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Actinide Carbonate Complexes and Their Importance in Actinide Environmental Chemistry

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Table 1. Oxidation States of Light Actinide Elements^a

Th	Pa	U	Np	Pu	Am	Cm
III (IV*)	III IV (V*)	III IV V (VI*)	III IV (V*) VI VII	(III) (IV*) (V) (VI) VII	(III*) IV V VI VII	(III*) IV

^a An asterisk indicates the most common oxidation states, and environmentally important states are in parentheses.

to approximately 38000 tons in 1985, and was predicted to reach 88500 tons in 1990.⁴ For the United States alone, it is estimated that by the year 2000 the accumulation of spent nuclear fuel will reach 40000 metric tons.⁵ The majority of this spent fuel and its decay products is expected to be stored in deep geologic repositories.³ Each repository site has its own unique conditions and intrinsic barrier properties; and the characteristics of these sites is under intense study in many countries.

The principle transport mechanism for migration of transuranic elements away from a repository is expected to be by action of water, and therefore the chemistry of transuranic elements under natural aquatic conditions is receiving a considerable amount of study. In order to understand the chemical behavior of transuranic elements in natural aquatic systems, one must consider a wide variety of complex geochemical processes such as sorption,^{6-11,53} precipitation/dissolution and redox equilibria,⁶ solubility,¹²⁻¹⁹ radiolysis,²⁰⁻³⁴ hydrolysis,^{35,36} humic acid complexation,³⁷⁻⁵² colloid generation,^{41,42,54-59} and the effects of other metal ions and other potential ligands on actinide speciation.^{3,4,60-62} Each of these topics is an active area of research and to describe them all is beyond the scope of this paper. There are many reviews which provide an overview of the chemical behavior of transuranic elements in natural aquatic systems.^{3,4,60-77}

Of the 14 5f elements following actinium in the periodic table, thorium, protactinium, and uranium occur naturally.⁷⁵ On the basis of nuclear properties, availability, and distribution, only six of the 14 actinide elements (thorium, uranium, neptunium, plutonium, americium, and curium) are of long-term environmental concern.⁶⁰ The known oxidation states of these elements are listed in Table 1,⁶⁰ with the most common oxidation state in aqueous solution denoted with an asterisk, and environmentally important oxidation states are in parentheses. The variety of accessible oxidation states for these ac-

1. Introduction

In the last decade we have dramatically increased our understanding of the chemistry of actinide elements with a potent emphasis on relevance to the environment. This flourishing chemistry of the 5f elements was stimulated by many factors, including inorganic chemists' interest in structural diversity, new synthetic methods, new chemical separations, and a need to understand the fate and transport properties of actinides in natural aquifer systems. The purpose of this review is to present the motivation behind environmentally important actinide carbonate research and to provide a modern reference in the area of actinide carbonate chemistry that reflects the developments and achievements in the field since Newton and Sullivan's thorough review of actinide carbonate solution chemistry.²

The vast majority of transuranic elements are produced in commercial nuclear reactors from uranium-based fuels.³ It was estimated that cumulative spent nuclear fuel from western nations amounted



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actinides in aqueous solutions makes this chemistry rather complex. Furthermore, multiple oxidation states of the same element may exist simultaneously; plutonium, for example, may exist in four oxidation states, Pu(III), Pu(IV), Pu(V), and Pu(VI) under particular solution conditions.⁷³ A number of the known oxidation states exist only under unusual conditions, such as extreme redox potentials, radiolysis, elevated temperatures, etc.



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they are released to the environment. It is convenient to divide actinide environmental contamination into categories of short- and long-term concerns for exposure and/or groundwater contamination. Short-term concerns involve actinide isotopes which have relatively short half-lives. Dilution and natural decay will effectively ease these kinds of actinide contamination problems. Long-term environmental concerns involve long-lived actinide isotopes (half-lives greater than hundreds of years) produced in large quantities which require extreme precautions in handling, isolation, and disposal.

Actinide elements released to the environment will eventually come into contact with water. Carbonate and bicarbonate are present in significant concentrations in many natural waters, and are exceptionally strong complexing agents for actinide ions. Therefore, carbonate complexes of actinide ions may play an important role in migration from a nuclear waste repository or in accidental site contamination. The potential for aquatic transport of actinides as a result of carbonate complexation is reflected in the formation of naturally occurring uranyl carbonate minerals such as rutherfordine, $\text{UO}_2(\text{CO}_3)$,⁷⁸ liebigite, $\text{Ca}_2[\text{UO}_2(\text{CO}_3)_3] \cdot 10-11\text{H}_2\text{O}$,⁷⁹ and andersonite, $\text{Na}_2\text{Ca}[\text{UO}_2(\text{CO}_3)_3] \cdot 6\text{H}_2\text{O}$.⁸⁰ It is our responsibility to understand and predict the fate of industrial and research byproducts, whether they originate at mines, nuclear reactor sites, or within long-term repositories of highly radioactive waste. To gain an understanding of the complex geochemical behavior of these materials, we must begin with a fundamental knowledge of actinide carbonate chemistry. Here we present a brief overview of processes basic to understanding actinide carbonate chemistry, and some general aspects of actinide chemistry such as hydrolysis and complexation equilibria.

1.1. Complexation Equilibria

Complexation is a dominant factor influencing actinide speciation in natural waters. By altering the

actinide speciation. The effective coordination numbers are "hard" Lewis acid complexes with carbonate ligands. Actinide trend: An-

Complexation of a variety of ligands starts its own literature. Their equilibrium activities in systems, in terms of reactions a formation written in

$mM + nL$

Equilibrium constants for the present make up the general solution model and zero formation zero ionic strength approach (SIT). For strength of appendix B thermodynamic

A detailed and the first actinide speciation to predict in differing accurate thermodynamic zation for nuclear energy series of thermodynamic and was the chemically published.⁸

1.2. Hydrolysis

Hydrolysis or precipitation in eq 2 for hydrolysis: comparison to express constant

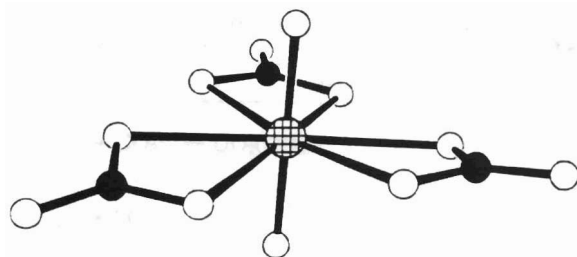
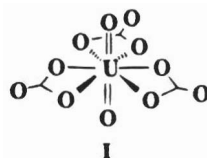
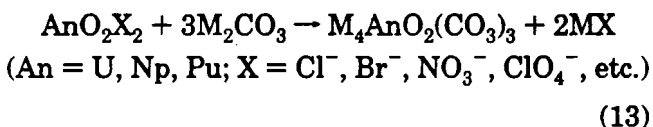


Figure 4. A ball-and-stick drawing illustrating the hexagonal bipyramidal coordination geometry found in the solid state structure of $\text{AnO}_2(\text{CO}_3)_3^{4-}$ complexes. The drawing was prepared from the fractional coordinates and unit cell parameters of synthetic andersonite, $\text{Na}_2\text{CaUO}_2(\text{CO}_3)_3 \cdot 6\text{H}_2\text{O}$, reported in ref 80. Hatched atoms = U; black = C; white = O.

complexes display a hexagonal bipyramidal coordination geometry where three bidentate carbonate ligands lie in a hexagonal plane, and the *trans* oxo ligands occupy coordination sites above and below the plane. The complex anions display approximately D_{3h} symmetry as shown qualitatively in I. Typical metrical



parameters for these structures have $\text{An}=\text{O}$ bond distances within the relatively narrow range of 1.7–1.9 Å, and $\text{An}-\text{O}$ bonds to the carbonate oxygens in the range 2.4–2.6 Å.



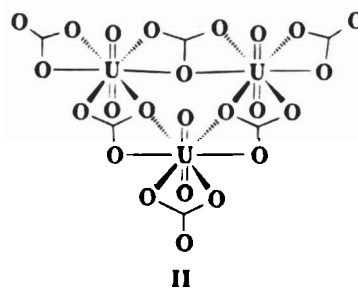
2.1.2. Solution Chemistry

Actinyl(VI) carbonate systems are usually quite complicated in that they consist of several different complex ions in rapid equilibria with one another and with the aquo ion or hydrolyzed species. Representative examples of the solution equilibria and their thermodynamic formation constants, taken from the recent literature, are listed in Table 2.

The aqueous U(VI) carbonate system has been very thoroughly studied, and there is little doubt about the compositions of the three monomeric complexes of general formula $\text{UO}_2(\text{CO}_3)$, $\text{UO}_2(\text{CO}_3)_2^{2-}$, and $\text{UO}_2(\text{CO}_3)_3^{4-}$ present under the appropriate conditions.⁸¹ There is also a great deal of evidence from emf, solubility, and spectroscopic data supporting the existence of polymeric solution species of formulas $(\text{UO}_2)_3(\text{CO}_3)_6^{6-}$, $(\text{UO}_2)_2(\text{CO}_3)(\text{OH})_3^-$, $(\text{UO}_2)_3\text{O}(\text{OH})_2(\text{HCO}_3)^+$, and $(\text{UO}_2)_{11}(\text{CO}_3)_6(\text{OH})_{12}^{2-}$ which form only under conditions of high metal ion concentration or high ionic strength.^{81,140} Determining the formation constant for the triscarbonato uranyl monomer, $\text{UO}_2(\text{CO}_3)_3^{4-}$, is complicated because this species is in equilibrium with the hexakiscarbonato uranyl trimer, $(\text{UO}_2)_3(\text{CO}_3)_6^{6-}$. Recently, Bidoglio *et al.* used thermal lensing spectroscopy (which is sensitive enough to allow the study of relatively dilute solutions where the trimer is not favored) to determine the equilibrium constant for the addition of one

carbonate to $\text{UO}_2(\text{CO}_3)_2^{2-}$ to form $\text{UO}_2(\text{CO}_3)_3^{4-}$, and used this value to calculate the formation constant, β_{13} .¹⁴³ The formation constants for the principal complexes have been determined by a large number of investigators using a wide variety of techniques, and have been critically reviewed by Grenthe *et al.*⁸¹

The trimetallic uranyl cluster $(\text{UO}_2)_3(\text{CO}_3)_6^{6-}$ has been the subject of a good deal of study, including ^{13}C and ^{17}O NMR spectroscopy,^{131,132,135,144,145} solution X-ray diffraction,¹³² potentiometric titration,^{133,140,141} single-crystal X-ray diffraction,¹³¹ and EXAFS spectroscopy in both the solid and solution states.¹³¹ The data in this area have consistently led to the proposal of a triangular cluster in solution (Figure 3) as shown qualitatively in II. This structural motif was proposed by Åberg on the basis of fits to solution X-ray diffraction data,¹³² and was based on the hexagonal $\text{AnO}_2(\text{CO}_3)$ layers in the solid state structures of $\text{KAnO}_2(\text{CO}_3)$ (An = Pu, Am),¹⁴⁶ which is a simple structural modification of the rutherfordine structure.⁷⁸



Ciavatta *et al.* were the first to propose the $(\text{UO}_2)_3(\text{CO}_3)_6^{6-}$ cluster based on potentiometric (emf) titration studies.¹⁴⁷ Åberg *et al.* reported ^{13}C NMR data for a sample at pH 5.7 (25 and 0 °C) which showed two ^{13}C NMR resonances consistent with the structure proposed in II.¹³² Several years later, Ferri *et al.* reported an ^{17}O NMR spectrum of a similar sample which displayed five ^{17}O NMR signals between δ 1130–1095 ppm in the expected 2:2:2:1:1 ratio,¹⁴⁵ and it was argued that this ^{17}O NMR spectrum confirmed the solution structure of $(\text{UO}_2)_3(\text{CO}_3)_6^{6-}$ as that shown in II. However, all five ^{17}O resonances appeared in the uranyl ($\text{O}=\text{U}=\text{O}$) chemical shift region of the ^{17}O NMR spectrum and are more consistent with five different uranyl oxygen environments. Subsequent ^{17}O NMR studies revealed a single uranyl ^{17}O resonance at δ 1105 ppm which is consistent with the proposed trimer structure, and the earlier assignment has been corrected.^{131,135,144}

EXAFS measurements performed at the uranium L_{III} edge for solid $[\text{C}(\text{NH}_2)_3]_6[(\text{UO}_2)_3(\text{CO}_3)_6]$, solid $\text{K}_4[\text{UO}_2(\text{CO}_3)_3]$, and a solution of $(\text{UO}_2)_3(\text{CO}_3)_6^{6-}$ gave further support of a trimeric structure for the $(\text{UO}_2)_3(\text{CO}_3)_6^{6-}$ ion.¹³¹ Figure 5 shows the EXAFS Fourier transforms for solid $\text{K}_4[\text{UO}_2(\text{CO}_3)_4]$ (top) and $[\text{C}(\text{NH}_2)_3]_6[(\text{UO}_2)_3(\text{CO}_3)_6]$ (bottom).¹³⁰ The EXAFS Fourier transform of $[\text{C}(\text{NH}_2)_3]_6[(\text{UO}_2)_3(\text{CO}_3)_6]$ shows five well-resolved peaks whose qualitative assignment based on the model trimeric structure II is straightforward. Peaks at 1.79, 2.45, and 2.90 Å in both transforms may be identified as distances from uranium to the uranyl oxygens, the six carbonate oxygens in the equatorial plane, and the carbonate

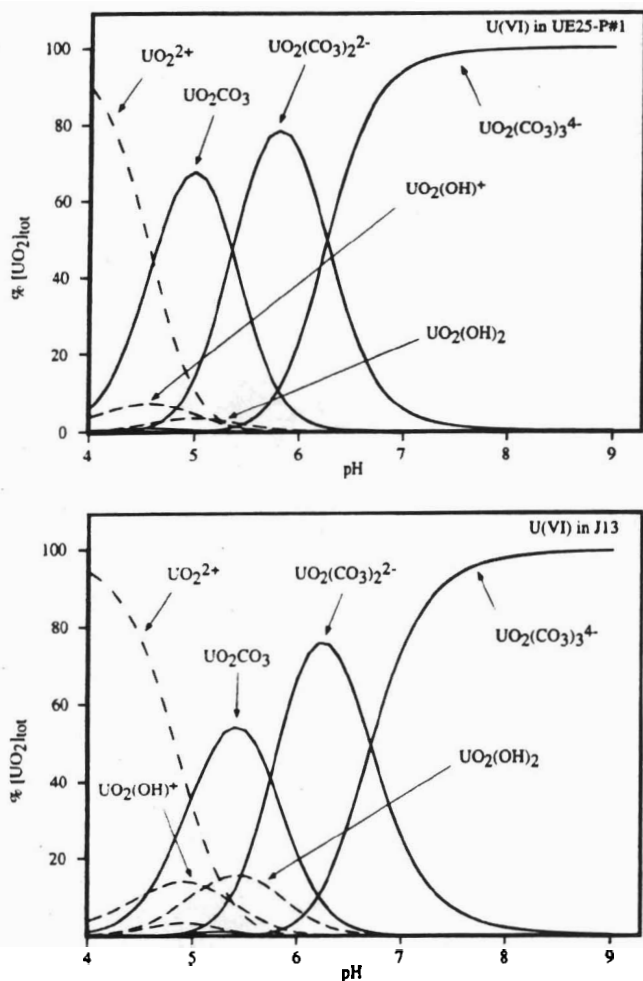


Figure 8. Calculated uranyl species distributions in carbonate solutions modeling Yucca Mountain UE25P#1 (top) and J-13 (bottom) groundwaters at 25 °C using NEA-suggested formation constants⁸¹ corrected to an ionic strength of 0.1 *m* using specific ion interaction theory. Solution conditions: (UE25P#1) $[UO_2^{2+}] = 1 \times 10^{-5}$ M, $[CO_3^{2-} + HCO_3^-] = 0.002$ M. (J-13) $[UO_2^{2+}] = 1 \times 10^{-5}$ M, $[CO_3^{2-} + HCO_3^-] = 0.0114$ M. Formation constants (25 °C, $I_m = 0.1$ m, log β): $ML = 8.80$; $ML_2 = 16.10$; $ML_3 = 21.65$; $M_3L_6 = 54.05$; $LH = 9.1$; $LH_2 = 16.05$. Hydrolysis constants (log *K*): $MOH = -5.38$; $M(OH)_2 = -10.50$; $M(OH)_3 = -19.19$; $M(OH)_4 = -32.58$; $M_2(OH)_2 = -5.84$; $M_3(OH)_4 = -12.35$; $M_3(OH)_5 = -16.20$; $M_3(OH)_7 = -31.46$; $M_2(OH) = -2.48$, where $M = UO_2$ and $L = CO_3$.

contain primarily sodium bicarbonate and very little other dissolved solids.^{162,163} Water samples with compositions that bracket the range of waters expected in the vicinity of Yucca Mountain have been chosen for solubility and speciation studies.¹⁶² These waters come from two sources: well J-13 and well UE25P#1. The water from well J-13 is expected to be representative of water from the unsaturated zone near the proposed emplacement area and has been recommended as a reference water. Well UE25P#1 taps the carbonate aquifer that underlies the emplacement horizon. Water from UE25P#1 has a total carbonate concentration (0.0114 M) that is approximately four times greater than J-13 (0.0028 M), and represents a reasonable upper boundary for carbonate concentrations. Calculated uranyl(VI) solution species distributions representative of these groundwater carbonate concentrations are shown in Figure 8. It is important to point out that there is no such thing as a "typical" species distribution diagram for

a given ion. The concentrations and thermodynamic constants used to calculate these distributions are listed in the figure caption. From the calculated species distributions shown in Figure 8, one can see that the chemistry of the uranyl ion is markedly influenced by carbonate complexation. Monomeric uranyl carbonate species $UO_2(CO_3)$, $UO_2(CO_3)_2^{2-}$, and $UO_2(CO_3)_3^{4-}$ are expected to dominate above pH 5, and the hydrolyzed species $UO_2(OH)_3^-$ is predicted to dominate at pH values near 11.0 (not shown in Figure 8). In the absence of other complexing ligands, carbonate complexation will dominate the speciation of the uranyl ion under near-neutral pH conditions as long as there is ample carbonate–bicarbonate available. At uranyl concentrations above 1×10^{-3} M, the trimeric cluster $(UO_2)_3(CO_3)_6^{6-}$ is present in significant concentrations. When the uranyl ion concentration exceeds the carbonate concentration, hydrolysis plays an increasingly important role. This is the primary difference in the predicted species distributions between carbonate solutions representative of UE25P#1 and J-13 waters shown in Figure 8. While the actual thermodynamic binding constants vary with each metal ion, the general trends in stable species of the Np(VI) and Pu(VI) analogs are anticipated to be similar to those shown in Figure 8. Thus one would expect to see monomeric actinyl(VI) carbonate complexes $AnO_2(CO_3)$, $AnO_2(CO_3)_2^{2-}$, and $AnO_2(CO_3)_3^{4-}$ dominating the speciation in these waters under conditions where An(VI) ions are stable.

2.2. Pentavalent Actinide Carbonate Complexes

2.2.1. Solid State and Structural Studies

There is a large body of evidence for the existence of three different types of actinyl(V) carbonate solids of general formula $M_{1,2n-1}AnO_2(CO_3)_n$ where $n = 1, 2,$ or 3 ; M is a monovalent cation, and $An = Np, Pu,$ or Am . The lack of data on U(V) complexes is due to the relative instability of the pentavalent oxidation state of uranium in aqueous solution.⁷³ The preparation of these solids is very sensitive to the concentration of the alkali metal carbonate or bicarbonate solution used in the synthesis and to the stability of the AnO_2^+ ion. Because of the greater stability of the Np(V) oxidation state relative to other actinide ions, it is not surprising that the neptunium system is by far the most well studied and understood.

Generally, monocation salts of formula $MNpO_2(CO_3)$ are prepared by the addition of fairly dilute (< 0.1 M) alkali metal carbonate or bicarbonate solutions to stock solutions of the NpO_2^+ ion stabilized in dilute acid. These so-called "double carbonate" salts precipitate from solution upon standing.^{164–170} In order to isolate pure samples of $MNpO_2(CO_3)$ it is important to add the carbonate solution to the actinyl solution in order to keep the concentration of alkali carbonate to a minimum with respect to the actinyl concentration. Use of alkali carbonate solutions of higher concentrations (0.5 – 2.0 M) in the syntheses results in the formation of quasi stable solutions from which pure solids of formula $M_3NpO_2(CO_3)_2$ precipitate overnight.^{171–173} Finally, the use of a large excess of alkali carbonate (such as 50% K_2CO_3 solutions) results in the formation of solids of general formula $M_5NpO_2(CO_3)_3$.¹⁷⁴ There are also reports of the existence of these solids with varying

Figure 9. from the fr

Figure 10 structure c ref 146. H

amounts exchange of the sol provides a se

For plu are added until the or $(NH_4)I$ extremely sium ame dilute acid alkali me The exact not be det peroxidis presence vided sol $RbAmO_2$ Like the r of alkali yield K_3A

MAnO general fo Pu, and A is due lar Zacharia co-worker Solid stat ion data $MAnO_2(C$ Cs, NH_4 types ha

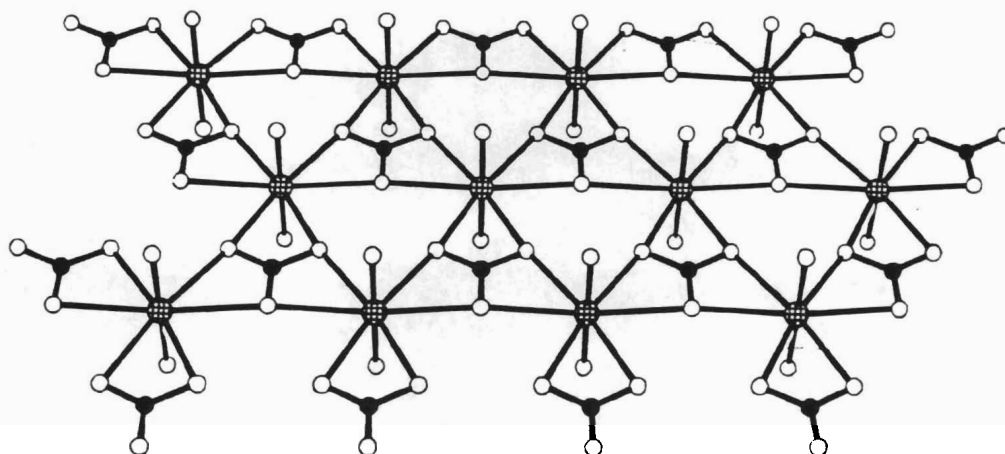


Figure 9. A ball-and-stick drawing illustrating a single $\text{PuO}_2(\text{CO}_3)$ layer in $\text{KPuO}_2(\text{CO}_3)$. The drawing was prepared from the fractional coordinates and unit cell parameters reported in ref 146. Hatched atoms = Pu; black = C; white = O.

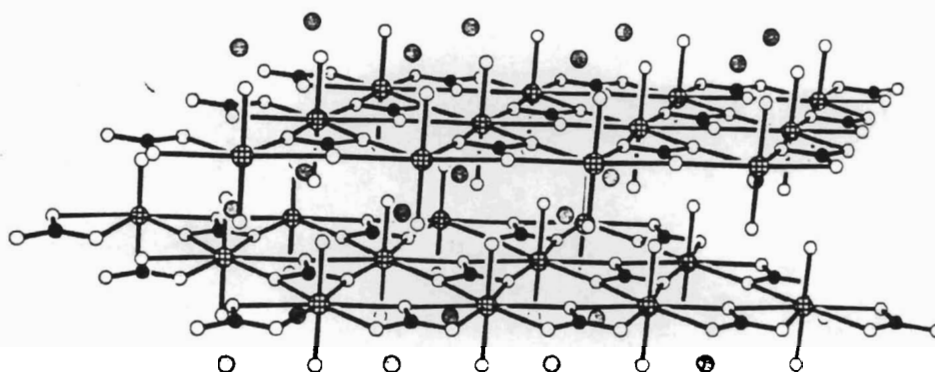


Figure 10. A ball-and-stick drawing illustrating the stacking of alternating $\text{PuO}_2(\text{CO}_3)^-$ and K^+ layers in the solid state structure of $\text{KPuO}_2(\text{CO}_3)$. The drawing was prepared from the fractional coordinates and unit cell parameters reported in ref 146. Hatched atoms = Pu; light gray = K; black = C; white = O.

amounts of waters of hydration and of their cation exchange properties.¹⁷⁵ A thorough understanding of the solid state structures of the compounds provides a satisfying explanation for these results.¹⁷³

For plutonium, when solid alkali carbonate salts are added to a PuO_2^+ solution (stabilized at pH = 2) until the pH reached 7, microcrystals of $\text{KPuO}_2(\text{CO}_3)$ or $(\text{NH}_4)\text{PuO}_2(\text{CO}_3)$ precipitated. These have been extremely well characterized.¹⁷⁰ Sodium and potassium americium(V) carbonates are prepared by heating dilute acid solutions of Am(III) and the corresponding alkali metal carbonate in solutions of hypochlorite.¹⁶⁷ The exact compositions of the resulting solids could not be determined. An analogous preparation using peroxodisulfate or ozone as chemical oxidants in the presence of rubidium or ammonium carbonate provided solids of composition $(\text{NH}_4)\text{AmO}_2(\text{CO}_3)$ and $\text{RbAmO}_2(\text{CO}_3)$, which have been well characterized.¹⁴⁶ Like the neptunium analogs, the use of a large excess of alkali carbonate in the americium reactions will yield $\text{K}_3\text{AmO}_2(\text{CO}_3)_2$ and $\text{K}_5\text{AmO}_2(\text{CO}_3)_3$ solids.

$\text{MANO}_2(\text{CO}_3)$. The actinyl(V) carbonate solids of general formula $\text{MANO}_2(\text{CO}_3)$ are well known for Np, Pu, and Am. Our understanding of these structures is due largely to the pioneering efforts of Ellinger and Zachariasen in the United States¹⁴⁶ and Volkov and co-workers in the former Soviet Union.^{164-166,172,173}

Solid state structures based on powder X-ray diffraction data have been determined for a wide variety of $\text{MANO}_2(\text{CO}_3)$ compounds where M = Na, Li, K, Rb, Cs, NH_4 ; and An = Np, Pu, and Am. Two structural types have been observed, depending on the size of

the univalent alkali metal cation. With the larger cations, a hexagonal structure is observed, as exemplified by $\text{KPuO}_2(\text{CO}_3)$ which crystallizes in the hexagonal space group $P6_3/mmc$ with two $\text{KPuO}_2(\text{CO}_3)$ moieties in the unit cell.¹⁴⁶ The reasonable assumptions of linear $\text{O}=\text{Pu}=\text{O}$ and carbonate $\text{C}-\text{O}$ distances of 1.94 and 1.28 Å allowed the other significant interactions in the structure to be deduced from the powder diffraction data. The coordination environment of the plutonyl ion is a hexagonal bipyramidal arrangement of oxygen atoms with the plutonyl units perpendicular to the hexagonal plane. Each plutonium atom forms six equatorial bonds with the oxygen atoms of three carbonate ligands in a bidentate manner with $\text{Pu}-\text{O}$ distances of 2.55 Å. The plane of hexagonal bipyramidal plutonyl units forms an infinite layer of $\text{PuO}_2(\text{CO}_3)^-$ which differs from the layers seen in rutherfordine. Figure 9 shows a ball and stick view of the structure, emphasizing the local coordination of the plutonyl ion in a single hexagonal $\text{PuO}_2(\text{CO}_3)^-$ layer. These hexagonal layers are separated by alternating layers of alkali metal cations as shown in Figure 10. Each potassium ion in the cation layer interacts with six carbonate and six plutonyl oxygen atoms with 2.96 and 2.98 Å separations, respectively. Figure 10 illustrates how these multiple layers are staggered with respect to the position of $\text{O}=\text{Pu}=\text{O}$ units.

In detailed studies of the corresponding neptunium(V) system, Volkov *et al.* noted a change in the crystal system from hexagonal to orthorhombic as the alkali metal cation size was decreased.¹⁶⁵ That is,

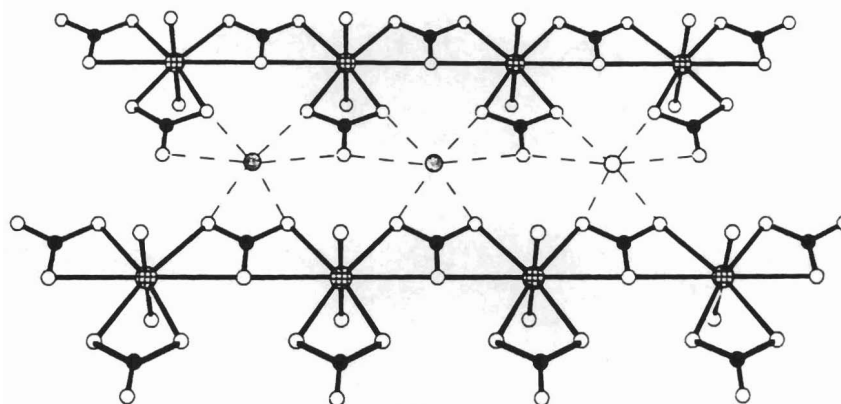
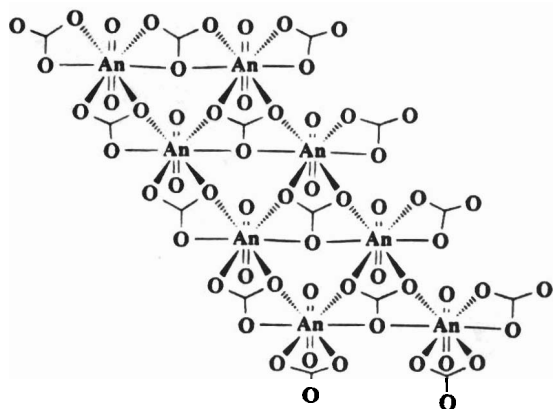
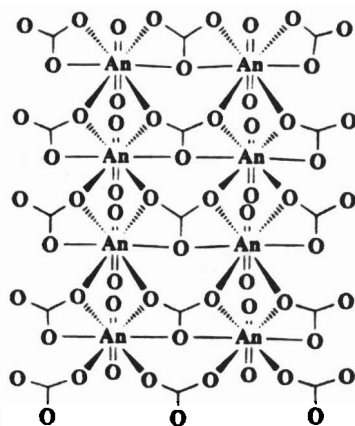


Figure 11. A ball-and-stick drawing illustrating a single $\text{KNpO}_2(\text{CO}_3)_2$ layer in the solid state structure of $\text{K}_3\text{NpO}_2(\text{CO}_3)_2$. The drawing was prepared from the fractional coordinates and unit cell parameters reported by in ref 166. Hatched atoms = Np; light gray = K; black = C; white = O.

in the series of neptunium(V) monocarbonates $\text{MNPo}_2(\text{CO}_3)$ with $\text{M} = \text{Cs}^+, \text{Rb}^+, \text{NH}_4^+, \text{K}^+, \text{Na}^+, \text{and Li}^+$, a hexagonal-to-orthorhombic phase change was observed within the $\text{NpO}_2(\text{CO}_3)$ layer at the potassium-sodium boundary. The solids maintain a layered structure, but the orthorhombic $\text{NpO}_2(\text{CO}_3)$ sheets now have the same structure as that found in rutherfordine (Figure 1). The hexagonal and orthorhombic structures are related by displacement of the chains of actinyl units through half a translation along the crystallographic a axis, illustrated qualitatively in III and IV. The orthorhombic structure



III
hexagonal



IV
orthorhombic

is more open than the hexagonal structure which

appears to allow for the closer contacts necessary for the smaller sodium and lithium cations.

Additional work by Volkov and co-workers demonstrated that the hexagonal structures containing potassium cations showed a definite swelling along the crystallographic c axis in the presence of water, and a corresponding shrinkage of the c axis with heating.¹⁶⁶ Thus, in the general case, the potassium monocarbonates of the pentavalent actinides have a more complex composition than just described, and may be represented by the general formula of $\text{KAnO}_2(\text{CO}_3)_n \cdot \text{H}_2\text{O}$ with intercalated water molecules.

$\text{M}_3\text{AnO}_2(\text{CO}_3)_2$. The actinyl(V) carbonate solids of general formula $\text{M}_3\text{AnO}_2(\text{CO}_3)_2$ ($\text{An} = \text{Np}, \text{Pu}, \text{Am}$, and $\text{M} = \text{Na}, \text{K}, \text{Rb}$) have been studied extensively by Volkov and co-workers.^{166,171,173} On the basis of powder X-ray diffraction data, these compounds are not rigorously isostructural, but the basic structural features are the same, and thus they will be described as one structural type. In the solid state, $\text{M}_3\text{AnO}_2(\text{CO}_3)_2$ compounds maintain the same orthorhombic layered structure as seen in $\text{MAnO}_2(\text{CO}_3)$ except that one half of the AnO_2^+ ions in the anionic carbonate layer have been replaced by alkali metal cations (M^+); this is shown as a ball-and-stick drawing of a single layer in Figure 11. One can envision from Figure 11 that M^+ and AnO_2^+ cations form alternating chains within the familiar hexagonal sheet and give rise to the approximate composition $[\text{M}_{0.5}(\text{AnO}_2)_{0.5}(\text{CO}_3)]$ within the layer. This is illustrated qualitatively in V (Chart 1). The cation and anion layers are now oriented such that an alkali metal cation, M^+ , lies directly above and below the linear AnO_2^+ ion of adjacent sheets (perpendicular to the layer represented in Figure 11). The anionic carbonate layer and the cationic potassium layers line up such that they are parallel to the crystallographic c axis, and this allows for an $\text{M}-\text{O}=\text{An}$ interaction between layers. In this way, a second infinite chain of $\text{O}=\text{An}=\text{O}-\text{M}-\text{O}=\text{An}=\text{O}$ units is formed, resulting in a maximally ordered structure. This second infinite chain is illustrated in the ball-and-stick drawing shown in Figure 12.

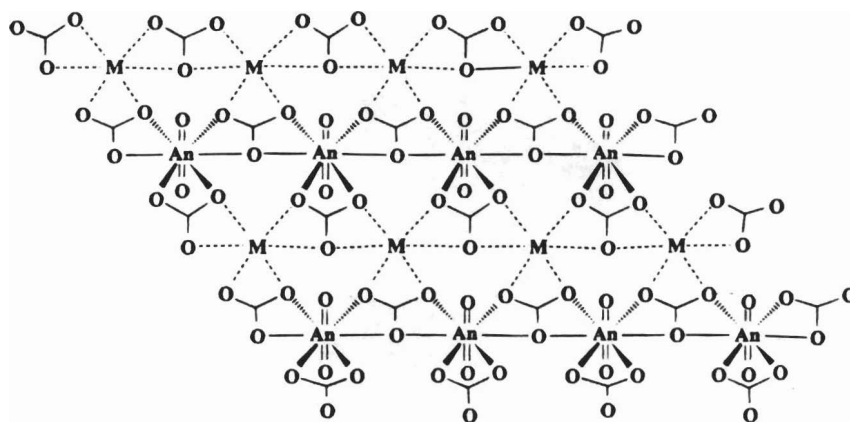
The observations noted above have been used by Volkov *et al.* to propose a believable unified structural theory for actinyl(V) carbonate solids.¹⁷³ The observation that alkali cations can occupy the same sites as the AnO_2^+ ions allows for a relatively straightfor-

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Chart 1



V

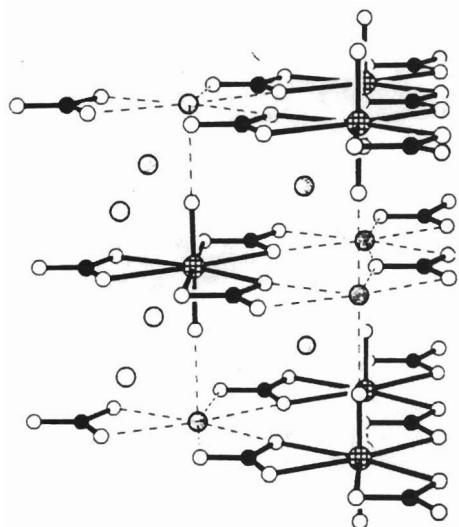


Figure 12. A ball-and-stick drawing illustrating the infinite stacking between $\text{KNpO}_2(\text{CO}_3)_2$ layers in the solid state structure of $\text{K}_3\text{NpO}_2(\text{CO}_3)_2$. The drawing was prepared from the fractional coordinates and unit cell parameters reported in ref 166. Hatched atoms = Np; light gray = K; black = C; and white = O.

ward explanation for the presence of nonstoichiometric solids such $\text{M}_4\text{AnO}_2(\text{CO}_3)_{2.5}n\text{H}_2\text{O}$. This solid could easily arise from further replacement of AnO_2^+ ions in the layers by alkali metal cations, M^+ . In this way it was proposed that solids of intermediate compositions $\text{M}_{1.3+2x}\text{AnO}_2(\text{CO}_3)_{2+x}n\text{H}_2\text{O}$, where $0 \leq x \leq 0.5$, could exist while still preserving the basic structural features. In addition, it has been shown that these carbonate compounds can contain varying numbers of water molecules, yet there are no free sites in these structures to accommodate the additional water molecules. Relying on the observation that AnO_2^+ ions can be replaced by M^+ ions in the structures, it seems reasonable that water molecules can occupy the site of the oxygen atoms of the linear AnO_2^+ unit thereby creating $\text{H}_2\text{O}-\text{M}^+-\text{OH}_2$ units along the crystallographic c axis, the axis known to swell in the presence of water. To the best of our knowledge, there are no X-ray diffraction studies reported for solids of formula $\text{M}_5\text{AnO}_2(\text{CO}_3)_3$.

Diffuse reflectance spectra recorded for $\text{NaNpO}_2(\text{CO}_3)$ and $\text{Na}_3\text{NpO}_2(\text{CO}_3)_2$ solids are compared in Figure 13.¹⁷⁶ The remarkable differences in the spectra of these solids can be attributed to the

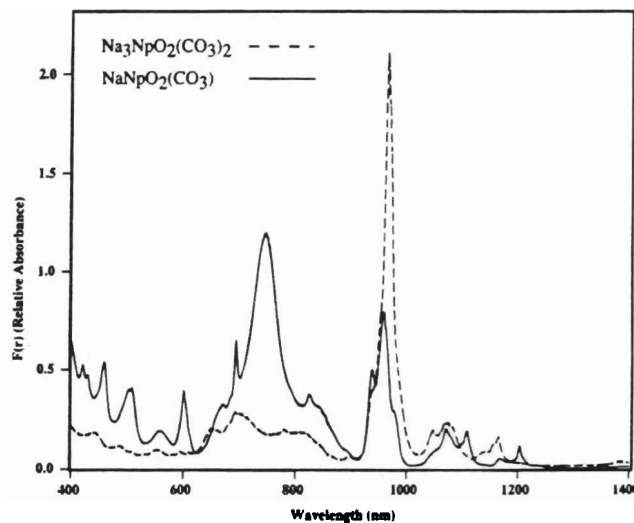


Figure 13. Comparison of the diffuse reflectance spectra of the solids $\text{NaNpO}_2(\text{CO}_3)$ (solid line) and $\text{Na}_3\text{NpO}_2(\text{CO}_3)_2$ (dashed line).

significant differences in the solid state structures as noted above (see Figures 9 and 11).

2.2.2. Solution Chemistry

As might be expected based on the relative stabilities of the oxidation states of actinide ions in aqueous solution, the carbonate complexes of Np(V) have been studied most extensively.

The Raman frequencies for the symmetric stretch of NpO_2^+ , PuO_2^+ , and AmO_2^+ were measured by Madic *et al.* to be 767, 748, and 730 cm^{-1} , respectively.¹⁰⁸ The Raman-active ν_1 symmetric stretching frequencies of the AnO_2^+ group for actinyl(V) species in carbonate solutions show little variation as the atomic number of the actinide increases. $\text{UO}_2(\text{CO}_3)_3^{4-}$ reduced to $\text{UO}_2(\text{CO}_3)_3^{5-}$ has a ν_1 Raman band at 759 cm^{-1} , and the NpO_2^+ ion in 2 M carbonate solution has a ν_1 Raman band at 755 cm^{-1} . The species present is thought to be $\text{NpO}_2(\text{CO}_3)_3^{5-}$. Both AmO_2^+ and PuO_2^+ in carbonate solutions have Raman bands at 755 cm^{-1} . In comparison with the ν_1 frequencies measured in acidic solutions, those in carbonate solutions show a small negative shift for ν_1 of Np(V) and a positive shift for ν_1 of Am(V). Madic *et al.* suggested that the differences between frequencies in noncomplexing media and in carbonate media may

Table 3. Representative Values for the Equilibrium Constants of the Carbonate Complexes of Pentavalent Actinides at Selected Ionic Strengths and 25 °C

equilibrium	I	log K	ref
Uranyl			
$UO_2^+ + 3CO_3^{2-} \rightleftharpoons UO_2(CO_3)_3^{5-}$	0	7.41(±0.27)	81
	3.0	6.54(±0.49)	181
Neptunyl			
$NpO_2^+ + CO_3^{2-} \rightleftharpoons NpO_2(CO_3)^-$	0	4.69(±0.13)	184
	0.1	4.34(±0.11)	183
	0.2	4.13(±0.03)	186
	0.5	4.2(±0.1)	181
	1.0	4.3(±0.2)	181
	3.0	5.09	127
	5.0 ^b	4.71(±0.04)	185
$NpO_2^+ + 2CO_3^{2-} \rightleftharpoons NpO_2(CO_3)_2^{3-}$	0.2	7.06(±0.05)	186
	0.5	6.4(±0.2)	181
	1.0	6.7(±0.3)	181
	3.0	8.15	127
	5.0 ^b	7.54(±0.05)	185
$NpO_2^+ + 3CO_3^{2-} \rightleftharpoons NpO_2(CO_3)_3^{5-}$	0.5	7.8(±0.3)	181
	1.0	8.5(±0.4)	181
	3.0	10.46	127
	5.0 ^b	9.63(±0.05)	185
Plutonyl			
$PuO_2^+ + CO_3^{2-} \rightleftharpoons PuO_2(CO_3)^-$	0	5.12(±0.07)	104
	0.5	4.60(±0.04)	104
$PuO_2^+ + 3CO_3^{2-} \rightleftharpoons PuO_2(CO_3)_3^{5-}$	1 ^a	10.0(±2.1)	100
Americyl			
$AmO_2^+ + CO_3^{2-} \rightleftharpoons AmO_2(CO_3)^-$	3 ^b	4.74(±0.09)	185
$AmO_2^+ + 2CO_3^{2-} \rightleftharpoons AmO_2(CO_3)_2^{3-}$	3 ^b	7.42(±0.03)	185
$AmO_2^+ + 3CO_3^{2-} \rightleftharpoons AmO_2(CO_3)_3^{5-}$	3 ^b	9.54(±0.13)	185

^a Na₂CO₃ electrolyte. ^b NaCl electrolyte; NaClO₄ was used to adjust the ionic strength in all other studies.

be related to hydrogen bonding between the oxygen of the actinyl ions and water molecules.¹⁵⁴

Wester and Sullivan measured the formal potentials for the reduction of AnO₂(CO₃)₃⁴⁻ to AnO₂(CO₃)₃⁵⁻ in 1 M Na₂CO₃ to be -0.538, +0.445, and +0.334 V for An = U,¹⁷⁷ Np,¹⁷⁸ and Pu,¹⁷⁹ respectively. They concluded that the carbonate radical, CO₃^{•-} can oxidize any of the AnO₂(CO₃)₃⁵⁻ species.

There have been a variety of studies on the thermodynamic formation constants for actinyl(V) complexes formed in carbonate media. A representative set of thermodynamic formation constants taken from the recent literature is given in Table 3.¹⁸⁰⁻¹⁸⁶ There is only one uranyl(V) species for which quantitative thermodynamic information is available, namely UO₂(CO₃)₃⁵⁻. The formation constant for this species was determined on the basis of the formation constant of UO₂(CO₃)₃⁴⁻ and the reduction potential of the equilibrium shown in eq 15.¹⁸⁰



There is ample spectrophotometric and solubility data supporting the formation of monomeric complex anions, NpO₂(CO₃)⁻, NpO₂(CO₃)₂³⁻, and NpO₂(CO₃)₃⁵⁻ in solution; and these correlate nicely with the known solid phase salts MNpO₂(CO₃), M₃NpO₂(CO₃)₂, and M₅NpO₂(CO₃)₃ (M = monovalent cation) which were discussed earlier. The formation constants for these species in solutions of ionic strength 0.1-3.5 m have been determined by a number of researchers using a variety of methods. The thermodynamic formation

constantly well understood (Table 3), but those for NpO₂(CO₃)₃⁵⁻ are more scattered, and there is no consensus. The most reliable estimates come from Riglet, who examined spectrophotometric data obtained at various ionic strengths.¹⁸¹

Bennett and co-workers determined the formation constant for PuO₂(CO₃)⁻ using photoacoustic spectroscopy (PAS), then employed the specific ion interaction theory (SIT) to calculate a formation constant at zero ionic strength (Table 3).¹⁰³ This value compares favorably with the corresponding log β₁₁ for the NpO₂(CO₃)⁻ analog (Table 3). No evidence for mixed hydroxy carbonate species was found in this study, in which hydrolysis behavior of the PuO₂⁺ ion was also investigated. The formation constant for the triscarbonate species, PuO₂(CO₃)₃⁵⁻ was determined by Liese using the formation constant of PuO₂(CO₃)₃⁴⁻ and the one electron reduction potential between the two species in analogy to eq 15.¹⁰⁰

Ferri, Grenthe, and Salvatore recalculated previous redox data of Bourges *et al.*¹⁸² for the AmO₂²⁺/AmO₂⁺ redox couple in carbonate media.¹⁸⁰ This reinterpretation indicates that AmO₂⁺ forms a limiting carbonate complex AmO₂(CO₃)₃⁵⁻ with approximately the same formation constant as found for the analogous uranyl(V) species. One problem with extrapolation of the formation constants of AnO₂(CO₃)₃⁵⁻ to zero ionic strength arises from the strong ion pairing between cations such as Na⁺ and the pentaanion.

2.2.3. Species Distribution in Aqueous Solutions

Like the actinyl(VI) ions, only monomeric complexes are expected in natural waters due to the low ionic strengths and low metal ion concentrations expected for these waters. In addition, there is no evidence in support of polynuclear actinyl(V) carbonate complexes.

We used the thermodynamic constants for neptunyl(V) hydrolysis and carbonate complexation to produce the expected species distributions under solution conditions representative of the bounding groundwaters found at the proposed Yucca Mountain repository. Calculated neptunyl species distributions under carbonate concentrations representative of those found in UE25P#1 and J-13 groundwaters are shown in Figure 14. We reiterate that there is no such thing as a "typical" species distribution diagram for a given actinyl(V) ion. Carbonate complexation is expected to dominate the speciation for the neptunyl ion under near-neutral pH and ambient conditions as long as there are ample carbonate ions present in solution. Under these solution conditions, monomeric neptunyl carbonate species NpO₂(CO₃)⁻, and NpO₂(CO₃)₂³⁻ are expected to dominate above pH = 7, and hydrolysis to form NpO₂(OH) is predicted to be unimportant, even at pH values near 11.0 (not shown in Figure 14). We also observe that the carbonate concentrations in these waters is simply not high enough to allow formation of the tris complex NpO₂(CO₃)₃⁵⁻ and this is consistent with the observation that the tris complex is only formed in 2 M carbonate solutions. In the J-13 water, with a factor of 4 less carbonate, NpO₂(CO₃)⁻ is predicted to be the dominant species even at pH = 9. There is some reason to expect that the carbonate concentrations

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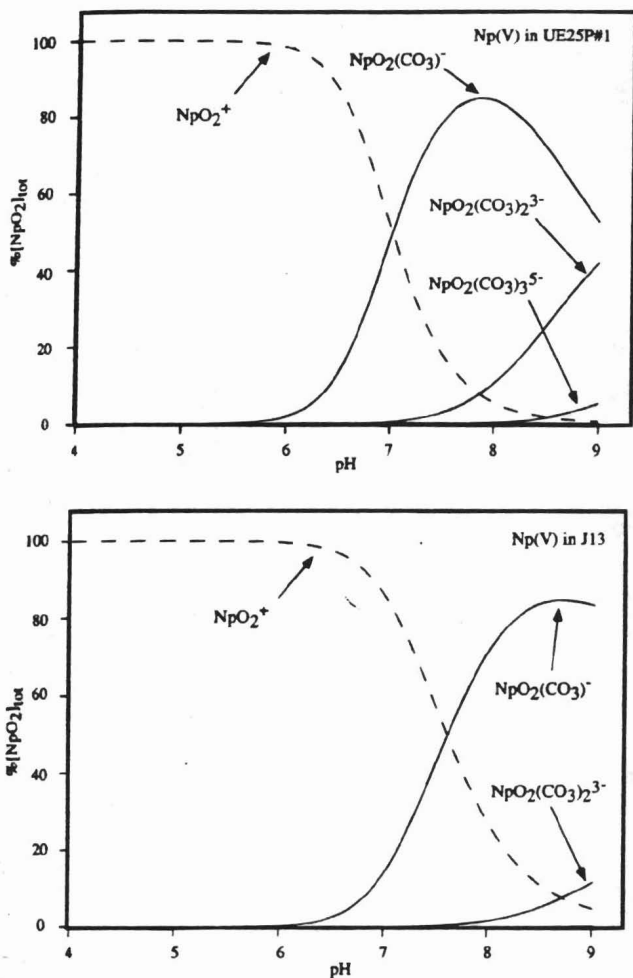


Figure 14. Calculated neptunyl species distributions in carbonate solutions modeling Yucca Mountain UE25P#1 (top) and J-13 (bottom) groundwaters at 25 °C. Np(V) carbonate binding constants were taken from Righet,¹⁸¹ ($I_m = 0.5\text{ m}$); hydrolysis constants were taken from Neck *et al.*⁹⁷ ($I_m = 0.1\text{ m}$); and ligand protonation constants were calculated for $I_m = 0.1\text{ m}$ using SIT and data from Grenthe *et al.*⁸¹ Solution conditions: (UE25P#1) $[\text{NpO}_2^{2+}] = 1 \times 10^{-5}\text{ M}$, $[\text{CO}_3^{2-} + \text{HCO}_3^-] = 0.002\text{ M}$. (J-13) $[\text{NpO}_2^{2+}] = 1 \times 10^{-5}\text{ M}$, $[\text{CO}_3^{2-} + \text{HCO}_3^-] = 0.0114\text{ M}$. Formation constants ($\log \beta$): $\text{ML} = 4.3$; $\text{ML}_2 = 6.5$; $\text{ML}_3 = 7.9$ ($I_m = 0.5\text{ m}$); $\text{LH} = 9.1$; $\text{LH}_2 = 16.05$ ($I_m = 0.1\text{ m}$). Hydrolysis constants ($\log K$): $\text{MOH} = -11.32$; $\text{M}(\text{OH})_2 = -23.42$ ($I_m = 0.1\text{ m}$), where $\text{M} = \text{NpO}_2$ and $\text{L} = \text{CO}_3$.

even at pH = 9. As with uranium, when the metal ion concentration exceeds the carbonate concentration, hydrolysis will play an increasingly important role. Uranyl(V) is not expected to be stable in groundwater solutions, and the Pu(V) ion is expected to behave similarly to Np(V) for a given groundwater solution.

2.3. Tetravalent Actinide Carbonate Complexes

2.3.1. Solid State and Structural Studies

A discussion of thorium carbonate and carbonate solids has been given by Bagnall.¹⁸⁷ Simple, neutral binary thorium(IV) carbonates of formula $\text{Th}(\text{CO}_3)_2$ and $\text{Th}(\text{CO}_3)_2 \cdot n\text{H}_2\text{O}$ ($n = 0.5$ and $3.00\text{--}3.57$) are claimed to form during the pyrolysis of $\text{Th}(\text{C}_2\text{O}_4)_2$, or by heating thorium hydroxide under CO_2 at 150 °C, respectively.¹⁸⁷ There are literature reports on solids of formula $\text{ThO}(\text{CO}_3)$ and $\text{Th}(\text{OH})_2(\text{CO}_3) \cdot 2\text{H}_2\text{O}$, but these solids are not well characterized.¹⁸⁷ The exist-

ence of the guanidinium complexes $[\text{C}(\text{NH}_2)_3][\text{An}(\text{CO}_3)_3]$ ($\text{An} = \text{Th}, \text{U}$) have also been claimed. It has been reported that addition of ethylenediammonium sulfate to uranium(IV) solutions of $(\text{NH}_4)_2\text{CO}_3$ or KHCO_3 results in the precipitation of $[\text{C}_2\text{H}_4(\text{NH}_3)_2][\text{U}(\text{CO}_3)_3(\text{H}_2\text{O})] \cdot 2\text{H}_2\text{O}$.¹⁸⁸ Hydrolysis of this complex occurs with dissolution to give $[\text{C}_2\text{H}_4(\text{NH}_3)_2][\text{U}_2(\text{OH})_2(\text{CO}_3)_5(\text{H}_2\text{O})_4] \cdot 2\text{H}_2\text{O}$ or $[\text{C}_2\text{H}_4(\text{NH}_3)_2][\text{U}(\text{OH})_2(\text{CO}_3)_2(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$. Tetracarbonato uranium salts of composition $[\text{C}(\text{NH}_2)_3]_4[\text{U}(\text{CO}_3)_4]$ and $[\text{C}(\text{NH}_2)_3]_3(\text{NH}_4)[\text{U}(\text{CO}_3)_4]$ have been reported.¹⁸⁸ The corresponding thorium salts with sodium or guanidinium cations have also been proposed.

The pentacarbonato salts of thorium(IV) and uranium(IV) are the most well studied of the tetravalent actinide carbonate solids. The salts of formula $\text{M}_6\text{An}(\text{CO}_3)_5 \cdot n\text{H}_2\text{O}$ ($\text{An} = \text{Th}, \text{U}$; $\text{M}_6 = \text{Na}_6, \text{K}_6, \text{TL}_6$, $[\text{Co}(\text{NH}_3)_6]_2$, $[\text{C}(\text{NH}_2)_3]_3[\text{NH}_4]_3$, $[\text{C}(\text{NH}_2)_3]_6$; $n = 4\text{--}12$) have all been reported.^{189–191} The sodium salt can be prepared by chemical or electrochemical reduction of $\text{Na}_4\text{UO}_2(\text{CO}_3)_3$, followed by the addition of Na_2CO_3 to form a precipitate. The potassium salt, $\text{K}_6\text{U}(\text{CO}_3)_5 \cdot 6\text{H}_2\text{O}$ can be prepared by dissolution of freshly prepared U(IV) hydroxide in K_2CO_3 solution in the presence of CO_2 ; and the guanidinium salt can be prepared by addition of guanidinium carbonate to a warm $\text{U}(\text{SO}_4)_2$ solution, followed by cooling.¹⁸⁸ The anhydrous sodium, thallium, and guanidinium salts can be prepared by heating the hydrated salts. It is well established that the hydrated salts of formula $\text{M}_6\text{An}(\text{CO}_3)_5 \cdot n\text{H}_2\text{O}$ contain bidentate carbonate ligands and that there are no water molecules bound directly to the central metal atom. All of the uranium(IV) complexes are readily air oxidized to uranium(VI) complexes, and therefore there is no structural information for the uranium analogs. The only single-crystal X-ray diffraction studies that we are aware of are for salts of $\text{Th}(\text{CO}_3)_5^{6-}$ and $\text{Th}(\text{CO}_3)_6^{8-}$.^{192–196,200}

Solid plutonium(IV) carbonate complexes of general formula $\text{M}_x(\text{Pu}(\text{CO}_3)_4)_n \cdot n\text{H}_2\text{O}$ have been prepared for a variety of alkali metal cations ($\text{M} = \text{Na}^+, \text{K}^+, \text{NH}_4^+$; $x = 4, 5, 6, 8$). The generic preparation involves dissolution of plutonium(IV) oxalate in the appropriate alkali metal carbonate solution. Addition of the resulting solution to a mixture of ethanol and water resulted in the plutonium(IV) carbonate compound adhering to the container walls, leaving the alkali carbonate and oxalate in solution. Standing in 99% ethanol or thermal dehydration converts the oil to an amorphous powder. Depending on reaction conditions, $\text{K}_4\text{Pu}(\text{CO}_3)_4 \cdot n\text{H}_2\text{O}$, $\text{K}_6\text{Pu}(\text{CO}_3)_5 \cdot n\text{H}_2\text{O}$, $\text{K}_8\text{Pu}(\text{CO}_3)_6 \cdot n\text{H}_2\text{O}$, and $\text{K}_{12}\text{Pu}(\text{CO}_3)_8 \cdot n\text{H}_2\text{O}$ have all been reported.¹⁹⁷ These compounds are all reported as green amorphous powders which are water soluble. $\text{K}_6[\text{Pu}(\text{CO}_3)_5] \cdot n\text{H}_2\text{O}$ can be isolated as brownish green crystals where $n = 3$ or 4. Sodium salts of formula $\text{Na}_4\text{Pu}(\text{CO}_3)_4 \cdot 3\text{H}_2\text{O}$, $\text{Na}_6\text{Pu}(\text{CO}_3)_5 \cdot 2\text{H}_2\text{O}$, and $\text{Na}_8\text{Pu}(\text{CO}_3)_6 \cdot 4\text{H}_2\text{O}$ have been claimed as light green crystalline compounds that appear to lose some water of hydration and crumble upon exposure to air.¹⁹⁸ Similarly, the $(\text{NH}_4)_4\text{Pu}(\text{CO}_3)_4 \cdot 4\text{H}_2\text{O}$ and $[\text{Co}(\text{NH}_3)_6]_2\text{Pu}(\text{CO}_3)_5 \cdot 5\text{H}_2\text{O}$ salts have been reported.¹⁹⁹ It is difficult to evaluate many of the plutonium(IV) carbonate reports without additional characterizing data. On the basis of the crystal structures of the

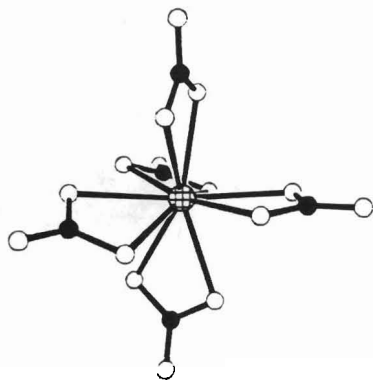


Figure 15. A ball-and-stick drawing illustrating the pseudo hexagonal bipyramidal coordination geometry of the $\text{Th}(\text{CO}_3)_5^{6-}$ anion in the solid state structure of $[\text{C}(\text{NH}_2)_3]_6[\text{Th}(\text{CO}_3)_5]$. The drawing was prepared from the fractional coordinates and unit cell parameters reported in ref 194. Hatched atoms = Th; black = C; and white = O.

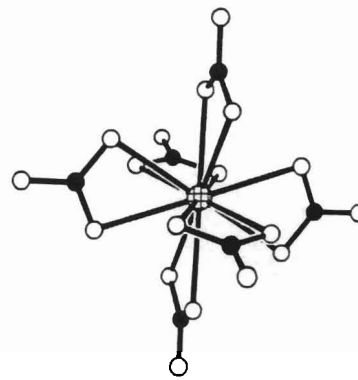


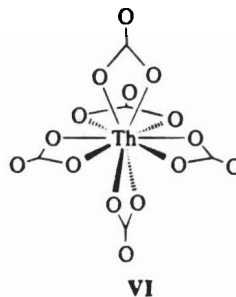
Figure 16. A ball-and-stick drawing illustrating the icosahedral coordination geometry (virtual T_h symmetry) of the $\text{Th}(\text{CO}_3)_6^{8-}$ anion in the solid state structure of tuluokite $\text{Na}_6\text{BaTh}(\text{CO}_3)_6 \cdot 6\text{H}_2\text{O}$. The drawing was prepared from the fractional coordinates and unit cell parameters reported in ref 200. Hatched atoms = Th; black = C; and white = O.

analogous thorium compounds, plutonium(IV) carbonate anions of formula $\text{Pu}(\text{CO}_3)_4^{4-}$, $\text{Pu}(\text{CO}_3)_5^{6-}$, and $\text{Pu}(\text{CO}_3)_6^{8-}$ seem reasonable, but higher-order anions may well be mixtures of the plutonium(IV) carbonate complexes and alkali carbonate.

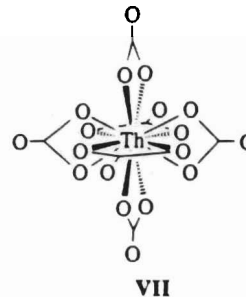
$\text{M}_6\text{An}(\text{CO}_3)_5$. Single crystals of $\text{Na}_6\text{Th}(\text{CO}_3)_5 \cdot 12\text{H}_2\text{O}$ were originally reported to possess monoclinic symmetry.¹⁸⁹ Two forms of this solid have since been shown to have triclinic crystal symmetry.¹⁹³⁻¹⁹⁵ The solid state structure has been determined from single-crystal X-ray diffraction data. In the solid state, the $\text{Th}(\text{CO}_3)_5^{6-}$ anion consists of a central thorium atom coordinated to 10 oxygen atoms of five bidentate carbonate ligands. The oxygen atoms are located at the vertices of an irregular decahedron. A ball-and-stick drawing of the solid state structure of the thorium hexaanion is shown in Figure 15. The Th–O distances range from 2.45 to 2.56 Å. After examining the solid state structure in detail, we prefer to view this complex structure as a modification of the well-known hexagonal bipyramidal coordination polyhedron seen in $\text{AnO}_2(\text{CO}_3)_3^{4-}$. Viewed in this way, the $\text{Th}(\text{CO}_3)_5^{6-}$ ion has three bidentate carbonate ligands in an approximately hexagonal plane, and two trans bidentate carbonate ligands occupying pseudo-axial positions as illustrated qualitatively in VI. The solid state structure was also reported for the guanidinium salt $[\text{C}(\text{NH}_2)_3]_6[\text{Th}(\text{CO}_3)_5]$,¹⁹⁴ and the correct space group has been subsequently assigned.¹⁹⁶

$\text{Na}_6\text{BaTh}(\text{CO}_3)_6 \cdot 6\text{H}_2\text{O}$. The only well-characterized actinide(IV) carbonate solid with six carbonates per metal atom is the recently reported mineral tuluokite $\text{Na}_6\text{BaTh}(\text{CO}_3)_6 \cdot 6\text{H}_2\text{O}$, discovered in pegmatite veins of the Khibinski alkaline Massif, in the former Soviet Union.²⁰⁰ The solid state structure was determined from single-crystal X-ray diffraction data. The three-dimensional structure consists of columns of barium and thorium icosahedra which alternate along the crystallographic *c* axis and share common polyhedral faces. The sodium atoms are found interspersed between the barium and thorium columns. The column of thorium atoms contains discrete molecules of $\text{Th}(\text{CO}_3)_6^{8-}$ anions; the basic structural features of this ion are shown in a ball-and-stick representation in Figure 16. The icosahedral

perpendicular planes formed by the trans carbonate ligands, giving virtual T_h symmetry as seen in Figure 16 and in VII. The average of the Th–O distances to the carbonate ligands is 2.62 Å, and average C–O distances are 1.30 Å.²⁰⁰ The interatomic distances between carbonate ligands and barium or sodium cations average 2.95 and 2.60 Å, respectively.²⁰⁰



VI



VII

2.3.2. Solution Chemistry

Whereas there is a great deal of qualitative information regarding anionic carbonate complexes of the tetravalent actinides, reliable quantitative data are rare. The most recent solution studies for thorium have been reported by Bruno *et al.*,⁸⁹ Grenthe *et al.*,⁹¹ João *et al.*,²⁰¹ and Östholms *et al.*²⁰² In the study by Östholms *et al.*,²⁰² the solubility of microcrystalline ThO_2 was examined as a function of pH and CO_2 partial pressure. The results were consistent with the presence of a thorium mixed hydroxo carbonate complex of formula $\text{Th}(\text{OH})_3(\text{CO}_3)^-$ and the pentacarbonate complex $\text{Th}(\text{CO}_3)_5^{6-}$; the formation constants were determined for both species.²⁰² The observation of a mixed hydroxy carbonate complex of a readily hydrolyzable tetravalent cation is not unreasonable, since complexes of this type have been found for other ions.²⁰³ In the case of uranium, there is quantitative data only for $\text{U}(\text{CO}_3)_5^{6-}$ and $\text{U}(\text{CO}_3)_4^{4-}$.^{204,205} Ciavatta *et al.* studied the redox equilibrium shown in eq 16 by both potentiometric and spectrophotometric techniques.²⁰⁴ The standard potential for the U(IV)–U(VI) redox couple was then used to estimate the value of $\log \beta_{15}$ for formation of the limiting complex $\text{U}(\text{CO}_3)_5^{6-}$ in eq 17. Pratopo *et al.* reanalyzed solubility data for uranium in a

Table 4. Representative Values for the Equilibrium Constants of the Carbonate Complexes of Tetravalent Actinides at Selected Ionic Strengths and Room Temperature

reaction	I	log K	ref
Thorium(IV)			
$\text{Th}^{4+} + 5\text{CO}_3^{2-} \rightleftharpoons \text{Th}(\text{CO}_3)_5^{6-}$	1.0 ^a	26.2(±0.2)	201
	2.5 ^a	26.3(±0.2)	201
	3.0	32.3	202
$\text{ThO}_2(\text{s}) + 4\text{H}^+ + 5\text{CO}_3^{2-} \rightleftharpoons \text{Th}(\text{CO}_3)_5^{6-}$	3.0	39.64(±0.4)	202
$\text{ThO}_2(\text{s}) + \text{H}^+ + \text{H}_2\text{O} + \text{CO}_3^{2-} \rightleftharpoons \text{Th}(\text{OH})_3(\text{CO}_3)^{-}$	3.0	6.78(±0.3)	202
Uranium(IV)			
$\text{U}^{4+} + 5\text{CO}_3^{2-} \rightleftharpoons \text{U}(\text{CO}_3)_5^{6-}$	0	34.0(±0.9)	81
	3.0	69.86(±0.55)	204
$\text{U}(\text{CO}_3)_4^{4-} + \text{CO}_3^{2-} \rightleftharpoons \text{U}(\text{CO}_3)_5^{6-}$	0	-1.12(±0.22)	205
Neptunium(IV)			
$\text{Np}^{4+} + 3\text{CO}_3^{2-} \rightleftharpoons \text{Np}(\text{CO}_3)_3^{2-}$	0.3	37.1(±1.2)	207
$\text{Np}^{4+} + 4\text{CO}_3^{2-} \rightleftharpoons \text{Np}(\text{CO}_3)_4^{4-}$	0.3	41.1(±1.4)	207
$\text{Np}^{4+} + 4\text{OH}^- + 2\text{CO}_3^{2-} \rightleftharpoons \text{Np}(\text{OH})_4(\text{CO}_3)_2^{4-}$	0.1	53.07(±0.44)	206
Plutonium(IV)			
$\text{Pu}^{4+} + \text{CO}_3^{2-} \rightleftharpoons \text{Pu}(\text{CO}_3)^{2+}$	0.3	17.0(±0.7)	100
$\text{Pu}^{4+} + 2\text{CO}_3^{2-} \rightleftharpoons \text{Pu}(\text{CO}_3)_2$	0.3	29.9(±0.96)	100
$\text{Pu}^{4+} + 3\text{CO}_3^{2-} \rightleftharpoons \text{Pu}(\text{CO}_3)_3^{2-}$	0.3	39.1(±0.82)	100
$\text{Pu}^{4+} + 4\text{CO}_3^{2-} \rightleftharpoons \text{Pu}(\text{CO}_3)_4^{4-}$	0.3	42.9(±0.75)	100
$\text{Pu}^{4+} + 5\text{CO}_3^{2-} \rightleftharpoons \text{Pu}(\text{CO}_3)_5^{6-}$	0.3	44.5(±0.77)	100
$\text{Pu}^{4+} + 2\text{CO}_3^{2-} + 4\text{OH}^- \rightleftharpoons \text{Pu}(\text{OH})_4(\text{CO}_3)_2^{4-}$	≈0.1	46.4(±0.7)	210

^a NH_4NO_3 electrolyte. ^b K_2CO_3 electrolyte, 20 °C; NaClO_4 was used to adjust the ionic strength in all other studies.

mixed hydroxo carbonato complex of formula $\text{U}(\text{OH})_2(\text{CO}_3)_2^{2-}$, and proposed a value for the formation constant,²⁰⁶ but more quantitative data are needed. A representative set of thorium(IV) and uranium(IV) carbonate equilibria and their formation constants are given in Table 4.



Moriyama and co-workers reported complexation constants of Np(IV) in carbonate solutions based on solubility data and suggested the formation of $\text{Np}(\text{CO}_3)_3^{2-}$ and $\text{Np}(\text{CO}_3)_4^{4-}$ in solution.²⁰⁷ More recently, Pratopo *et al.* reported a solubility study of the Np(IV) carbonate system and concluded that mixed hydroxo carbonato complexes were required to explain the data. Pratopo *et al.* proposed the formation of $\text{Np}(\text{OH})_4(\text{CO}_3)_2^{4-}$ above pH = 10, and $\text{Np}(\text{OH})_2(\text{CO}_3)_2^{2-}$ below pH = 10.²⁰⁶ Representative thermodynamic formation constants for neptunium(IV) taken from the recent literature are listed in Table 4.

There is a great deal of scatter in the Pu(IV) carbonate formation constants reflecting the extreme difficulties encountered when working with aqueous Pu(IV). The Pu(IV) aquo ion is notoriously unstable in aqueous solution, being prone to rapid hydrolysis—the formation of colloidal Pu(IV) is a pervasive problem in all Pu(IV) complexation studies. Silva described spectrophotometric and complex competition experiments leading to a lower limit for the binding constant for $\text{Pu}(\text{CO}_3)^{2+}$ of $\log \beta_{11} > 13$.²⁰⁸ Lierse performed solubility studies of Pu(IV) in carbonate solutions and interpreted the results in terms of stepwise formation constants for the series of ions $\text{Pu}(\text{CO}_3)^{2+}$, $\text{Pu}(\text{CO}_3)_2$, $\text{Pu}(\text{CO}_3)_3^{2-}$, $\text{Pu}(\text{CO}_3)_4^{4-}$, and $\text{Pu}(\text{CO}_3)_5^{6-}$ in analogy with the reported solid phases and these values are given in Table 4.¹⁰⁰ Lierse's value for the first complex formation constant of $\log \beta_{11} = 17$ is many orders of magnitude

lower than the original values discussed by Newton and Sullivan² and appears to be a much more reasonable value for a monobidentate ligand complex. It is likely that the stepwise formation constants will be highly correlated and careful consideration of the mathematical and statistical details is necessary. Hobart *et al.* attempted to use a complex-competition method to determine the carbonate complexation of Pu(IV) using the citrate ion.²⁰⁹ They determined that mixed hydroxo carbonato compounds of general formula $\text{Pu}(\text{OH})_x(\text{CO}_3)_y$ must be present, but the values for x and y could not be determined from the data.²⁰⁹ The equilibria were quite complicated and multiple mixed ligand complexes were detected. Yamaguchi *et al.* studied the solubility of Pu(IV) in carbonate solutions and concluded that mixed hydroxo carbonato complexes were needed in order to fit the data.²¹⁰ They interpreted their results in terms of the formation of $\text{Pu}(\text{OH})_2(\text{CO}_3)_2^{2-}$ below pH = 10, and $\text{Pu}(\text{OH})_4(\text{CO}_3)_2^{4-}$ at pH greater than 10.²¹⁰

Americium(IV) is generally very unstable with respect to reduction or disproportionation in non-complexing aqueous solutions, but it can be stabilized in carbonate solutions. Bourges and co-workers reported formal potentials for the Am(III)–Am(IV) couple in carbonate solution and concluded that there were two more carbonate ligands bound to the Am(IV) ion than in the Am(III) complex.¹⁸² This observation prompted Grenthe and co-workers to propose the formation of $\text{Am}(\text{CO}_3)_5^{6-}$ with $\log \beta_{15} \approx 40$. This value agrees relatively well with that reported for the uranium analog.¹²⁷

From a perusal of the variety of proposed An(IV) carbonate species and their corresponding thermodynamic formation constants (Table 4), there is clearly no uniform, accurate model. For example, the major species for Th(IV) and U(IV) are clearly identified as $\text{Th}(\text{CO}_3)_5^{6-}$ and $\text{U}(\text{CO}_3)_5^{6-}$; while for Np(IV) $\text{Np}(\text{CO}_3)_3^{2-}$ and $\text{Np}(\text{CO}_3)_4^{4-}$ are proposed; while for Pu(IV) the entire series, $\text{Pu}(\text{CO}_3)_n^{4-2n}$ ($n = 1-5$), has been proposed. Clearly the widely scattered nature

of the carbonate formation constants for tetravalent plutonium, and the question of whether mixed hydroxo carbonates $\text{Pu}(\text{OH})_n(\text{CO}_3)_2^{n-}$ ($n = 2$ or 4) or $\text{Pu}(\text{CO}_3)_n^{4-2n}$ ($n = 1-5$) are the predominant solution species, illustrate the difficulty in identifying properly the solution species and determining their thermodynamic stabilities. Most studies of Th, U, Np, and Pu do indicate that mixed hydroxo carbonate complexes are important in describing the aqueous solution behavior.

2.3.3. Species Distribution in Aqueous Solutions

Thorium and plutonium are expected to be present as trivalent ions in natural water systems. It is also quite evident from consideration of available thermodynamic data that the thorium(IV) and plutonium(IV) carbonate systems are quite complicated, and the plutonium system is in need of further study. The data for thorium(IV) indicate that the predominant Th(IV) complex in many natural waters will be $\text{Th}(\text{CO}_3)_5^{6-}$ (in the absence of ligands other than hydroxide and carbonate).²⁰² The most recent data on plutonium indicate that hydroxo carbonate complexes are likely to form; but we believe that these species are, at best, defined only as $\text{Pu}(\text{OH})_x(\text{CO}_3)_y$, where the values of x and y have yet to be determined satisfactorily. The tendency of Pu(IV) to hydrolyze and form colloidal $\text{PuO}_2 \cdot 2\text{H}_2\text{O}$ will be very strong in natural waters. The present state of understanding is clearly insufficient for accurate predictions of the fate and transport of tetravalent actinide ions in natural water systems.

2.4. Trivalent Actinide Carbonate Complexes

2.4.1. Solid State and Structural Studies

The only data available for trivalent actinide carbonate solids exist for americium and curium. Americium(III) carbonate solids have been prepared by addition of a CO_2 -saturated solution of NaHCO_3 to aqueous solutions of Am(III). The resulting pink precipitate was washed with a CO_2 -saturated solution. Thermogravimetric data are consistent with the formulation of $\text{Am}_2(\text{CO}_3)_3 \cdot 4\text{H}_2\text{O}$.²¹¹ Treatment of $\text{Am}_2(\text{CO}_3)_3$ with either 0.5 M NaHCO_3 or 1.5 M Na_2CO_3 solutions produces $\text{NaAm}(\text{CO}_3)_2 \cdot 4\text{H}_2\text{O}$ and $\text{Na}_3\text{Am}(\text{CO}_3)_3 \cdot 3\text{H}_2\text{O}$, respectively.²¹¹ Acidified Am(III) solutions maintained under varying partial pressures of CO_2 yield solids which Runde *et al.* characterized as orthorhombic $\text{Am}(\text{OH})(\text{CO}_3)$ or $\text{Am}_2(\text{CO}_3)_3$ based on X-ray powder diffraction data, and comparison with neodymium and europium analogs.²¹² This confirmed Silva and Nitsche's earlier characterization of solid $\text{Am}(\text{OH})(\text{CO}_3)$, but an earlier report of a hexagonal form of $\text{Am}(\text{OH})(\text{CO}_3)$ could not be confirmed.²¹³

Curium(III) carbonate solids have been prepared by addition of a Cm(III) hydrochloric acid solution to a dilute potassium carbonate solution. The solid is believed to be $\text{Cm}_2(\text{CO}_3)_3$ by analogy with americium.²¹⁴

2.4.2. Solution Chemistry

Americium(III) carbonate complexation has been studied by spectrophotometry, solubility, potentiometry,

Table 5. Representative Values for the Equilibrium Constants of the Carbonate Complexes of Trivalent Actinides at Selected Ionic Strengths and Room Temperature

reaction	I	$\log K$	ref
Americium(III)			
$\text{Am}^{3+} + \text{CO}_3^{2-} \rightleftharpoons \text{Am}(\text{CO}_3)^+$	0	7.6	183
	0.1	6.69(± 0.15)	215
	0.1	5.08(± 0.92)	218
	0.3	6.48(± 0.03)	216
	5.0 ^a	5.7(± 0.4)	185
$\text{Am}^{3+} + 2\text{CO}_3^{2-} \rightleftharpoons \text{Am}(\text{CO}_3)_2^-$	0	12.3	183
	0.1	9.27(± 2.2)	218
	0.3	9.94(± 0.24)	183
	5.0 ^a	9.7(± 0.5)	185
	0	15.2	183
$\text{Am}^{3+} + 3\text{CO}_3^{2-} \rightleftharpoons \text{Am}(\text{CO}_3)_3^{3-}$	0.1	12.12(± 0.85)	218
	5.0 ^a	12.9(± 0.2)	185
	0.1	12.15(± 0.15)	218
$\text{Am}^{3+} + 2\text{CO}_3^{2-} + \text{OH}^- \rightleftharpoons \text{Am}(\text{OH})(\text{CO}_3)_2^-$	0.1	16.16(± 0.14)	218
$\text{Am}^{3+} + \text{CO}_3^{2-} + 2\text{OH}^- \rightleftharpoons \text{Am}(\text{OH})_2(\text{CO}_3)^-$	0.1	18.29(± 0.17)	218

^a NaCl electrolyte; NaClO_4 was used to adjust the ionic strength in all other studies.

al. used absorption spectrophotometry to determine $\log \beta_{11}$ for formation of $\text{Am}(\text{CO}_3)^+$ in 0.1 M perchlorate solution.²¹⁵ Felmy and co-workers studied the solubility of $\text{Am}(\text{OH})(\text{CO}_3)$ over a wide range of conditions and proposed the formation of $\text{Am}(\text{CO}_3)^+$, $\text{Am}(\text{CO}_3)_2^-$, and $\text{Am}(\text{CO}_3)_3^{3-}$, consistent with the known solids.¹⁸³ Meinrath and Kim examined the absorption and photoacoustic spectroscopy of Am(III) species under a 1% CO_2 atmosphere. $\text{Am}_2(\text{CO}_3)_3$ precipitated and was found to be the solubility-controlling solid under those conditions. Parallel solubility and spectroscopic studies were performed, and the data were consistent with the formation of $\text{Am}(\text{CO}_3)^+$ and $\text{Am}(\text{CO}_3)_2^-$.²¹⁶ Meinrath and Kim's value for $\log \beta_{11}$ is in good agreement with that reported by Nitsche. Bernkoff and Kim used a model containing mono-, bis-, and triscarbonate complexes as well as mixed hydroxo carbonate complexes to fit americium carbonate solubility data.²¹⁸ Giffaut and Vitorge reported evidence for radiolytic oxidation of $^{241}\text{Am}(\text{III})$ to $^{241}\text{Am}(\text{V})$ under CO_2 atmospheres and indicated that the slow kinetics of precipitation can induce experimental uncertainties in solubility measurements for these intensely radioactive isotopes.²¹⁷ Representative thermodynamic formation constants for Am(III) carbonate complexes are given in Table 5. There is not sufficient direct evidence to substantiate or refute the formation of $\text{Am}(\text{CO}_3)_3^{3-}$. When the carbonate complexation constants for Am(III) carbonates are compared with the hydrolysis constants, it becomes clear (see discussion below) that hydrolysis is competitive with carbonate complexation in the trivalent americium system. This raises the question of mixed hydroxo carbonate solution species and implies that more data is needed in this area.

2.4.3. Species Distribution in Aqueous Solutions

Americium(III) and curium(III) are the only trivalent actinides expected to be present at significant concentrations in natural waters systems. We used the thermodynamic formation constants for americium(III) hydrolysis and carbonate complexation to produce the expected species distributions under solution conditions representative of groundwater

% (Am³⁺)_{tot}

% (Am³⁺)_{tot}

Figure in ca (top) carbo and F and J from are fo [Am³⁺] [Am³⁺] Form = 9.1 = -7 = Am

repos for ca and J 17. 7 tions figure distri of the by car tratio Am(C above predic (not s) compl define carbor (CO₃)⁻ mately

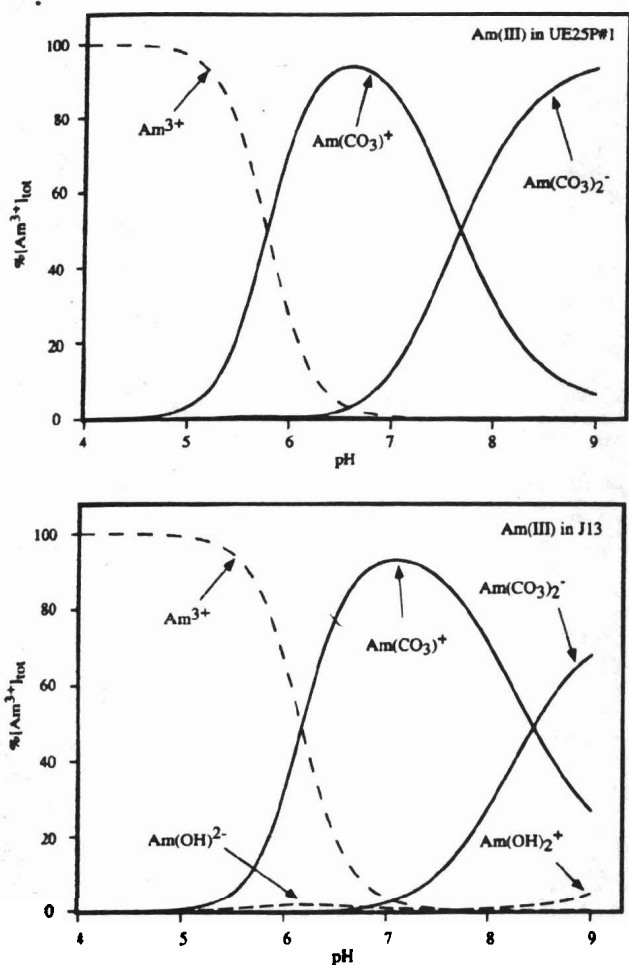


Figure 17. Calculated americium(III) species distributions in carbonate solutions modeling Yucca Mountain UE25P#1 (top) and J-13 (bottom) groundwaters at 25 °C. Am(III) carbonate formation constants were taken from Meinrath and Kim;²¹⁶ hydrolysis constants were taken from Stadler and Kim;²³ and ligand protonation constants calculated from SIT using data from Grenthe *et al.*⁸¹ All constants are for 0.1 *m* ionic strength. Solution conditions: (UE25P#1) $[Am^{3+}] = 1 \times 10^{-8}$ M, $[CO_3^{2-} + HCO_3^-] = 0.002$ M; (J-13) $[Am^{3+}] = 1 \times 10^{-8}$ M, $[CO_3^{2-} + HCO_3^-] = 0.0114$ M. Formation constants ($\log \beta$): $ML = 6.48$; $ML_2 = 9.94$; $LH = 9.1$; $LH_2 = 16.05$. Hydrolysis constants ($\log K$): $MOH = -7.46$; $M(OH)_2 = -15.32$; $M(OH)_3 = -26.88$, where $M = Am$ and $L = CO_3$.

repository. Calculated Am(III) species distributions for carbonate solutions representative of UE25P#1 and J-13 groundwater solutions are shown in Figure 17. Thermodynamic constants and solution conditions used in the calculations are included in the figure caption. From the calculated Am(III) species distributions, it is clear once again that the chemistry of the trivalent actinide ion is markedly influenced by carbonate complexation at low metal ion concentrations. Monomeric americium carbonate species $Am(CO_3)^+$, and $Am(CO_3)_2^-$ are expected to dominate above pH 6, and hydrolysis to form $Am(OH)_2^+$ is predicted to dominate at high pH values near 11.0 (not shown in Figure 17). We did not include the tris complex $Am(CO_3)_3^{3-}$, because its identity is not well defined. In the J-13 water, with a factor of 4 less carbonate than UE25P#1, the concentrations of $Am(CO_3)^+$ and $Am(CO_3)_2^-$ are predicted to be approximately equal near pH 8.5, while this change in the dominant species would occur at nearly pH 7.5 in the more carbonaceous UE25P#1 water. Carbonate com-

plexation is expected to dominate the speciation for the Am(III) ion under near-neutral pH conditions as long as there are ample carbonate ions present in solution.

3. Concluding Remarks

Both carbonate and hydroxide strongly complex actinide ions and will affect the mobility of actinide ions in natural groundwater systems. Therefore, identification of the carbonate complexes and determination of the thermodynamic parameters associated with their formation is a crucial area of study. A great deal of new data on actinide carbonate complexes has appeared since the critical solution chemistry review by Newton and Sullivan.² Advances in the last decade can be attributed, in part, to the application of many new techniques for the study of actinide speciation including, photothermal (PAS, PTL)²¹⁹⁻²³¹ and laser-induced fluorescence (LIF) spectroscopies,^{224,228,232} extended X-ray absorption fine structure (EXAFS),¹³¹ laser resonance ionization mass spectroscopy,²³³ improved trace analyses,²³⁴ combined extraction methods,^{183,225} and NMR spectroscopy.^{131,132,145,159} It is expected that further applications of these new techniques will greatly expand our understanding of these systems in the future.

In general, actinyl(VI) carbonate systems are quite complicated in that they consist of several complex ions in rapid equilibria with one another and with the aquo ion or hydrolyzed species. In the solid state, $AnO_2(CO_3)$, $M_6(AnO_2)_3(CO_3)_6$, and $M_4AnO_2(CO_3)_3$ are well characterized for uranium, while the analogous neptunium and plutonium solids are not as well defined, and the americium solids are unknown. In aqueous solution there is little doubt that the important species are $AnO_2(CO_3)$, $AnO_2(CO_3)_2^{2-}$, $AnO_2(CO_3)_3^{4-}$, and $(AnO_2)_3(CO_3)_6^{6-}$ (for $An = U, Np,$ and Pu). For uranyl there is also a great deal of evidence for additional polymeric species $(UO_2)_2(CO_3)(OH)_3^-$, $(UO_2)_3O(OH)_2(HCO_3)^+$, and $(UO_2)_{11}(CO_3)_6(OH)_{12}^{2-}$; the corresponding neptunyl, plutonyl, and americyl carbonate systems need further study.

Pentavalent actinide carbonate solids of general formula $M_{(2n-1)}AnO_2(CO_3)_n$ ($n = 1$ or 2 , M is a monovalent cation, and $An = Np, Pu,$ or Am) have been structurally characterized, and a unified picture of these salts has been presented. In aqueous solution, the carbonate complexes $AnO_2(CO_3)_n^{(2n-1)-}$ ($n = 1, 2,$ or 3 , $An = Np, Pu,$ or Am) have been observed. Consistent quantitative data are available for all three monocarbonato complexes and for the bicarbonato neptunyl complex.

Tetravalent actinide carbonate solids have only been well studied for thorium and uranium. Only pentacarbonato and hexacarbonato salts of formula $M_6An(CO_3)_5 \cdot nH_2O$ ($An = Th, U$) and $Na_6BaTh(CO_3)_6 \cdot 6H_2O$ have been structurally characterized. The aqueous solution chemistry of the tetravalent actinide carbonate complexes is extremely complex. Thermodynamic data are widely scattered, and the question remains whether mixed hydroxo carbonato complexes $An(OH)_n(CO_3)_2^{n-}$ ($n = 2$ or 4) or $An(CO_3)_n^{4-2n}$ ($n = 1-5$) are the predominant solution species. There are recent data which support the formation of $Th(OH)_3(CO_3)^-$ and $Th(CO_3)_5^{6-}$ as the

only important solution species, and also data which suggest that complexes of formula $An(OH)_x(CO_3)_y^{(2y+x-4)-}$ are important U, Np, and Pu solution species.

The compositions of trivalent actinide carbonate solids are well established, but structural details are not known. In aqueous solution, there is evidence for the stepwise formation of $An(CO_3)^+$, $An(CO_3)_2^-$, and $An(CO_3)_3^{3-}$ for $An = Am$ and Cm , but the question of mixed hydroxo carbonate solution species remains unanswered.

Clearly there are many areas of actinide carbonate research that require further study to define the nature of contaminants, to predict how actinides may behave in natural systems, to explore alternative methods for industrial processes and effluent treatment, to find acceptable methods for remediation and transuranic waste storage, and to manage responsibly the transuranic elements so their unique properties may be utilized.

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