

5.6 Plutonium Geochemistry and K_d Values

5.6.1 Overview: Important Aqueous- and Solid-Phase Parameters Controlling Retardation

In the ranges of pH and conditions typically encountered in the environment, plutonium can exist in all 4 oxidation states, namely +3, 4, +5, and +6. Under oxidizing conditions, Pu(IV), Pu(V), and Pu(VI) are common, whereas, under reducing conditions, Pu(III) and Pu(IV) would exist. Dissolved plutonium forms very strong hydroxy-carbonate mixed ligand complexes, therefore, its adsorption and mobility is strongly affected by these complex species. Under conditions of low pH and high concentrations of dissolved organic carbon, it appears that plutonium-organic complexes may be control adsorption and mobility of plutonium in the environment.

If plutonium is present as a distinct solid phase (amorphous or partly crystalline $\text{PuO}_2 \cdot x\text{H}_2\text{O}$) or as a solid solution, the upper limits of aqueous plutonium concentrations would be in the 10^{-12} to 10^{-9} M range. Dissolved plutonium in the environment is typically present at $\leq 10^{-15}$ M levels indicating that adsorption may be the principal phenomenon that regulates the mobility of this actinide.

Plutonium can adsorb on geologic material from low to extremely high affinities with K_d values ranging from 11 to 300,000 ml/g. Plutonium in the higher oxidation state adsorbed on iron oxide surfaces may be reduced to the tetravalent state by Fe(II) present in the iron oxides.

Two factors that influence the mobilization of adsorbed plutonium under environmental pH conditions (>7) are the concentrations of dissolved carbonate and hydroxyl ions. Both these ligands form very strong mixed ligand complexes with plutonium, resulting in desorption and increased mobility in the environment.

5.6.2 General Geochemistry

Plutonium is produced by fissioning uranium fuel and is used in the construction of nuclear weapons. Plutonium has entered the environment either through accidental releases or through disposal of wastes generated during fuel processing and the production and detonation of nuclear weapons. Plutonium has 15 isotopes, but only 4 of these isotopes namely, ^{238}Pu [$t_{1/2}$ (half life) = 86 y], ^{239}Pu ($t_{1/2}$ = 24,400 y), ^{240}Pu ($t_{1/2}$ = 6,580 y), ^{241}Pu ($t_{1/2}$ = 13.2 y), are of environmental concern due to their abundances and long-half lives.

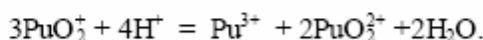
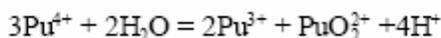
In the range of pH and redox conditions typically encountered in the environment, plutonium can exist in 4 oxidation states, namely +3, +4, +5, and +6 (Allard and Rydberg, 1983). Plutonium oxidation states are influenced by factors such as pH, presence of complexants and reductants, radiolysis, and temperature (Choppin, 1983). Observations indicate that under very low plutonium concentrations and oxidizing environmental conditions, the disproportionation¹ reactions of plutonium are not significant (Cleveland, 1979). Under reducing conditions, Pu(III) species would be dominant up to pH values approaching about 8.5, beyond which the Pu(IV) species are known to be the dominant species. However, under oxidizing conditions and at pH values greater than 4.0, plutonium can exist in +4,+5, and +6 oxidation states (Keeney-Kennicutt and Morse, 1985). A number of investigators believe that under oxidizing conditions, the +5 state to be the dominant redox state (Aston, 1980; Bondietti and Trabalka, 1980; Nelson and Orlandini, 1979; Rai *et al.*, 1980b).

Of the contaminated sites considered in EPA/DOE/NRC (1993), radioactive contamination by ^{238}Pu , ^{239}Pu , and/or ^{240}Pu has been identified at 9 of the 45 Superfund National Priorities List (NPL) sites. The reported contamination includes airborne particulates, plutonium-containing soils, and plutonium dissolved in surface- and groundwaters.

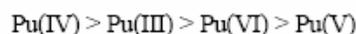
5.6.3 Aqueous Speciation

Dissolved plutonium forms complexes with various inorganic ligands such as hydroxyl, carbonate, nitrate, sulfate, phosphate, chloride, bromide, and fluoride; with many naturally occurring organic ligands such as acetate, citrate, formate, fulvate, humate, lactate, oxalate, and tartrate; and with

¹ Disproportionation is a chemical reaction in which a single compound serves as both oxidizing and reducing agent and is thereby converted into more oxidized and a more reduced derivatives (Sax and Lewis, 1987). For the reaction to occur, conditions in the system must be temporarily changed to favor this reaction (specifically, the primary energy barrier to the reaction must be lowered). This is accomplished by a number of ways, such as adding heat or microbes, or by radiolysis occurring. Examples of plutonium disproportionation reactions are:



synthetic organic ligands such as EDTA and 8-hydroxyquinoline derivatives (Cleveland, 1979). Plutonium(IV) hydrolyzes more readily than all other redox species of plutonium (Baes and Mesmer, 1976). The order of hydrolysis of plutonium redox species follows the sequence



(Choppin, 1983). Plutonium hydrolytic species may have up to 4 coordinated hydroxyls. The tendency of plutonium in various oxidation states to form complexes depends on the ionic potential defined as the ratio (z/r) of the formal charge (z) to the ionic radius (r) of an ion. Among plutonium redox species, Pu(IV) exhibits the highest ionic potential and therefore forms the strongest complexes with various ligands. Based on the equilibrium constants ($K_{r,298}^{\circ}$) for the plutonium complexation reactions, ligands, such as chloride and nitrate, form weak complexes ($\log K_{r,298}^{\circ}$ of 1 to 2) with plutonium, whereas fluoride, sulfate, phosphate, citrate, and oxalate form stronger complexes ($\log K_{r,298}^{\circ}$ of 6 to 30). Among the strongest complexes of plutonium are the hydroxy-carbonate mixed ligand complexes [e.g., $\text{Pu}(\text{OH})_2(\text{CO}_3)_2^{\pm}$] (Tait *et al.*, 1995; Yamaguchi *et al.*, 1994). Additionally, dissolved organic matter (fulvic and humic material) may also form complexes with plutonium. Although the nature of these complexes and their stability constants have not been fully characterized, it is believed that humic complexes of plutonium may be the dominant soluble species in natural environments at lower pH (below 5 to 6) values (Allard and Rydberg, 1983).

Because dissolved plutonium can exist in multiple redox states and form hydrolytic and complex species in solution, it is useful to assess the probable dominant plutonium aqueous species that may exist in typical ground water. Therefore, the aqueous speciation of dissolved plutonium was calculated as a function of pH using the MINTEQA2 code and a concentration of 3.2×10^{-10} mg/l (1.36×10^{-15} M) total dissolved plutonium. This concentration is based on the maximum activity of $^{239,240}\text{Pu}$ measured by Simpson *et al.* (1984) in 33 water samples taken from the highly alkaline Mono Lake in California. The species distribution was calculated assuming that multiple plutonium valence states might be present based on thermodynamic equilibrium considerations. This calculation is dependent on redox conditions as well as the pH and composition of the water. Therefore, a set of oxic conditions that might be associated with surface or near-surface disposal facilities or contaminated sites were selected for these illustrative calculations. These redox conditions are based on an experimentally determined pH/Eh relationship described in Lindsay (1979) for suspensions of sandy loam and distilled water. In a series of acid and base titrations, the pH/Eh response of the soil/water suspension was determined to vary according to the equation

$$pe + pH = 15.23 \quad (5.1)$$

where pe = negative log of the electron activity.¹

¹ The electron activity is defined as unity for the standard hydrogen electrode.

The pe is related to Eh by the equation

$$pe = (2.303RT/F) pe \quad (5.2)$$

where R = universal gas constant (1.9872 cal/mol·K)

T = temperature in degrees kelvin

F = Faraday constant (96,487 coulombs/equivalent).

At 25.0°C (298 K),

$$Eh(\text{mV}) = 5.92 pe \quad (5.3)$$

Using Equations 5.1 and 5.3, an Eh value was calculated for each pH value used as an input for the MINTEQA2 calculations of plutonium aqueous speciation. The plutonium aqueous species that were included in the computation scheme are tabulated in Table 5.10. Thermodynamic data for these species were taken primarily from Lemire and Tremaine (1980) and other secondary sources and database modifications described by Krupka and Serne (1996).

Results are plotted as a species distribution diagram (Figure 5.3). The data show that, under very low pH (~3 - 3.5) conditions, PuF_3^{2+} and PuO_2^+ are the dominant species of plutonium. The free ionic species, PuO_2^+ appears to be the dominant form within the pH range of 4 to 5. Within the pH range of 5.5 to 6.5, the main species of plutonium appear to be PuO_2^+ , and $\text{Pu}(\text{OH})_2(\text{CO}_3)_2^{2-}$, with minor species being the neutral hydrolytic species $\text{Pu}(\text{OH})_4^0(\text{aq})$ and the phosphate complex $\text{Pu}(\text{HPO}_4)_4^+$. At pH values exceeding 6.5, the bulk of the dissolved plutonium (~90 percent) would be comprised of the $\text{Pu}(\text{OH})_2(\text{CO}_3)_2^{2-}$ species with a minor percentage of $\text{Pu}(\text{OH})_4^0(\text{aq})$. These illustrative computations indicate that, under pH conditions that typically exist in surface and groundwaters (>6.5), the dominant form of dissolved plutonium would be the tetravalent complex species, $\text{Pu}(\text{OH})_2(\text{CO}_3)_2^{2-}$.

Polymeric species of plutonium may not occur under environmental conditions because the total plutonium concentrations in nature are at least 7 orders of magnitude less than the concentrations required for the formation of such species (Choppin, 1983). It is important to note that the speciation of plutonium would change significantly with changing redox conditions, pH, the types and total concentrations of complexing ligands and major cationic constituents.

5.6.4 Dissolution/Precipitation/Coprecipitation

Allard and Rydberg (1983) calculated that the aqueous concentrations of plutonium in nature may be controlled by the solubility of the solid phase $\text{PuO}_2 \cdot x\text{H}_2\text{O}$. Many observations show that plutonium associated with soils and particulate organic matter is present in tetravalent oxidation state (Nelson and Lovett, 1980; Nelson *et al.*, 1987; Silver, 1983). Calculations by Allard and Rydberg (1983) based on available thermodynamic data show that, under reducing conditions, the solubility of dissolved

plutonium would be limited by the solid phase PuO_2 at pH values greater than 8, and by the solid phase $\text{Pu}_2(\text{CO}_3)_3$ of trivalent plutonium at lower pH values.

Table 5.10. Plutonium aqueous species included in the speciation calculations.

Redox State	Aqueous Species
Pu(III)	Pu^{3+} , PuOH^{2+} , $\text{Pu}(\text{OH})_2^+$, $\text{Pu}(\text{OH})_3^0(\text{aq})$ PuCO_3^+ , $\text{Pu}(\text{CO}_3)_2$, $\text{Pu}(\text{CO}_3)_3^{2-}$ PuSO_4^+ , $\text{Pu}(\text{SO}_4)_2$ $\text{PuH}_2\text{PO}_4^{2+}$, PuCl^{2+}
Pu(IV)	Pu^{4+} , PuOH^{3+} , $\text{Pu}(\text{OH})_2^{2+}$, $\text{Pu}(\text{OH})_3$, $\text{Pu}(\text{OH})_4^0(\text{aq})$ $\text{Pu}(\text{OH})_4(\text{CO}_3)_2^{4-}$, $\text{Pu}(\text{OH})_2(\text{CO}_3)_2^{2-}$ PuSO_4^{2+} , $\text{Pu}(\text{SO}_4)_2^0(\text{aq})$, PuHPO_4^{2+} , $\text{Pu}(\text{HPO}_4)_2^0(\text{aq})$, $\text{Pu}(\text{HPO}_4)_3^{2-}$, $\text{Pu}(\text{HPO}_4)_4^{4-}$ PuCl^{3+} , PuF^{3+} , PuF_2^{2+} , PuF_3^+ , $\text{PuF}_4^0(\text{aq})$
Pu(V)	PuO_2^+ , $\text{PuO}_2\text{OH}^0(\text{aq})$, $(\text{PuO}_2)_2\text{OH}^+$
Pu(VI)	PuO_2^{2+} , PuO_2OH^+ , $\text{PuO}_2(\text{OH})_2^0(\text{aq})$, $\text{PuO}_2(\text{OH})_3$, $(\text{PuO}_2)_2(\text{OH})_2^{2+}$, $(\text{PuO}_2)_3(\text{OH})_3^+$ $\text{PuO}_2\text{CO}_3^0(\text{aq})$, $\text{PuO}_2(\text{CO}_3)_2^{2-}$, $\text{PuO}_2(\text{CO}_3)_3^{4-}$ PuO_2Cl^+ , PuO_2F^+ , $\text{PuO}_2\text{F}_2^0(\text{aq})$, PuO_2F_3 , $\text{PuO}_2\text{F}_4^{2-}$ $\text{PuO}_2\text{SO}_4^0(\text{aq})$, $\text{PuO}_2\text{H}_2\text{PO}_4^+$

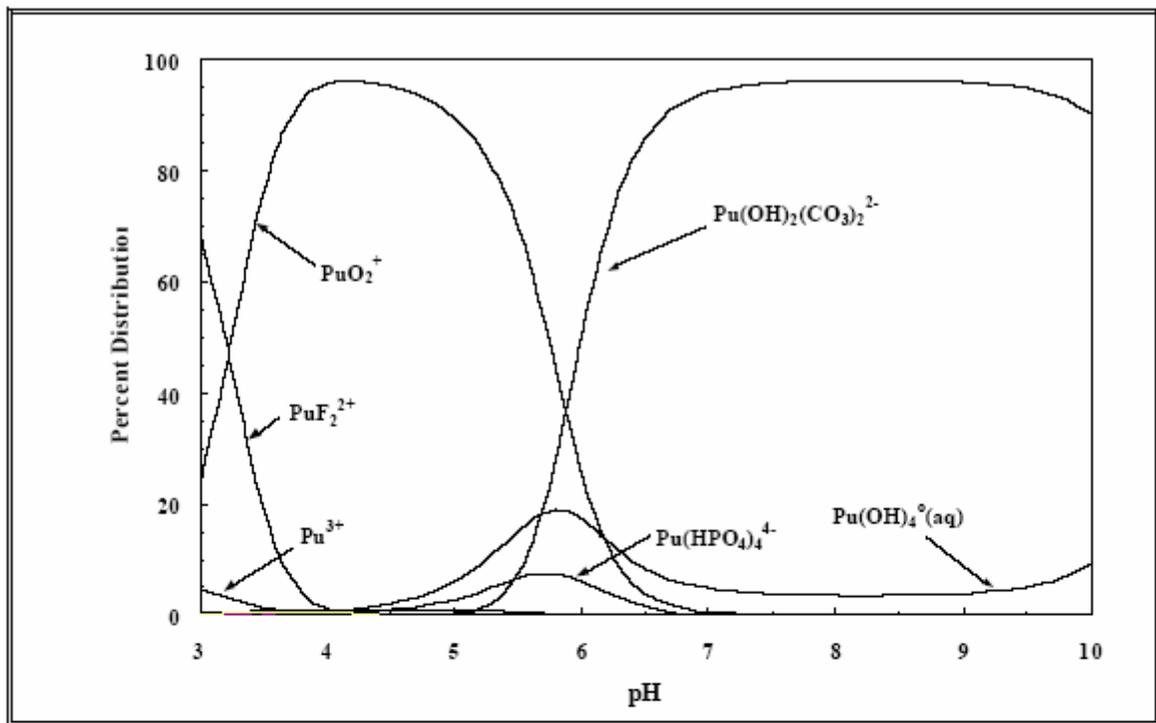


Figure 5.3. Calculated distribution of plutonium aqueous species as a function of pH for the water composition in Table 5.1. [The species distribution is based on a concentration of 3.2×10^{-10} mg/l (1.36×10^{-15} M) total dissolved plutonium.]

Laboratory studies conducted by Rai *et al.* (1980a), Delegard (1987), and Yamaguchi *et al.* (1994) indicated that a freshly precipitated amorphous $\text{PuO}_2 \cdot x\text{H}_2\text{O}$ phase controls the equilibrium solubility of plutonium. Solubility on aged precipitates by Rai *et al.* (1980a) and Delegard (1987) also showed that equilibrium plutonium concentrations would be controlled by a partially crystallized $\text{PuO}_2 \cdot x\text{H}_2\text{O}$ phase at concentrations about 2 orders of magnitude less than that of amorphous $\text{PuO}_2 \cdot x\text{H}_2\text{O}$. Therefore, under oxidizing conditions, amorphous $\text{PuO}_2 \cdot x\text{H}_2\text{O}$, if present in soils, may control soluble plutonium concentrations near 10^{-8} M. Under alkaline conditions with high dissolved carbonate concentrations, dissolved plutonium concentrations may increase to micromolar levels. When dissolved carbonate is not present, $\text{PuO}_2 \cdot x\text{H}_2\text{O}$ may control plutonium concentrations at about 10^{-10} M (Rai *et al.*, 1980a).

5.6.5 Sorption/Desorption

Plutonium is known to adsorb onto soil components such as clays, oxides, hydroxides, oxyhydroxides, aluminosilicates and organic matter. Depending on the properties of the substrate, pH, and the composition of solution, plutonium would adsorb with affinities varying from low ($K_d = 11$ ml/g) to extremely high ($K_d = 300,000$ ml/g) (Baes and Sharp, 1983; Coughtrey *et al.*, 1985; Thibault *et al.*, 1990).

A number of studies indicate that iron hydroxides adsorb and reduce penta- and hexavalent plutonium to its tetravalent state at the solid surface. Experimental data showed that tetra- and pentavalent plutonium aqueous species oxidize to hexavalent form upon adsorption onto manganese dioxide surfaces whereas, pentavalent plutonium adsorbed on goethite disproportionate into tetra and hexavalent forms (Keeney-Kennicutt and Morse, 1985). Subsequently, the hexavalent form of plutonium was observed to have been reduced to tetravalent state. Additionally, these reactions were found to occur faster under light conditions than under dark conditions suggesting photochemical catalysis of adsorbed plutonium redox change reactions.

Laboratory studies have indicated that increasing carbonate concentrations decreased adsorption of tetra- and pentavalent plutonium on goethite surfaces (Sanchez *et al.*, 1985). Phenomenon similar to the reduction and suppression of plutonium adsorption in the presence of carbonate ions have also been observed for other actinides which also form strong hydroxy-carbonate mixed ligand aqueous species. These data suggest that plutonium would be most mobile in high pH carbonate-rich groundwaters.

Some studies indicate that the mass of plutonium retarded by soil may not be easily desorbed from soil mineral components. For example, Bunzl *et al.* (1995) studied the association of $^{239+240}\text{Pu}$ from global fallout with various soil components. They determined the fractions of plutonium present as readily exchangeable, bound to carbonates, bound to iron and manganese oxides, bound to organic matter, and residual minerals. For soils at their study site in Germany, the results indicated that 30–40 y after deposition of the plutonium, the readily exchangeable fraction of plutonium was less than 1 percent. More than 57 percent of the plutonium was sorbed to organic matter and a considerable mass sorbed to the oxide and mineral fractions.

5.11 Uranium Geochemistry and K_d Values

5.11.1 Overview: Important Aqueous- and Solid-Phase Parameters Controlling Retardation

In essentially all geologic environments, +4 and +6 are the most important oxidation states of uranium.

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Uranium(VI) species dominate in oxidizing environments. Uranium(VI) retention by soils and rocks in alkaline conditions is poor because of the predominance of neutral or negatively charged species. An increase in CO_2 pressure in soil solutions reduces U(VI) adsorption by promoting the formation of poorly sorbing carbonate complexes. Uranium(IV) species dominate in reducing environments. Uranium(IV) tends to hydrolyze and form strong hydrolytic complexes. Uranium(IV) also tends to form sparingly soluble precipitates that commonly control U(IV) concentrations in groundwaters. Uranium(IV) forms strong complexes with naturally occurring organic materials. Thus, in areas where there are high concentrations of dissolved organic materials, U(IV)-organic complexes may increase U(IV) solubility. There are several ancillary environmental parameters affecting uranium migration. The most important of these parameters include redox status, pH, ligand (carbonate, fluoride, sulfate, phosphate, and dissolved carbon) concentrations, aluminum- and iron-oxide mineral concentrations, and uranium concentrations.

5.11.2 General Geochemistry

Uranium (U) has 14 isotopes; the atomic masses of these isotopes range from 227 to 240. All uranium isotopes are radioactive. Naturally-occurring uranium typically contains 99.283 percent ^{238}U , 0.711 percent ^{235}U , and 0.0054 percent ^{234}U by weight. The half-lives of these isotopes are 4.51×10^9 y, 7.1×10^8 y, and 2.47×10^5 y, respectively. Uranium can exist in the +3, +4, +5, and +6 oxidation states, of which the +4 and +6 states are the most common states found in the environment.

The mineralogy of uranium-containing minerals is described by Frondel (1958). Uranium in the +4 and +6 oxidation states exists in a variety of primary and secondary minerals. Important U(IV) minerals include uraninite (UO_2 through $\text{UO}_{2.25}$) and coffinite [USiO_4] (Frondel, 1958; Langmuir, 1978). Aqueous U(IV) is inclined to form sparingly soluble precipitates, adsorb strongly to mineral surfaces, and partition into organic matter, thereby reducing its mobility in groundwater. Important U(VI) minerals include camotite [$(\text{K}_2(\text{UO}_2)_2(\text{VO}_4)_2)$], schoepite ($\text{UO}_3 \cdot 2\text{H}_2\text{O}$), rutherfordine (UO_2CO_3), tyuyamunite [$\text{Ca}(\text{UO}_2)_2(\text{VO}_4)_2$], autunite [$\text{Ca}(\text{UO}_2)_2(\text{PO}_4)_2$], potassium autunite [$\text{K}_2(\text{UO}_2)_2(\text{PO}_4)_2$], and uranophane [$\text{Ca}(\text{UO}_2)_2(\text{SiO}_3\text{OH})_2$] (Frondel, 1958; Langmuir, 1978). Some of these are secondary phases which may form when sufficient uranium is leached from contaminated wastes or a disposal system and migrates downstream. Uranium is also found in phosphate rock and lignite¹ at concentrations that can be commercially recovered. In the presence of lignite and other sedimentary carbonaceous substances, uranium enrichment is believed to be the result of uranium reduction to form insoluble precipitates, such as uraninite.

Contamination includes airborne particulates, uranium-containing soils, and uranium dissolved in surface- and groundwaters. Of the contaminated sites considered in EPA/DOE/NRC (1993), radioactive contamination by ^{234}U , ^{235}U , and/or ^{238}U has been identified at 35 of the 45 Superfund

¹ Lignite is a coal that is intermediate in coalification between peat and subbituminous coal.

National Priorities List (NPL) sites and 26 of the 38 NRC Site Decommissioning Site Plan (SDMP) sites.

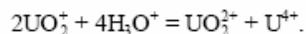
5.11.3 Aqueous Speciation

Because of its importance in nuclear chemistry and technology, a great deal is known about the aqueous chemistry of uranium [reviewed by Baes and Mesmer (1976), Langmuir (1978), and Wanner and Forest (1992)]. Uranium can exist in the +3, +4, +5, and +6, oxidation states in aqueous environments. Dissolved U(III) easily oxidizes to U(IV) under most reducing conditions found in nature. The U(V) aqueous species (UO_2^+) readily disproportionates to U(IV) and U(VI).¹ Consequently, U(IV) and U(VI) are the most common oxidation states of uranium in nature. Uranium will exist in the +6 and +4 oxidation states, respectively, in oxidizing and more reducing environments.

Both uranium species, UO_2^{2+} and U^{4+} , hydrolyze readily. The U^{4+} ion is more readily hydrolyzed than UO_2^{2+} , as would be expected from its higher ionic charge. Langmuir (1978) calculated U(IV) speciation in a system containing typical natural water concentrations of chloride (10 mg/l), fluoride (0.2 mg/l), phosphate (0.1 mg/l), and sulfate (100 mg/l). Below pH 3, UF_2^{2+} was the dominant uranium species. The speciation of dissolved U(IV) at pH values greater than 3 is dominated by hydrolytic species such as $\text{U}(\text{OH})_3^+$ and $\text{U}(\text{OH})_4^0(\text{aq})$. Complexes with chloride, fluoride, phosphate, and sulfate were not important above pH 3. The total U(IV) concentration in solution is generally quite low, between 3 and 30 $\mu\text{g/l}$, because of the low solubility of U(IV) solid phases (Bruno *et al.*, 1988; Bruno *et al.*, 1991). Precipitation is discussed further in the next section.

Dissolved U(VI) hydrolyses to form a number of aqueous complexes. The distribution of U(VI) species is presented in Figures 5.6a-b and 5.7. The distribution of uranyl hydrolytic species (Figures 5.6a-b) was calculated as a function of pH using the MINTQA2 code. The U(VI) aqueous species included in the speciation calculations are listed in Table 5.16. The thermodynamic data for these aqueous species were taken primarily from Wanner and Forest (1992). Because dissolved uranyl ions can be present as polynuclear² hydroxyl complexes, the hydrolysis of uranyl ions under oxic conditions is therefore dependent on the concentration of total dissolved uranium. To demonstrate this aspect of uranium chemistry, 2 concentrations of total dissolved uranium, 0.1 and 1,000 $\mu\text{g/l}$, were used in these calculations. Hem (1985, p. 148) gives 0.1 to 10 $\mu\text{g/l}$ as the range for dissolved uranium in

¹ Disproportionation is defined in the glossary at the end of this letter report. This particular disproportionation reaction can be described as:



² A polynuclear species contains more than 1 central cation moiety, *e.g.*, $(\text{UO}_2)_2\text{CO}_3(\text{OH})_3$ and $\text{Pb}_4(\text{OH})_4^{4+}$.

most natural waters. For waters associated with uranium ore deposits, Hem states that the uranium concentrations may be greater than 1,000 $\mu\text{g/l}$.

In a U(VI)-water system, the dominant species were UO_2^{2+} at pH values less than 5, $\text{UO}_2(\text{OH})_2^{\text{aq}}$ at pH values between 5 and 9, and $\text{UO}_2(\text{OH})_3$ at pH values between 9 and 10. This was true for both uranium concentrations, 0.1 $\mu\text{g/l}$ (Figure 5.6a) and 1,000 $\mu\text{g/l}$ dissolved U(VI) (Figure 5.6b). At 1,000 $\mu\text{g/l}$ dissolved uranium, some polynuclear species, $(\text{UO}_2)_3(\text{OH})_5^+$ and $(\text{UO}_2)_2(\text{OH})_3^{2+}$, were calculated to exist between pH 5 and 6. Morris *et al.* (1994) using spectroscopic techniques provided additional proof that an increasing number of polynuclear species were formed in systems containing higher concentrations of dissolved uranium.

A large number of additional uranyl species (Figure 5.7) are likely to exist in the chemically more complicated system such as the water composition in Table 5.1 and 1,000 $\mu\text{g/l}$ dissolved U(VI). At pH values less than 5, the UO_2F^+ species dominates the system, whereas at pH values greater than 5, carbonate complexes [$\text{UO}_2\text{CO}_3^{\text{aq}}$, $\text{UO}_2(\text{CO}_3)_2^{\text{aq}}$, $\text{UO}_2(\text{CO}_3)_3^{\text{aq}}$] dominate the system. These calculations clearly show the importance of carbonate chemistry on U(VI) speciation. For this water composition, complexes with chloride, sulfate, and phosphate were relatively less important. Consistent with the results in Figure 5.7, Langmuir (1978) concluded that the uranyl complexes with chloride, phosphate, and sulfate were not important in a typical groundwater. The species distribution illustrated in Figure 5.7 changes slightly at pH values greater than 6 if the concentration of total dissolved uranium is decreased from 1,000 to 1 $\mu\text{g/l}$. At the lower concentration of dissolved uranium, the species $(\text{UO}_2)_2\text{CO}_3(\text{OH})_3$ is no longer present as a dominant aqueous species.

Sandino and Bruno (1992) showed that UO_2^{2+} -phosphate complexes [$\text{UO}_2\text{HPO}_4^{\text{aq}}$ and UO_2PO_4] could be important in aqueous systems with a pH between 6 and 9 when the total concentration ratio $\text{PO}_4(\text{total})/\text{CO}_3(\text{total})$ is greater than 0.1. Complexes with sulfate, fluoride, and possibly chloride are potentially important uranyl species where concentrations of these anions are high. However, their stability is considerably less than the carbonate and phosphate complexes (Wanner and Forest, 1992).

Organic complexes may also be important to uranium aqueous chemistry. The uncomplexed uranyl ion has a greater tendency to form complexes with fulvic and humic acids than many other metals with a +2 valence (Kim, 1986). This has been attributed to the greater "effective charge" of the uranyl ion compared to other divalent metals. The effective charge has been estimated to be about +3.3 for U(VI) in UO_2^{2+} . Kim (1986) concluded that, in general, +6 actinides, including U(VI), would have approximately the same tendency to form humic- or fulvic-acid complexes as to hydrolyze or form carbonate complexes. This suggests that the dominant reaction with the uranyl ion that will take place in a groundwater will depend largely on the relative concentrations of hydroxide, carbonate, and organic material concentrations. He also concluded, based on comparison of stability constants, that the tendency for U^{6+} to form humic- or fulvic-acid complexes is less than its tendency to hydrolyze or form carbonate complexes. Importantly, U(IV) and U(VI) can form stable organic complexes, thereby increasing their solubility and mobility.

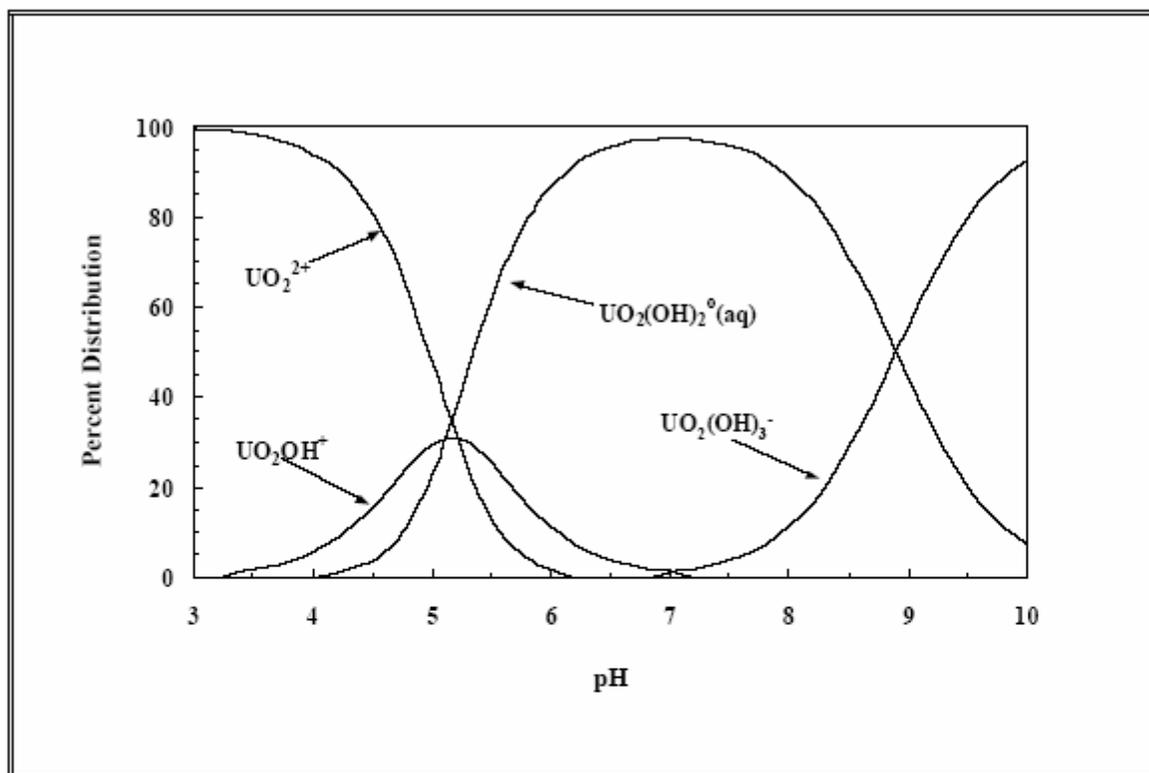
Table 5.16. Uranium(VI) aqueous species included in the speciation calculations.

Aqueous Species
UO_2^{2+} , UO_2OH^+ , $UO_2(OH)_2^0(aq)$, $UO_2(OH)_3^-$, $UO_2(OH)_4^{2-}$, $(UO_2)_2OH^{3+}$, $(UO_2)_2(OH)_3^{2+}$, $(UO_2)_3(OH)_4^{3+}$, $(UO_2)_3(OH)_5^{2+}$, $(UO_2)_3(OH)_6^+$, $(UO_2)_4(OH)_7^+$, $U_6(OH)_{15}^{9+}$
$UO_2CO_3^0(aq)$, $UO_2(CO_3)_2^{2-}$, $UO_2(CO_3)_3^{4-}$, $UO_2(CO_3)_4^{6-}$, $(UO_2)_3(CO_3)_6^{6-}$, $(UO_2)_{11}(CO_3)_8(OH)_{12}^{12-}$, $(UO_2)_2CO_3(OH)_3$
UO_2PO_4 , $UO_2HPO_4^0(aq)$, $UO_2H_2PO_4^+$, $UO_2H_3PO_4^{2+}$, $UO_2(H_2PO_4)_2^0(aq)$, $UO_2(H_2PO_4)(H_3PO_4)^+$,
$UO_2SO_4^0(aq)$, $UO_2(SO_4)_2^{2-}$
$UO_2NO_3^+$
UO_2Cl^+ , $UO_2Cl_2^0(aq)$, UO_2F^+ , $UO_2F_2^0(aq)$, $UO_2F_3^-$, $UO_2F_4^{2-}$
$UO_2SiO(OH)_3^+$

5.11.4 Dissolution/Precipitation/Coprecipitation

Dissolution, precipitation, and coprecipitation have a much greater effect on the concentrations of U(IV) than on the concentration of U(VI) in groundwaters. In most cases, these processes will likely not control the concentration of U(VI) in oxygenated groundwaters far from a uranium source. Near a uranium source, or in reduced environments, these processes tend to become increasingly important and several (co)precipitates may form depending on the environmental conditions (Falck, 1991; Frondel, 1958). Reducing conditions may exist in deep aquifers, marsh areas, or engineered barriers that may cause U(IV) to precipitate. Important U(IV) minerals include uraninite (compositions ranging from UO_2 to $UO_{2.25}$), coffinite ($USiO_4$), and ningyoite [$CaU(PO_4)_2 \cdot 2H_2O$] (Fron­del, 1958; Langmuir, 1978). Important U(VI) minerals include camotite [$(K_2(UO_2)_2(VO_4)_2)$], schoepite ($UO_3 \cdot 2H_2O$), therfordine (UO_2CO_3), tyuyamunite [$Ca(UO_2)_2(VO_4)_2$], autunite [$Ca(UO_2)_2(PO_4)_2$], potassium autunite [$K_2(UO_2)_2(PO_4)_2$], and uranophane [$Ca(UO_2)_2(SiO_3OH)_2$] (Fron­del, 1958; Langmuir, 1978). Autunite, a U(VI) mineral, is found in the oxidized zones of uranium ore deposits and uraninite, a

U(IV) mineral, is a primary mineral in reducing ore zones (Fron del, 1958). The best way to model the concentration of precipitated uranium is not with the K_d construct, but through the use of solubility



constants.

Figure 5.6a. Calculated distribution of U(VI) hydrolytic species as a function of pH at 0.1 $\mu\text{g/l}$ total dissolved U(VI). [The species distribution is based on U(VI) dissolved in pure water (*i.e.*, absence of complexing ligands other than OH) and thermodynamic data from Wanner and Forest (1992).]

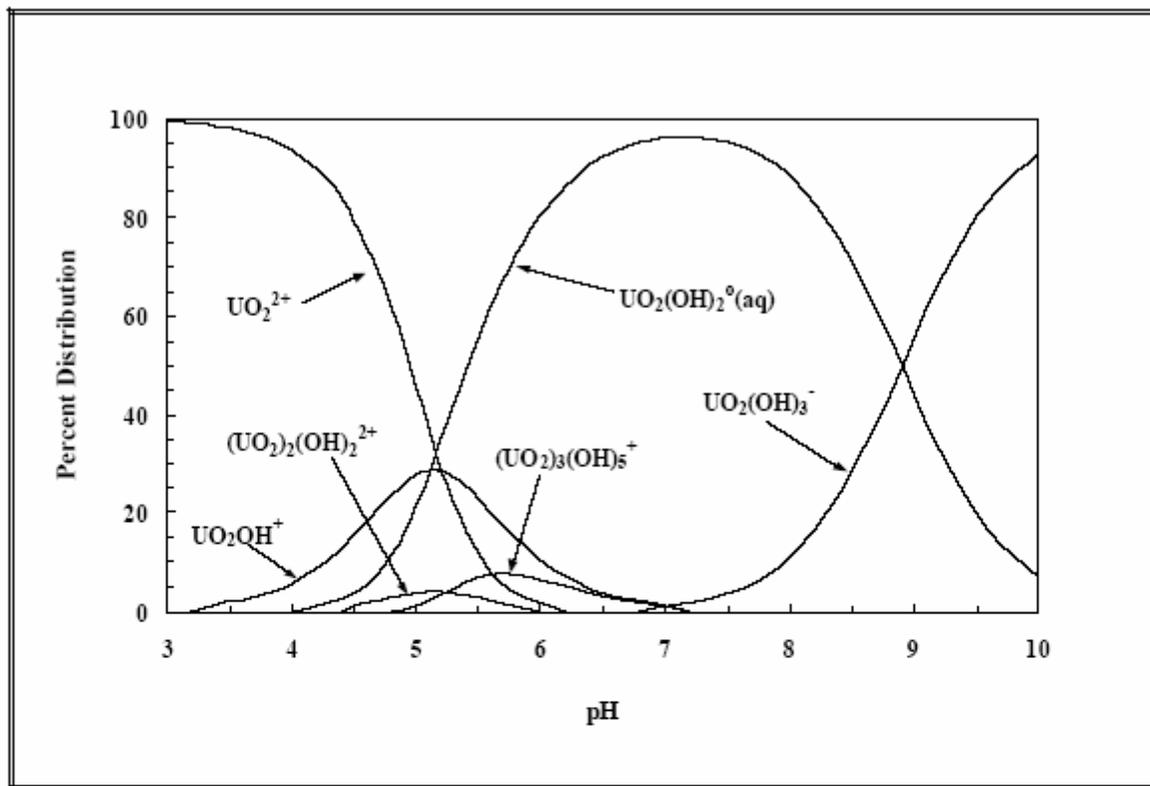


Figure 5.6b. Calculated distribution of U(VI) hydrolytic species as a function of pH at 1,000 $\mu\text{g/l}$ total dissolved U(VI). [The species distribution is based on U(VI) dissolved in pure water and thermodynamic data from Wanner and Forest (1992).]

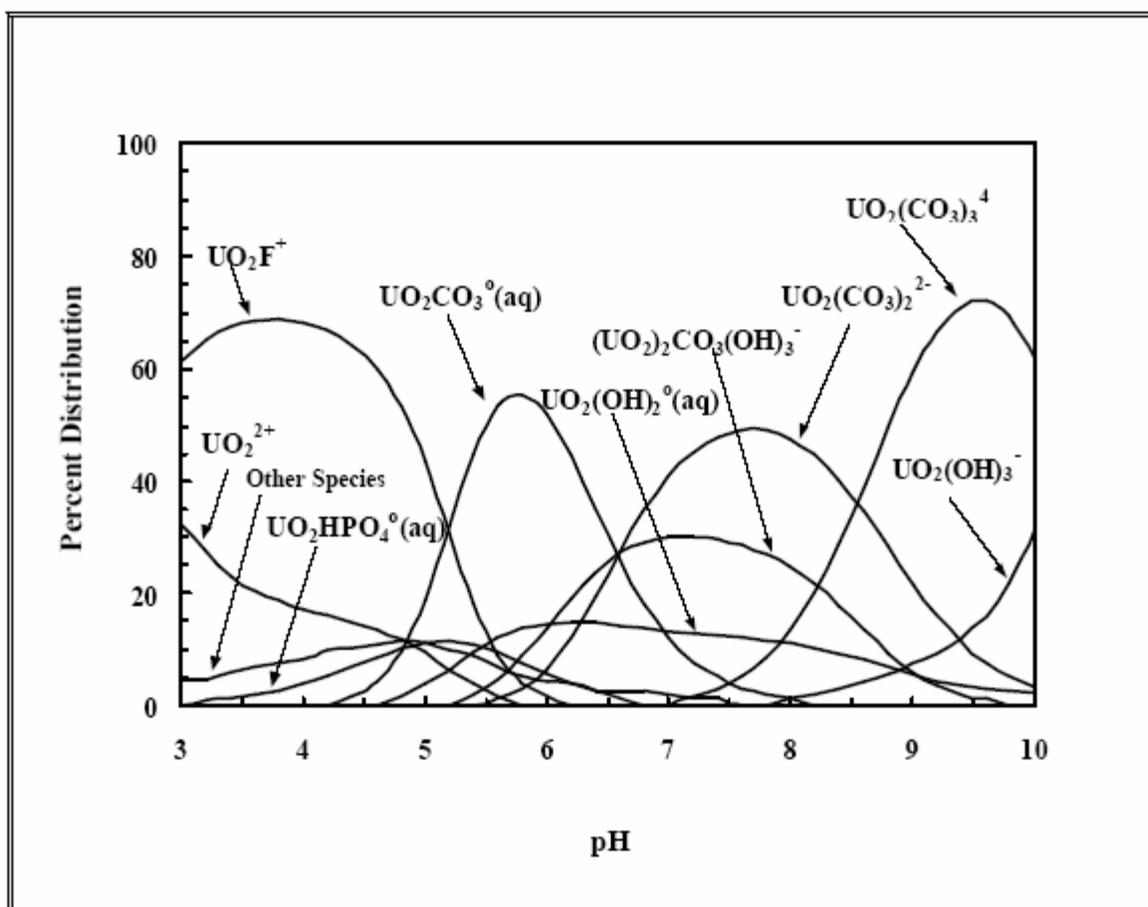


Figure 5.7. Calculated distribution of U(VI) aqueous species as a function of pH for the water composition in Table 5.1. [The species distribution is based on a concentration of 1,000 $\mu\text{g/l}$ total dissolved U(VI) and thermodynamic data from Wanner and Forest (1992).]

5.11.5 Sorption/Desorption

In low ionic strength solutions with low U(VI) concentrations, dissolved uranyl concentrations will likely be controlled by cation exchange and adsorption processes. The uranyl ion and its complexes adsorb onto clays (Ames *et al.*, 1982; Chisholm-Brause *et al.*, 1994), organics (Borovec *et al.*, 1979; Read *et al.*, 1993; Shanbhag and Chopin, 1981), and oxides (Hsi and Langmuir, 1985; Waite *et al.*, 1994). As the ionic strength of an oxidized solution increases, other ions, notably Ca^{2+} , Mg^{2+} , and K^+ , will displace the uranyl ion from soil exchange sites, forcing it into solution. For this reason, the uranyl

ion is particularly mobile in high ionic-strength solutions. Not only will other cations dominate over the uranyl ion in competition for exchange sites, but carbonate ions will form strong soluble complexes with the uranyl ion, further lowering the activity of this ion while increasing the total amount of uranium in solution (Yeh and Tripathi, 1991).

Some of the sorption processes to which uranyl ion is subjected are not completely reversible. Sorption onto iron and manganese oxides can be a major process for extraction of uranium from solution (Hsi and Langmuir, 1985; Waite *et al.*, 1994). These oxide phases act as a somewhat irreversible sink for uranium in soils. Uranium bound in these phases is not generally in isotopic equilibrium with dissolved uranium in the same system, suggesting that the reaction rate mediating the transfer of the metal between the 2 phases is slow.

Naturally occurring organic matter is another possible sink for U(VI) in soils and sediments. The mechanisms by which uranium is sequestered by organic matter have not been worked out in detail. One possible process involves adsorption of uranium to humic substances through rapid ion-exchange and complexation processes with carboxylic and other acidic functional groups (Boggs *et al.*, 1985; Borovec *et al.*, 1979; Idiz *et al.*, 1986; Shanbhag and Choppin, 1981; Szalay, 1964). These groups can coordinate with the uranyl ion, displacing waters of hydration, to form stable complexes. A process such as this probably accounts for a significant fraction of the organically bound uranium in surface and subsurface soils. Alternatively, sedimentary organics may act to reduce dissolved U(VI) species to U(IV) (Nash *et al.*, 1981).

Uranium sorption to iron oxide minerals and smectite clay has been shown to be extensive in the absence of dissolved carbonate (Ames *et al.*, 1982; Hsi and Langmuir, 1985; Kent *et al.*, 1988). However, in the presence of carbonate and organic complexants, sorption has been shown to be substantially reduced or severely inhibited (Hsi and Langmuir, 1985; Kent *et al.*, 1988).

Aqueous pH is likely to have a profound effect on U(VI) sorption to solids. There are 2 processes by which it influences sorption. First, it has a great impact on uranium speciation (Figures 5.6a-b and 5.7) such that poorer-adsorbing uranium species will likely exist at pH values between about 6.5 and 10. Secondly, decreases in pH reduce the number of exchange sites on variable charged surfaces, such as iron-, aluminum-oxides, and natural organic matter.