Actinide Science: Fundamental and Environmental Aspects

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Nuclear test explosions and reactor wastes have deposited an estimated 16×10^{15} Bq of plutonium into the world's aquatic systems. However, plutonium concentration in open ocean waters is orders of magnitude less, indicating that most of the plutonium is quite insoluble in marine waters and has been incorporated into sediments. Actinide ions in waters often are not in a state of thermodynamic equilibrium and their solubility and migration behavior is related to the form in which the nuclides were introduced into the aquatic system. Actinide solubility depends on such factors as pH(hydrolysis), E_H(oxidation state), reaction with complexants (e.g. carbonate, phosphate, humic acid, etc.), sorption to surfaces of minerals and/or colloids, etc., in the water. The most significant of these variables is the oxidation state of the metal ion. The simultaneous presence of more than one oxidation state for some actinides (e.g. plutonium) in a solution complicates actinide environmental behavior. Both $Np(V)O_2^+$ and $Pu(V)O_2^+$, the most significant soluble states in natural oxic waters are relatively noncomplexing and resistant to hydrolysis and subsequent precipitation but can undergo reduction to the Pu(IV) oxidation state with its different elemental behavior. The solubility of NpO_2^+ can be as high as 10^{-4} M while that of PuO_2^+ is more limited by reduction to the insoluble tetravalent species, $Pu(OH)_4$, ($pK_{SP}{\sim}56$). The net solubility of hexavalent UO_2^{2+} in sea water is also limited by hydrolysis; however, it has a relatively high concentration due to formation of carbonate complexes. The insoluble trivalent americium hydroxocarbonate, $Am(CO)_3(OH)$, is the limiting species for the solubility of Am(III) in sea water. Thorium is found exclusively as the tetravalent species and its solubility is limited by the formation of quite insoluble $Th(OH)_4$. The chemistry of actinide ions in the environment is reviewed to show the spectrum of reactions that can occur in natural waters which must be considered in assessing the environmental behavior of actinides. While much is understood about sorption of actinides on surfaces, the mode of migration of actinides in such waters and the potential effects of these radioactive specials on marine biota, much more information is needed for a satisfactory understanding of the behavior of the actinides in the environment.

1. Introduction

Since 1945, over 2×10^{20} Bq of radioactivity have been released into the atmosphere due to nuclear weapons tests. Controlled and uncontrolled releases of radioactivity from nuclear reactor systems amount to a total of 5.3×10^{18} Bq (ca. 2.5% of that from tests). The large majority of the total release has been deposited in the oceans of the world. Plutonium concentration in surface ocean waters is on the order of 10^{-5} Bq/kg, indicating that most of the 16×10^{15} Bq of plutonium estimated to be deposited by nuclear weapons testing has already been incorporated in sea bottom sediments. This is consistent with the estimate that of the 8×10^{14} Bq of plutonium discharged into the Irish Sea from controlled releases of low level waste from the nuclear fuel reprocessing plant at Sellafield, U.K., only about 7% has moved into the Atlantic ocean. These data have led to studies on the nature of actinide sorption, the mode of migration, and the potential effects of these radionuclides on marine biota.

2. Complexation

The actinides form strongly ionic bonds. Such cations are classified as "hard" acids, and interact preferentially with "hard" base complexants containing oxygen and fluorine donors (including the oxygen atoms of water molecules). Binding in aqueous media to softer donor atoms, such as nitrogen, sulfur, etc., occurs via chelation with multidentate ligands, which contain bonds to both the soft donor and hard oxygen donor.

In ionic bonds, the bond strength increases with the effective charge density of the metal, the order of increasing complexation strength of actinide ions is:

$$Na^+ \ll Ca^{2+} < AnO_2^+ < An^{3+} < AnO_2^{2+} < An^{4+} \qquad (1)$$
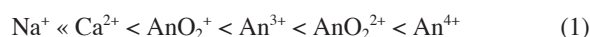
This trend reflects the experimental evaluation of the effective charge density of NpO_2^+ as $+2.2$ and of UO_2^{2+} as $+3.3$.[1]

Electrostatic interaction and steric interference are the primary factors in the structure of the complexes and in the number of water molecules bound in the first coordination sphere of the actinide cation. Observed total coordination numbers in the solid state range from 6 to 12 for simple actinide complexes and from 2 to 8 for dioxo actinide (V) and (VI) compounds. The similarities between lanthanide and actinide aminocarboxylate complexes (formation constants, bonding enthalpies and number of inner sphere waters)[2] and the data for lanthanide complexes in solution indicate that the analogous actinide compounds should have coordination numbers of 8 or 9 for trivalent, An(III),[3] 7 or 8 for tetravalent, An(IV),[4] 4 for pentavalent, An(V)O_2^+, and 6 for haxavalent, An(VI)O_2^{2+} cations.

Actinide cations form inner sphere complexes (anion and cation in direct contact) with strongly negative anions such as humics, carbonate, bicarbonate, sulfate, fluoride, and most carboxylate ligands. Conversely, weaker, outer sphere complexes (anion and cation separated by bridging water molecule) form for actinides with weakly basic ligands such as chloride, bromide, iodide, and perchlorate ions.

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3. Actinide Oxidation States

The variety of oxidation states, Table 1, of the actinide cations, and the simultaneous presence in solution of more than one of these states complicate actinide behavior in solution amd makes it difficult to predict the behavior with changes in E_H, pH, ligand concentrations, etc. For some of the actinides of environmental interest, (e.g. Am(III), Cm(III), Th(IV)) only one oxidation state is formed. Uranium is in the tetravalent state in reducing waters and in the hexavalent state in oxidizing waters. In oxic waters, neptunium is found in the pentavalent state as NpO_2^+ unless the solution is strongly oxidizing when NpO_2^{2+} forms.[5] Plutonium may exist in several oxidation states, from IV through VI, in solution. Trivalent plutonium is present only in anoxic or strongly acidic waters. The dominant soluble specie of plutonium in natural aerobic waters is PuO_2^+.[6-10] Reduction of PuO_2^+ to Pu(IV) due to the insolubility of $Pu(OH)_4$ is a major factor in plutonium behavior in environmental waters. Under reducing conditions and in the presence of enhanced levels of organics, Pu(III) is the dominant state and is often complexed to humics.[11-15] In surface ocean waters both $Pu(V)O_2^+$ and Pu^{4+} forms have been reported.[16, 17] However, the concentration of "dissolved" Pu(IV) measured is very dependent on the size of the filters used, indicating that most of the reported "dissolved" Pu(IV) in natural waters is in colloidal form.

TABLE 1: Available Actinide Oxidation States* in Sea Water, pH = 8.2, I = 0.7m

Actinide	Oxidation State
Th	**IV**
U	IV, **VI**
Np	IV, **V**, VI
Pu	III, **IV**, **V**, VI
Am	**III**
Cm	**III**

*The most common oxidation states denoted in bold

The concentrations of the different oxidation states of actinides are dependent on pH, E_H, and the presence of suspended particulates. Each actinide oxidation state has different chemical behavior, complicating prediction of the geochemical behavior. In general, increasing pH and/or E_H favors higher oxidation states. Also, the plutonium redox behavior may be affected by photolytic peroxide formation at organic and inorganic surfaces.[4] The reduction potentials of U, Np and Pu at pH 0, 8, and 14 are presented in Figure 1.
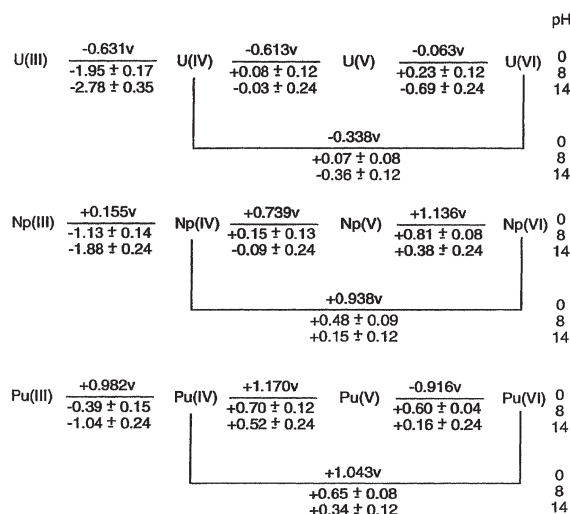
Figure 1. Redox potentials of U, Np and Pu at pH = 0, 8, and 14.

4. Environmental Species

The environmental behavior of the actinide species is dependent on whether the actinides are injected in the environment as source-dependent or source-independent species.[16a] The oxides of uranium and plutonium formed in the very high temperature weapon explosions are highly refractory oxides which do not react with the surrounding media but remain in the forms in which they are injected into the environment, usually as solid particles, for long periods of time. Over this period of time, these refractory "source specific" species are modified to become "source independent" species whose behavior is dependent on the conditions of the ecosystem in which they exist. Source independent species not only originate from the release of nuclides which are originally source-dependent but, also, include actinides and other radionuclides released into natural waters from nuclear processing plants, laboratory research, etc. which are never in a refractory form. The kinetics of these source independent species are sufficiently rapid that either an equilibrium, or, a steady state model, can describe their behavior over time. Development of a useful geochemical database for prediction of the behavior for such source-independent actinide species has been a major goal in research on actinide environmental behavior.

5. Solubility, Hydrolysis and Carbonate Complexation

Actinide solubility depends on such factors as pH, E_H, reaction with complexants (e.g. carbonate, phosphate, humic acid, etc.), sorption to surfaces of minerals and/or colloids, etc., in the water.[18-20] Table 2 lists some techniques for oxidation state measurements and their sensitivities. Actinide cations have strong ion–dipole interaction with water molecules and binding of water of hydration extends beyond the first hydration sphere. The total hydration is dependent on the effective charge of the actinide cation and the number of coordination sites not occupied by ligands.

TABLE 2: Approximate Detection Limits of Actinides in Oxidation State Speciation

Technique	Approximate Detection Limits
Nuclear Magnetic Resonance	$10^{-1} - 10^{-4}$ M
X-ray Absorption Spectroscopy	$10^{-1} - 10^{-4}$ M
Visible Absorption Spectroscopy	$\geq 10^{-5}$ M
Laser-Induced Photoacoustic Spectroscopy	$10^{-5} - 10^{-9}$ M
Laser-Induced Thermal Lensing Spectroscopy	$10^{-5} - 10^{-9}$ M
Time-Resolved Laser Fluorescence Spectroscopy	$10^{-5} - 10^{-9}$ M

Techniques to determine oxidation state of actinides and their concentration sensitivities.

In carbonate-free environments, $Am(OH)^{2+}$ and $Am(OH)_2^+$ form the major species of Am(III) at pH 8.2, in carbonate-rich waters, $Am(CO_3)^+$, $Am(CO_3)_2^-$, and $Am(OH)_2^+$ are significant components. Because of the strong sorption characteristics of the hydroxyl species, americium is sorbed onto colloids, sediments and humics. The OECD–NEA[21] has reviewed americium hydrolysis while general actinide hydrolysis has been reviewed by Fuger[22] and Rizkalla and Choppin.[23] The speciation of soluble Am(III) in sea water is given in Figure 2.

Hydrogen peroxide has been shown to be a reducing agent in sea and natural waters for the higher oxidation states of plutonium.[24] The reduction of plutonium in natural waters can result from the photolytic formation of peroxide from the organics present. Tracer level Pu(VI) in organic-free synthetic sea water at pH 8 has been shown to be reduced to Pu(V) in
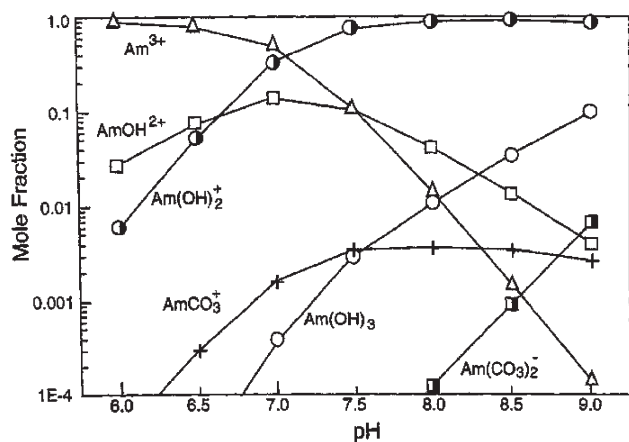
Figure 2. Speciation of Am(III) in sea water as a function of pH.

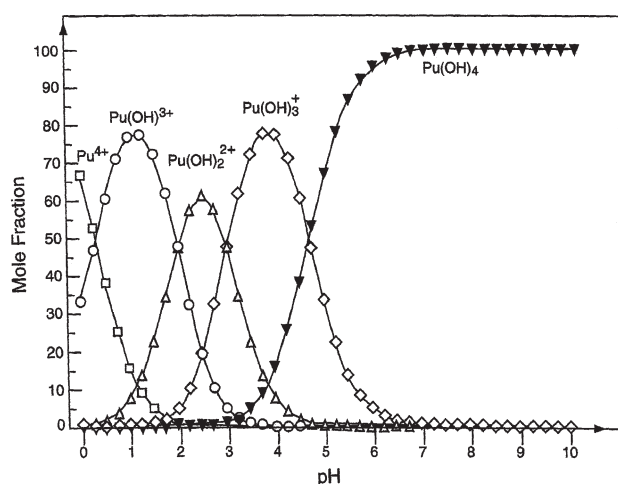**Figure 4.** Speciation of U(VI) O_2^{2+} as a function of pH in oxic waters.

Figure 3. Pattern of hydrolysis of Pu(IV) as a function of pH in oxic waters.

only a few minutes. Reduction of Pu(V) has a slower rate due to the weak tendency of pentavalent plutonium to complex or react with other components of the solution.[25]

Thorium(IV) is capable of forming both mono-and polymeric hydrolysis products. In dilute solution ($\leq 10^{-4}$ M), as the pH increases above 2, the species, $Th(OH)^{3+}$, $Th(OH)_3^+$ and, at higher pH, $Th(OH)_4$ were identified.[26, 27] An(IV) cations do not form carbonate complexes in significant levels as hydrolysis is a stronger dominant reaction, leading to the very insoluble An(OH)$_4$ species. Figure 3 shows the pattern of hydrolysis of Pu(IV) as a function of pH.

The pentavalent cation AnO_2^+ comprises ca. 95% of the total concentration of soluble neptunium and plutonium in solutions with carbonate concentrations $\leq 10^{-4}$ M. The solubility of NpO_2^+ may be as high as 10^{-4} M,[28] while the solubility of PuO_2^+, $10^{-8} – 10^{-6}$ M, is limited by the formation of the insoluble tetravalent species, $Pu(OH)_4$, (pK_{SP} ~56). Pentavalent neptunium hydrolyzes in solutions with pH > 9. In waters where $[CO_3^{2-}] \geq 10^{-4}$ M, $NpO_2(CO_3)^-$, $NpO_2(CO_3)_2^{3-}$, and $NpO_2(CO_3)_3^{5-}$ species may be present. For more complete data of neptunium carbonate complexation, see References 29–31. The stability of NpO_2^+ makes it very useful as a chemical analogue for PuO_2^+. The redox potential of Pu(V) – Pu(IV) and the strong hydrolysis of Pu (IV) limits the concentration of PuO_2^+ in marine and natural waters.

Study of uranyl (VI) hydrolysis is complicated by the formation of polymeric species. In concentrations below 10^{-6} M, $UO_2(OH)^+$ is the dominant hydrolysis species in solution while above this concentration, polymeric forms such as $(UO_2)_2(OH)_2^{2+}$, $(UO_2)_3(OH)_4^{2+}$ and $(UO_2)_3(OH)_2^{4+}$ and $(UO_2)_3(OH)_5^+$ form.[32] Carbonate complexes are estimated to account for 90 – 100% of the urani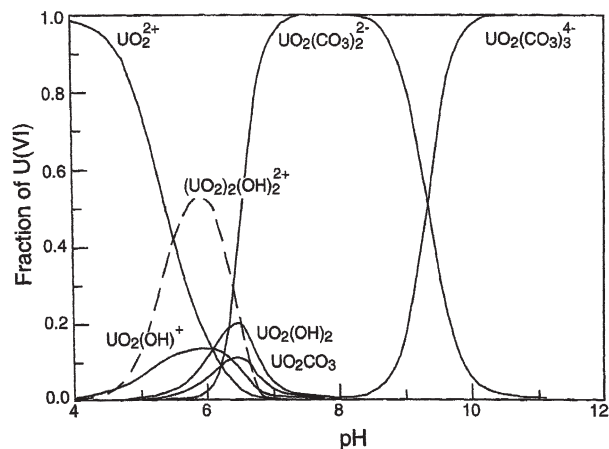um dissolved in ocean waters.[33] Uranyl carbonate complexes exist as UO_2CO_3, $UO_2(CO_3)_2^{2-}$, and $(UO_2)(CO_3)_3^{4-}$ and are discussed in the literature.[32, 34] Kinetics of exchange and activation parameters have been studied by ^{13}C NMR.[35, 36] Figure 4 presents the speciation of UO_2^{2+} as a function of pH.

6. Role of Organics

An important factor in actinide redox and complexation environmental behavior is the effects of organics in aquatic systems. Of particular interest is the role of humic acids since these are ubiquitous in natural waters, including sea water. The size of humics in sea water and other natural waters normally falls in the range of colloidal particles. As the dissolved organic carbon content increases the concentration of plutonium in the aqueous phase usually decreases due to reduction of PuO_2^+ to hydrolyzed, insoluble Pu(IV) by the humics. Addition of $An(V)O_2^+$ and $An(VI)O_2^{2+}$ to solutions of humic acids has shown that the humics reduce the plutonium fairly rapidly to the tetravalent state at which point hydrolysis occurs.[37] The hydrolytic product may precipitate or sorb to solids or to colloidal species. Colloids in sea water generally are usually carbonate or oxide mineral systems; however, in many cases, they have a surface coating of humic acid (pseudo-colloids). Colloids of this latter type sorb the hydrolyzed species even more strongly than simpler colloid systems.

To summarize the role of humics, humic interactions with actinides include redox activity, coulombic attraction due to the net anionic charge of the humic (condensation binding), and direct site-specific binding to the humics. The existence of these two types of binding, accompanied by the different dissociative kinetic rates requires that predictive models for actinides in marine and natural waters incorporate both kinetic and thermodynamic behavior. The source specific nature of humics complicates significantly the characterization of actinide-humic interactions.

7. Sorption

Since carbonate anions form strong complexes with actinides in solution, carbonate minerals can be expected to provide excellent surfaces for actinide sorption. The important role of sorption in actinide immobilization and transport has been discussed by many authors.[38–40] As actinide sorption is influenced by the charge of the cations as well as by steric effects, sorption strength follows the same trend as complexation. In neutral and basic media, actinides interact with hydroxyl moieties of polysilicic acid, hydrated iron oxides, as well as the surface hydroxyl groups of colloidal materials.

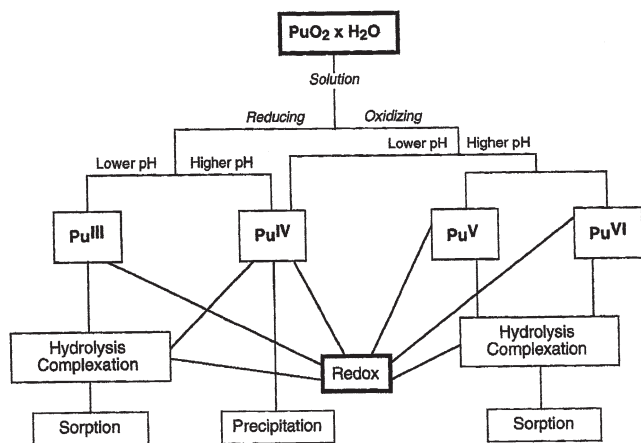Particles may have net positive or negative surface charges

Figure 5. Schematic of behavior of plutonium in natural waters.

depending on the pH. For a more complete discussion of surface charge models the reviews of Silva and Nitsche[21] and Stumm and Morgan[41] are recommended.

$Am(OH)_3$ sorbs readily to many types of surface. Am(III) sorption[42] onto calcite and aragonite surfaces is both rapid and extensive, and less than 1% could be desorbed readily. Americium(III) is more extensively sorbed onto aragonite compared to calcite, although both minerals consist of $CaCO_3$. The preference for aragonite was attributed to competition by Mg^{2+} for aragonite binding sites, resulting in suppression of Am sorption.

NpO_2^+ and UO_2^{2+} sorb very weakly onto colloids. Keeney-Kennicutt and Morse[5] report that NpO_2^+ sorbs onto marine carbonate sediment irreversibly; however, NpO_2^+ sorbs less strongly onto minerals other than carbonates[37] and organics.[43]

Plutonium sorbs more extensively, by several orders of magnitude, in the (III) and (IV) oxidation states than in the higher V and VI states.[8] In the Baltic Sea, 99% of the total plutonium inventory sorbs onto sediment as Pu(IV),[19] consistent with observations that Pu sorbed onto coastal soils along the Irish Sea exists exclusively as Pu(IV).[44] Because of the strong affinity of $Pu(OH)_4$ for sediments and suspended particulates, Pu(IV) sorption is the limiting factor in Pu transport processes.[4] Figure 5 summarizes the behavior of plutonium in natural waters.

8. Summary

The chemical state of actinide elements released to the environment, combined with the complexity and diversity of their environment behavior, creates difficulties in modeling their behavior over the lifetime of their radioactivity. Some of that diversity and the associated problems in assessing their behavior over long periods have been addressed in this paper. Much progress has been made in our understanding of the environmental behavior of actinides but much remains a challenge to understand in order to predict their future safety in repositories.

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