4) colloid formation. These processes control the overall chemical behavior of Pu in the environment and determine how much and how rapidly plutonium will move around in environmental systems. All four processes must be considered if one wants to understand and predict the chemical behavior and transport properties of plutonium in the environment. Detailed knowledge of the plutonium species and charges is essential because the nature and extent of precipitation, complexation, sorption, and colloid formation are strongly dependent on them. In addition, because these processes are not independent of one another, they must be considered simultaneously.

Oxidation States

The single most important property of plutonium is its oxidation state because the processes of precipitation, complexation, sorption, and colloid formation differ considerably from one oxidation state to another. Plutonium is known to exhibit several oxidation states, +3 through +7,[9] depending on solution conditions, and because of similar redox potentials connecting the various oxidation states, it is possible for two or more to coexist in solution at one time.[10] Water has an important oxidation–reduction chemistry that puts limits on the oxidation states that plutonium can exhibit in aqueous solutions.

Identification of Oxidation States

The method to be used for the quantitative determination of the oxidation states of plutonium in aqueous solutions depends on the concentration range of the plutonium. For concentrations of Pu less than micromolar, chemical separation techniques offer the only avenues. Above this concentration, spectroscopic techniques may be used.

Coprecipitation, selective sorption, liquid chromatography, and solvent-extraction techniques have been used with varying degrees of success to isolate and determine the oxidation states of Pu in aqueous systems and have been discussed in the literature.[11,12] Of these, solvent-extraction schemes have been used most often in recent times because they can give a rapid and nearly complete separation of oxidation states at trace levels. Choppin and Bertrand have proposed a series of solvent extractions at differing pH values using TTA (thenoyltrifluoroacetone).[13,14] However, Schramke et al. later showed that significant amounts of PuO_2^{2+} can be reduced to PuO_2^{+} by the organic extractant during the separation procedure if an oxidant is not present.[15] Choppin et al.[12] have proposed an actinide oxidation-state separation scheme for environmental samples, adapted from earlier work by Saito and Choppin[16] based on the organic extractant DBM (dibenzoylmethane) in chloroform. The use of this extractant has the advantage that the near-neutral pH of most environmental samples does not require adjustment to more acid conditions for the extraction step, as is the case with the other extractants mentioned here, thus minimizing the possible effects of pH adjustment on the oxidation-state distribution. Nitsche and co-workers used a combination of TTA, HDEHP (di-2-ethylhexylphosphoric acid), and hexone extractions at varying pH for oxidation-state determinations of Pu.[17] This same group later changed the scheme to substitute PMBP (1-phenyl-3-methyl-4-benzoyl-pyrazol-5-one) for TTA and added a step that included oxidation by dichromate for oxidation-state determinations at pH = 0 in synthetic brine solutions.[18] PMBP was found to be more efficient as an extractant than TTA and was more resistant to decomposition by oxidants such as dichromate. This is shown in Table I.

While chemical separation methods provide a sensitive method for determining the amounts of Pu in solution in a given oxidation state, they give no information about the nature of the solution species. Absorption spectroscopy methods are considered to be one of the most reliable techniques for the detection and characterization of solution species[19,20] and have been widely used for the characterization of actinides in solutions.[21,22] For example, spectra are shown in Figure 1 for Pu^{3+}, Pu^{4+}, PuO_2^{+}, and PuO_2^{2+}.[21] The major absorption peak wavelengths for Pu in the oxidation states of environmental importance are given in Table II. In addition to the identification, the quantity of the solution species can be obtained from the measured absorption peaks through the use of Beer's law.[23]

Unfortunately, conventional absorption spectrometers have detection limits of between 0.01 mM and 1 mM for plutonium,[24] depending on their molar absorptivities, while the solubilities of plutonium solids in aqueous solutions of near-neutral pH are generally 2 or more orders of magnitude less. With the advent of high-powered pulsed lasers in recent years, new laser-based techniques have been developed for measuring very weak sample absorbance.[25] These techniques—photoacoustic spectroscopy (PAS),[26] thermal deflection spectroscopy (TDS),[27] and thermal lensing spectroscopy (TLS)[28]—are referred to as photothermal spectroscopies and are potentially 3 orders of magnitude more sensitive than absorption spectroscopy using conventional spectrometers, while supplying the same information.[29]

Table I: Chemical Separation Methods for Determining Trace Concentrations of Pu(III, IV, V, VI) in Environmental Samples.

	Oxidation-State Distribution	
Method	**Organic Phase**	**Aqueous Phase**
PMBP extraction at pH = 0	(+4)	(+3, +5, +6, p)[a]
PMBP extraction at pH = 0 w/$Cr_2O_7^{2-}$	(+3, +4)	(+5, +6, p)
HDEHP extraction at pH = 0	(+4, +6)	(+3, +5, p)
HDEHP extraction at pH = 0 w/$Cr_2O_7^{2-}$	(+3, +4, +5, +6)	(p)

[a] p = Pu(IV) polymer.
PMBP is 1-phenyl-3-methyl-4-benzoyl-pyrazol-5-one.
HDEHP is di-2-ethylhexylphosphoric acid.

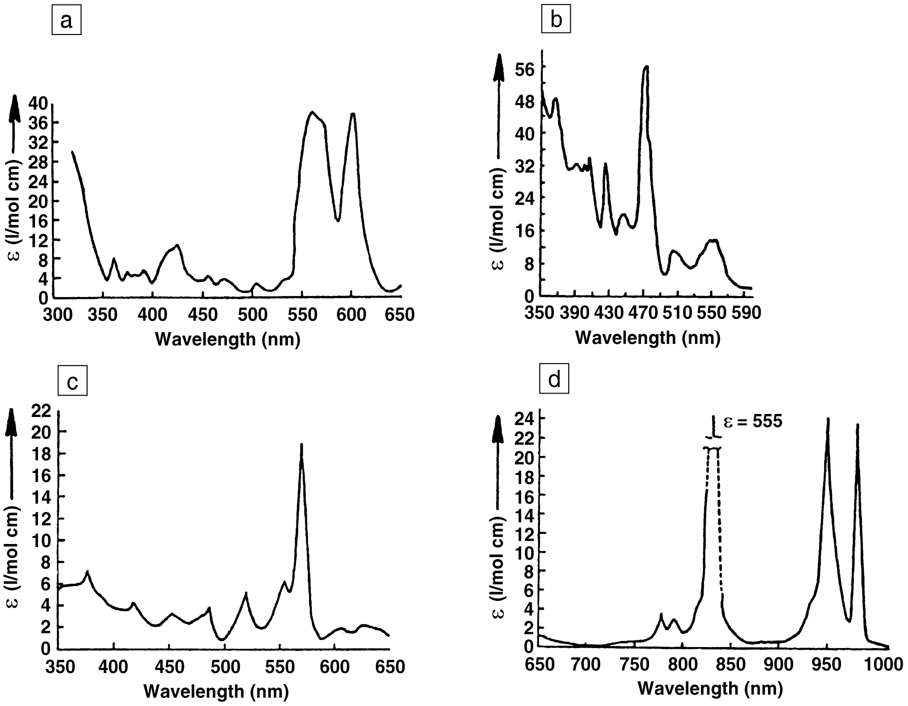

Figure 1. Optical-absorption spectrum of (a) Pu^{3+}, (b) Pu^{4+}, (c) PuO_2^{+}, and (d) PuO_2^{2+}. (From Reference 21.)

The detection limits obtained by PAS for Pu in the oxidation states of environmental importance are given in Table II.

Table II: Optical-Absorption Spectroscopy Parameters for Major Absorption Peaks of Plutonium Ions of Environmental Importance.

Ion	Wavelength (nm)	Molar Absorption (M^{-1} cm^{-1})	Sensitivity (M)	Sensitivity (ppm)
Pu(III)	600	38	1×10^{-7}	0.03
Pu(IV)	470	55	1×10^{-7}	0.03
PuO_2^+	568	19	5×10^{-7}	0.10
PuO_2^{2+}	830	550	1×10^{-7}	0.03

Solid Phases

Important Solid Phases

Precipitation can occur if there is a sufficient concentration of the plutonium in solution to exceed the solubility-product constant for the formation of a solid phase. This effect will limit the amount of the plutonium in solution in the vicinity of the solid phase at any given time and thus will tend to have a retarding effect on the rate of movement of Pu in the environment. In Table III, the compositions of groundwaters taken from a number of sources are shown.[30] The common anions are hydroxide, carbonate, sulfate, phosphate, fluoride, chloride, nitrate, and silicate. Hydroxide, carbonate, sulfate, phosphate, and fluoride form insoluble compounds with all four oxidation states of plutonium, while chloride and nitrate compounds are quite soluble.[31] The silicate compounds of plutonium have not been investigated, however, U^{4+} and U^{6+} form insoluble compounds with silica—for example, coffinite, uranophane, sodium boltwoodite, soddyite, and sodium weeksite[32]—and plutonium would be expected to exhibit similar behavior. The solubilities and solid phases exhibited by Pu in all of the oxidation states possible under environmental conditions have not been investigated. Because of the similarity in the electronic structure[33] and charge to ion size,[34] actinides in a given oxidation state tend to exhibit similar chemical properties, and this effect can be used to estimate plutonium behavior from the known behavior of other actinides.

Identification of Solid Phases

The identification and characterization of solid phases have long relied on the results from the measurement of x-ray powder diffraction patterns of the solids. However, solids obtained under environmental conditions are frequently amorphous and not amenable to this method of analysis. With the availability of third-generation synchrotrons[35] and the development of new fluorescence detectors[36] that can process high count rates, x-ray absorption spectroscopy (XAS) is becoming a powerful technique for studying the speciation of actinides in the environment.[37–39] XAS is particularly useful for investigating noncrystalline and polymeric actinide compounds that cannot be identified by x-ray diffraction analysis. Reports on the use of this technique for the characterization of plutonium solids are rather sparse; however, it has been used to study a number of uranium and neptunium compounds (e.g., see References 40–43).

X-ray absorption near edge structure (XANES) spectroscopy, usually within 50 eV of the adsorption edge, can provide information about the local structure, coordination number, and oxidation state of an actinide in solution, solid form, or at a solution–solid interface.[35] Peak shifts in the spectra with oxidation state are easily detected. Conradson et al. have shown that XANES spectroscopy is an efficient method for determining the oxidation states of Pu in a variety of matrices.[44] An example of plutonium XANES spectra from Reference 44 is shown in Figure 2. The edge energies were observed to shift progressively to higher energy with increasing valence, with an average 1.68-eV increase per formal oxidation-state increase. In addition, the general spectral shape of the (III) and (IV) species was clearly different from the dioxo-containing (V) and (VI) species.

Table III: Composition of Various Natural Groundwaters (from Reference 30).

Analysis	Rainwater	Surface Water[a]	Bedrock Water[b]	YMP[c] J-13 Water	YMP[c] UE-25p#1 Water	Ocean	Mono Lake Brine
Depth (m)	0	0.50	≤500	. . .	. . .	0–20	. . .
Age (yr)	0	≤10	≥100	. . .	. . .	. . .	. . .
pH	4–6	7.3–8.4 (7.9)	7–10	6.9	6.7	8.1	. . .
E_h (V)	0.9	0.0–0.3	−0.05	0.7	0.36	0.8	. . .
O_2 (mg/l)[d]	10	1–10	<0.1	5.7	. . .	≤9	. . .
Na^+	0.3–20	1–20 (12)	10–100[e]	45	171	10,766	22,000
K^+	0.1–4	0.3–8 (4)	1–5	5.3	13.4	399	. . .
Ca^{2+}	0.5–5	2–100 (25)	20–60	11.5	87.8	413	. . .
Mg^{2+}	0.1–0.5	3–30 (10)	15–30	1.76	31.9	1292	. . .
Fe (total)	. . .	0.1–1	5–30	0.04	<0.1	0.02	1
F^-	. . .	≤0.1	0.5–2	2.1	3.5	1.4	48
Cl^-	0.1–20	0.5–90 (10)	5–50[e]	6.4	37	19.353	. . .
Br^-	. . .	. . .	. . .	. . .	. . .	67	. . .
CO_3^{2-} (total)[e]	≤1	60–200	5–400	118–143	960	~140	28,300
NO_3^-	0.1–4	≤10	<1	10.1	<0.1	<0.7	. . .
PO_4^{3-} (total)	0	≤0.1	≤0.1	. . .	. . .	≤0.1	20
SO_4^{2-} (total)[f]	≤20 (1–5)	3–300 (20)	1–15	18.1	129	2712	8300
SiO_2 (total)	0	3–15	5–30	66	66	0.01–7	. . .
SH^- [g]	0	0	<1	. . .	. . .	<0.05	. . .
NH_3 [g]	<0.5	<0.1	<0.5	. . .	. . .	<0.05	. . .
Organic carbon	. . .	1–50	<1	0.15	. . .	~1	. . .

[a] Lakes, rivers, and shallow wells; typical values within parentheses.
[b] Swedish granite.
[c] Yucca Mountain Project (Nevada) wells.
[d] All concentrations in mg/l.
[e] Mainly as HCO_3^-.
[f] For relict water, the value may be 500–3000 mg/l.
[g] SH^- and NH_3 only occur in reducing waters ($E_h < 0$), except for surface waters in industrial areas.

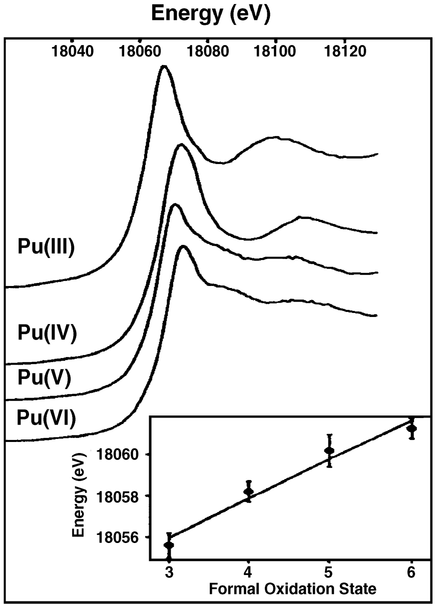

Figure 2. X-ray absorption near edge structure (XANES) spectra for aqueous Pu^{3+}, Pu^{4+}, PuO_2^{+}, and PuO_2^{2+}. Reprinted from Reference 44 with permission of Elsevier Science.

Extended x-ray absorption fine structure (EXAFS) spectroscopy gives additional information on coordination numbers and bond lengths to first, second, and even more distant neighbor atoms.[35,45] This information is very useful for understanding the chemical state, bonding, and bond lengths of actinide related to (1) speciation and complexation studies in aqueous and nonaqueous solutions; (2) adsorption processes at solid–solution interfaces involving minerals, mineral assemblies, rocks, and soils; and (3) adsorption and incorporation of radionuclides in microorganisms and other biological materials. Conradson has recently reported on the study of the Pu–O bonding in Pu(IV) colloid and dioxide.[45]

Aqueous Species

A number of inorganic and organic ligands that can form complexes with plutonium ions in solution may be present in groundwater. The charge of the solution complex can vary widely. Complexation tends to increase the amount of plutonium in solution and thus increase migration rates. This represents an important path for the migration of actinides in the environment.

Inorganic and Organic Complexes

The inorganic ligands in groundwater responsible for the complexation of plutonium are the same ones discussed under precipitation, namely, hydroxide, carbonate, sulfate, phosphate, chloride, fluoride, nitrate, and silicate. Complexation can occur with more than one ligand or plutonium ion, so several species may be associated with a given ligand.

In addition to the inorganic ligands in groundwater, there are naturally occurring organic ligands that can complex plutonium rather strongly and could affect plutonium transport. The interaction of plutonium ions with environmental organic material such as anthropogenic and natural dissolved organics and microbes is complex. These substances can also form colloids and therefore contribute to the formation of actinide pseudocolloids. The transport of organic actinide complexes, especially with EDTA (ethylenediaminetetracetic acid), was observed at ORNL and at Maxey Flats Disposal Site in Kentucky.[46,47]

Humic and fulvic acids were identified as the most important natural organic ligands.[48–52] They are ubiquitous to natural waters and range in concentration from 1 ppm at the ocean's surface, to 5 ppm in surface waters, to 50 ppm in dark-brown swamps.[53] Their names are derived from their method of isolation. Humic and fulvic acids are the alkaline-soluble fraction of soils, leaving behind insoluble humin. Acidification of this extract to pH 2 precipitates humic acid, and fulvic acid remains in solution. Humic and fulvic acids are polyelectrolytes with molecular weights ranging from 1000 amu to more than 10,000 amu, and from 500 amu to 2000 amu, respectively.[54] Their constitution, and thus their functionality toward metal actinide binding, depends very much on their origin. Although no two humic acids are completely alike, they all have in common many structural elements that can coordinate with plutonium. A proposed structure, representative for humic acids, is shown in Figure 3.[55]

Microbial Interaction

Microbes in soil, sediment, and water can have a significant influence on the plutonium source term. They exhibit the highest biodiversity of any living organism and sometimes can adapt quickly to changing living conditions.[56–58] Certain strains can even survive under harsh environmental conditions such as low or high temperature, high pressure, highly acidic and basic media, and high-radiation fields.[59–61] Compared with processes involving inorganic constituents, relatively little is known about bacterial interaction with plutonium. Several comprehensive reviews of the current understanding are available in the literature.[62–67]

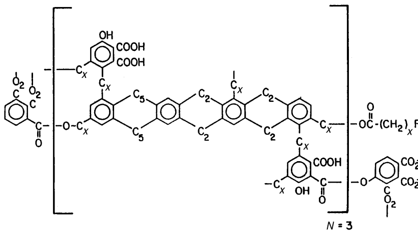

Figure 3. Hypothetical structural relationships in aqueous humic material based on degradation products of permanganate. (From Reference 55.)

Actinides may be stabilized or precipitated either by enzymatic and direct or indirect microbial action. The chemical form of the actinide, the presence of electron acceptors and donors, and the environmental condition play important roles in the type, rate, and magnitude of microbial activity. Redox conditions influence the solubility of actinides. Enzymatic reduction from a higher to a lower, less soluble oxidation state can occur. Microbes can produce extracellular chelating agents in response to a low availability of soluble iron. Siderophores, low-molecular-weight iron chelators, were identified to have a very high complexation affinity for Pu(IV), U(IV), U(VI), and Th(IV), and were shown to solubilize PuO_2.[68–71] Tetravalent actinides are bound preferentially because their charge-to-radius ratios are similar to Fe(III). Panak and co-workers have shown that the uptake of UO_2^{2+} by strains of the bacteria *Thiobacillus ferrooxidans* is primarily through the formation of stable inner-sphere complexes with the biomass.[72] These authors have also shown that the bacteria can oxidize Fe^{2+} to Fe^{3+}, and the Fe^{3+} can in turn oxidize U^{4+} to UO_2^{2+}, thus solubilizing the UO_2.[72,73] UO_2^{2+} can also be reduced by sulfur-reducing bacteria with subsequent precipitation of less soluble U^{4+} compounds.[73]

Identification of Solution Species

Complexation or colloid formation produces changes in the optical-absorption spectra that can frequently be used to identify the complex species or detect colloid formation. In the spectra of Pu^{4+}, the absorption wavelength of the uncomplexed hydrated ion is shifted from 470 nm to 486 nm with the formation of carbonate complexes. Because the concentrations of both complexed and uncomplexed species can be obtained from an analysis of the absorption spectra, this method is frequently used to measure complex-formation constants of actinides, for example, the carbonate complexation of Pu(IV)[74] and Pu(V).[75]

XAS is a new and powerful method for the study of the nature of solution species.

Not only can species be identified and thermodynamic constants evaluated, but bond strengths and distances to near neighbors can also be calculated. The structures of the aqueous nitrate complexes have been studied by EXAFS as a function of nitrate concentration.[76] The Pu was shown to be highly coordinated (coordination numbers of 11–12) for the first shell of oxygen nearest neighbors. The average plutonium–oxygen (nitrate) bond length was found to be 2.49 Å, and the average plutonium–oxygen (water) bond length was estimated to be 2.38 Å. EXAFS has also recently been utilized for the investigation of the chloride complexation of several actinides, including Pu^{3+}.[77] At low chloride concentrations, a hydration number of 10.2 and chloride bond length of 2.51 Å were found for Pu^{3+}. This ion showed a decrease in the hydration number (40%) and no inner-sphere complexation for chloride concentrations <14 M. A number of U(VI) inorganic and organic complexes have been investigated via EXAFS.[78–81]

Adsorption Processes

The plutonium ions may attach themselves to mineral or rock surfaces in contact with the aqueous phase. This process is similar to the precipitation process since it removes plutonium ions from solution. Thus, this process tends to reduce the concentration of plutonium ions in solution and produce a retarding effect on the migration rate. Plutonium ions in groundwater can attach themselves reversibly or irreversibly onto rock or mineral surfaces, solids, and sediments. According to Stumm and Morgan,[82] this adsorption process may result from short-range chemical forces (e.g., covalent bonding, hydrophobic bonding, and hydrogen bridges). These processes are frequently irreversible, for example, precipitation of a solid phase. Sorption may also result from long-range forces, (i.e., electrostatic and van der Waals attractions). Electrostatic adsorption is frequently rapid and reversible (e.g., ion-exchange reactions).

Identification of Surface Species

The so-called surface-complexation, or site-binding, model has been successfully used to describe the adsorption reactions of solution species on solid structures.[83–85] The disadvantage of this model is the difficulty in experimentally determining the model parameters and surface-reaction constants for a given solute. Usually, a set of surface reactions and species are proposed based on the knowledge of the solution speciation of the solute. The reaction constants for the proposed reactions are then derived by fitting computer-calculated adsorption curves using the model to experimental data.[86,87] Because this process typically involves a large number of potentially adjustable parameters, it is likely to lead to nonunique parameter-fitting and does not always lead to consistent sets of parameters for the same systems. However, recently XAS has been applied to the characterization of the adsorbed species and surface reactions,[88–90] and a direct determination of the sorbed species and surface reactions appears possible. The information that can be obtained by this method includes the mode of sorption (inner- or outer-sphere complexes or precipitation: mono-, bi-, or tridentate binding), the structure of the surface complex or precipitate (monomers, dimers, and/or more complex hydroxo-bridged metal-ion oligomers), and the composition of the surface complex or precipitate.[91]

Colloids

Plutonium ions can form or become associated with colloidal-sized particles. This represents another means for transmitting actinides through the geosphere. Plutonium in this form will not behave like a dissolved species and may exhibit considerably different migration behavior than the dissolved species. Depending on the nature of the colloid and the solution conditions, this process may enhance or retard migration of the plutonium. The role of colloids in facilitating actinide transport is far from clear; however, greatly enhanced transport of plutonium associated with colloids over that predicted for ionic species has been observed. At a site at Los Alamos, plutonium and americium were detected in monitoring wells over a mile away from a liquid-waste source and found by ultracentrifugation to be present as colloids.[92] The results of an actinide analysis of samples taken from an artificial, oligotrophic lake in northwest Wales, which was used as a source of cooling water for a nuclear-power plant, showed $^{239,240}Pu$ concentrations in the range of 6.4–12.5 fCi/l and associated primarily with colloidal-sized particles.[93] Recently, Kersting and co-workers have reported detecting $^{239,240}Pu$ in groundwater samples taken from aquifers at the Nevada Test Site.[94] The $^{240}Pu/^{239}Pu$ isotope ratio of the samples established that an underground nuclear test 1.3 km north of the sample site was the origin of the plutonium. The plutonium was found to be associated with colloidal-sized particles.

Depending on their size and charge relative to the surrounding porous media, colloids can move more rapidly or more slowly than the average groundwater velocity.[95,96] The sign and magnitude of the electrical charge of a colloid, the ζ potential, generally is a function of the pH of the solution, and there is a specific pH where they are uncharged. When uncharged particles pass through a porous media or thin fracture, they are usually transported without retention by convection and diffusion due to Brownian motion. The water velocity distribution is generally parabolic, the maximum velocity at the center being about two times the average velocity of the water.[95,96] Particles will randomly sample this velocity variation, but will not reach the walls due to their size. Therefore, their average velocity will be greater than the average groundwater velocity; the larger colloids will travel more rapidly than the smaller ones. If the colloids have the same charge as the surrounding media, repulsion will tend to increase the colloids' relative velocity even more as they are kept even further away from the walls and will tend to inhibit wall adsorption. In addition, colloid particles that are larger than some pore diameters will be excluded from passage through them and experience a shorter overall path length (size exclusion) and, again, an apparent higher velocity than the average water velocity. If the particles have a charge that is opposite that of the surrounding surfaces, retention mechanisms (wall absorption) will decrease the particle velocity relative to that of the groundwater. Failure to account for colloid formation and transport could lead to serious underestimations of the rate of transport of plutonium contaminants in the environment.

Summary and Outlook

In this article, a number of major sources and interaction processes for environmental contamination with plutonium have been outlined. While emphasis has been on laboratory studies, we should grasp the opportunity to study the contaminated sites, not merely assess their level of contamination, in order to gain a better understanding of actinide behavior in these more complex systems, which even the most sophisticated laboratory experiments cannot accurately simulate. The contaminated sites can be used as anthropogenic analogues that should aid us to better identify and prioritize the immobilization and remobilization processes. Field measurements should guide the design of laboratory experiments, and in turn, the understanding that is gathered in the laboratory should be used in directing the field measurements. This is an iterative process, and it should aid in designing more complex laboratory experiments that still can be described by first principles. Once the relatively simple but already complex laboratory system is understood, a new component can be added to it, and the influence of this added component on the overall system can be determined.

Future directions should focus on the development of a better understanding of the plutonium sorption processes at the molecular level through improvements in the detection limits of existing methods, for example, x-ray absorption spectroscopy and laser-based spectroscopic techniques, and the development of new techniques. This will include the development of lower detection limits for the measurement of plutonium speciation in real systems.

In order to provide a better understanding of environmental plutonium behavior, the research disciplines involved need to work more closely together. Actinide chemists, materials scientists, geochemists, soil scientists, mineralogists, microbiologists, physicists, and other pertinent scientists need to form multidisciplinary teams that are able to go beyond the borders of their individual disciplines. Only then will we be able to identify and better understand the major transport-controlling phenomena for plutonium migration in the environment. Accepting this challenge will contribute to better, more efficient, and possibly cheaper remediation and cleanup methods, as well as secure a bright and very interesting future for actinide materials chemistry.

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