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Actinide Carbonate Complexes and Their Importance in Actinide Environmental Chemistry

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Contents

1. Introduction 25
1.1. Complexation Equilibria 26
1.2. Hydrolysis 27
1.3. The Carbonate–Bicarbonate Ligand System 29
2. Carbonate Complexes of the Actinide Elements 29
2.1. Hexavalent Actinide Carbonate Complexes 29
2.1.1. Solid State and Structural Studies 29
2.1.2. Solution Chemistry 32
2.1.3. Species Distribution in Aqueous Solutions 35
2.2. Pentavalent Actinide Carbonate Complexes 36
2.2.1. Solid State and Structural Studies 36
2.2.2. Solution Chemistry 39
2.2.3. Species Distribution in Aqueous Solutions 40
2.3. Tetravalent Actinide Carbonate Complexes 41
2.3.1. Solid State and Structural Studies 41
2.3.2. Solution Chemistry 42
2.3.3. Species Distribution in Aqueous Solutions 44
2.4. Trivalent Actinide Carbonate Complexes 44
2.4.1. Solid State and Structural Studies 44
2.4.2. Solution Chemistry 44
2.4.3. Species Distribution in Aqueous Solutions 44
3. Concluding Remarks 45
4. Acknowledgments 46
5. References 46

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 structure discovery, 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 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 precipitation/dissolution and redox equilibria,6 solubility,12–19 radiolysis,20–34 hydrolysis,35,36 humic acid complexation,37–52 colloid generation,51,42,54–59 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.80 The known oxidation states of these elements are listed in Table 1.80 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-
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Actinide Carbonylation. The effectiveness of covalent bonding is the basis for the "hard" nature of the actinide carboxylate complexes. They are the result of the electrostatic interactions of the charged actinide ion and the negatively charged oxygen atom of the carboxylate group. The presence of these interactions makes the chemistry of the actinides more complex than that of the lanthanides.

In aqueous solutions, the actinide ions are highly soluble and form a variety of complexes with ligands such as carbonate, phosphate, and hydroxide. The formation constants of these complexes are important in understanding the behavior of the actinides in natural waters. The actinides are known to form complexes with ligands such as carbonate and bicarbonate, which are present in natural waters. These complexes are important in understanding the behavior of the actinides in natural waters. The actinides are known to form complexes with ligands such as carbonate and bicarbonate, which are present in natural waters. These complexes are important in understanding the behavior of the actinides in natural waters.
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 An–O bond distances within the relatively narrow range of 1.7–1.9 Å, and An–O bonds to the carbonate oxygens in the range 2.4–2.6 Å.

\[
\text{AnO}_2X_2 + 3M_2CO_3 \rightarrow M_4\text{AnO}_2(\text{CO}_3)_2 + 2M\text{X} \quad (\text{An} = \text{U, Np, Pu}; X = \text{Cl}^-, \text{Br}^-, \text{NO}_3^-, \text{ClO}_4^-, \text{etc.})
\]

(13)

### 2.1. 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 $\text{UO}_2(\text{CO}_3)_2$, $\text{UO}_2(\text{CO}_3)_2^{2-}$, and $\text{UO}_2(\text{CO}_3)_3^{4-}$ present under the appropriate conditions. There is also a great deal of evidence from emf, solubility, and spectroscopic data supporting the existence of polymeric solution species of formulas $\text{UO}_2(\text{CO}_3)_2^{6-}$, $\text{UO}_2(\text{CO}_3)_3\text{OH}^{3-}$, $\text{UO}_2\text{O}(\text{OH})_2(\text{HCO}_3)^-$, and $\text{UO}_2\text{H}(\text{CO}_3)_2\text{OH}^{2-}$ which form only under conditions of high metal ion concentration or high ionic strength. Determining the formation constant for the triscarbonate uranyl monomer, $\text{UO}_2(\text{CO}_3)_3^{4-}$, is complicated because this species is in equilibrium with the hexakiscarbonate uranyl trimer, $\text{UO}_2(\text{CO}_3)_6^{6-}$. 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 $\text{UO}_2(\text{CO}_3)_3^{2-}$ to form $\text{UO}_2(\text{CO}_3)_3^{4-}$, and used this value to calculate the formation constant, $\beta_{U(\text{CO}_3)_2}$. 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.

The trinuclear uranyl cluster ($\text{UO}_2(\text{CO}_3)_6^{6-}$ has been the subject of a good deal of study, including $^{13}C$ and $^{17}O$ NMR spectroscopy, solution EXAFS spectroscopy, and EXAFS spectroscopy in both the solid and solution states. 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, 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), which is a simple structural modification of the rutherfordine structure. Ciavatta et al. were the first to propose the ($\text{UO}_2(\text{CO}_3)_6^{6-}$ cluster based on potentiometric (emf) titration studies. 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. Several years later, Ferri et al. reported an $^{17}O$ NMR spectrum of a similar sample which displayed five $^{17}O$ NMR signals between $\delta$ 1130–1095 ppm in the expected 2:2:1:1 ratio, and it was argued that this $^{17}O$ NMR spectrum confirmed the solution structure of ($\text{UO}_2(\text{CO}_3)_6^{6-}$ as that shown in II. However, all five $^{17}O$ resonances appeared in the uranyl (O=U=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 $\delta$ 1105 ppm which is consistent with the proposed trimer structure, and the earlier assignment has been corrected. EXAFS measurements performed at the uranium L$_{\text{III}}$ edge for solid $\text{[C(NH}_2)_3\text{H}_3(\text{UO}_2\text{H}_3\text{CO}_3\text{H}_3]}$, solid $\text{K}_2[\text{UO}_2(\text{CO}_3)_3]$, and a solution of $\text{UO}_2(\text{CO}_3)_6^{6-}$ give further support of a trimeric structure for the ($\text{UO}_2(\text{CO}_3)_6^{6-}$ ion. Figure 5 shows the EXAFS Fourier transforms for solid $\text{K}_2[\text{UO}_2(\text{CO}_3)_3]$ (top) and $\text{[C(NH}_2)_3\text{H}_3(\text{UO}_2\text{H}_3\text{CO}_3\text{H}_3]}$ (bottom). The EXAFS Fourier transform of $\text{[C(NH}_2)_3\text{H}_3(\text{UO}_2\text{H}_3\text{CO}_3\text{H}_3]}$ 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 ions...
contain primarily sodium bicarbonate and very little other dissolved solids.\textsuperscript{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.\textsuperscript{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 ground-water 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 $\text{UO}_2^{2+}$, $\text{UO}_2\text{CO}_3^{2+}$, and $\text{UO}_2\text{CO}_3^{4-}$ are expected to dominate above pH 5, and the hydrolyzed species $\text{UO}_2(\text{OH})_2^{3+}$ 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 $1 \times 10^{-3}$ M, the trimeric cluster $(\text{UO}_2)_3(\text{CO}_3)_6^{5-}$ 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 $\text{AnO}_2\text{CO}_3$, $\text{AnO}_2\text{CO}_3^{2-}$, and $\text{AnO}_2\text{CO}_3^{3-}$ 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 $\text{M}_{2n-1}\text{AnO}_2\text{CO}_3$, where $n = 1$, 2, or 3; $M$ is a monovalent cation; and $\text{An} = \text{Np}$, $\text{Pu}$, or $\text{Am}$. The lack of data on U(V) complexes is due to the relative instability of the pentavalent oxidation state of uranium in aqueous solution.\textsuperscript{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 $\text{AnO}_2^{2+}$ 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 $\text{MNpO}_2\text{CO}_3$ are prepared by the addition of fairly dilute (0.1 M) alkali metal carbonate or bicarbonate solutions to stock solutions of the $\text{NpO}_2^{2+}$ ion stabilized in dilute acid. These so-called “double carbonate” salts precipitate from solution upon standing.\textsuperscript{164-170} In order to isolate pure samples of $\text{MNpO}_2\text{CO}_3$ 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 $\text{M}_2\text{NpO}_2\text{CO}_3$ precipitate overnight.\textsuperscript{171-173} Finally, the use of a large excess of alkali carbonate (such as 50% $\text{K}_2\text{CO}_3$ solutions) results in the formation of solids of general formula $\text{M}_2\text{NpO}_2\text{CO}_3\text{H}_2$.\textsuperscript{174} There are also reports of the existence of these solids with varying amounts of exchange of the solid acts as a source of Al.

For plutonium, a crystal that can be grown from aqueous solution is due to the presence of the highly basic (0.1 M) alkali metal carbonate solution.\textsuperscript{175} Like the actinides, the uranyl system yields K-stable $\text{K}_{2}\text{UO}_2\text{CO}_3$.

![Figure 8](image1.png)  
*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 constants corrected to an ionic strength of 0.1 M using specific ion interaction theory. Solution conditions: (UE25P#1) $[\text{UO}_2^{2+}] = 1 \times 10^{-8}$ M, $[\text{CO}_3^{2-} + \text{HCO}_3^{-}] = 0.002$ M; (J-13) $[\text{UO}_2^{2+}] = 1 \times 10^{-3}$ M, $[\text{CO}_3^{2-} + \text{HCO}_3^{-}] = 0.0114$ M. Formation constants (25 °C, $I_m = 0.1$ m, log $\beta$): ML = 8.60; ML$_2$ = 16.10; ML$_3$ = 21.65; M$_3$L$_4$ = 54.05; LH = 9.1; LH$_2$ = 16.05. Hydrolysis constants (log $K$): MOH = −5.38; M(OH)$_2$ = −10.56; 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$_4$(OH)$_6$ = −31.46; M$_5$(OH)$_7$ = −2.48, where $M = \text{UO}_2$ and $L = \text{CO}_3$.*

![Figure 9](image2.png)  
*Figure 9. Structure of PuO$_2$ (ref. 146).*
amounts of waters of hydration and of their cation exchange properties. A thorough understanding of the solid state structures of the compounds provides a satisfying explanation for these results.

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 KPuO$_2$(CO$_3$) or (NH$_4$)$_3$PuO$_2$(CO$_3$) precipitated. These have been extremely well characterized. Sodium and potassium americium(III) carbonates are prepared by heating dilute acid solutions of Am(III) and the corresponding alkali metal carbonate in solutions of hypochlorite. The exact compositions of the resulting solids could not be determined. An analogous preparation using peroxydisulfate or ozone as chemical oxidants in the presence of rubidium or ammonium carbonate provided solids of composition (NH$_4$)$_3$AmO$_2$(CO$_3$) and RbAmO$_2$(CO$_3$), which have been well characterized.

Like the neptunium analogs, the use of a large excess of alkali carbonate in the americium reactions will yield K$_3$AmO$_2$(CO$_3$)$_2$ and K$_6$AmO$_2$(CO$_3$)$_3$ solids.

MANO$_3$(CO$_3$). The actinyl(III) carbonate solids of general formula MANO$_2$(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 States and Volkov and co-workers in the former Soviet Union.

Solid state structures based on powder X-ray diffraction data have been determined for a wide variety of MANO$_2$(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 KPuO$_2$(CO$_3$) which crystallizes in the hexagonal space group $P6_3/mmc$ with two KPuO$_2$(CO$_3$) moieties in the unit cell. The reasonable assumptions of linear O=Pu=O and carbonate C–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 Pu–O distances of 2.55 Å. The plane of hexagonal bipyramidal plutonyl units forms an infinite layer of PuO$_2$(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 PuO$_2$(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 O=Pu=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. That is, the structure of KPuO$_2$(CO$_3$)$_2$ changes from hexagonal to orthorhombic as the divalent potassium ion is replaced by the monovalent sodium ion.
in the series of neptunium(V) monocarbonates M\(\text{NpO}_2\)\((\text{CO}_3)_2\) with \(M =\) Cs\(^+\), Rb\(^+\), NH\(_4\)\(^+\), K\(^+\), Na\(^+\), and Li\(^+\), a hexagonal-to-orthorhombic phase change was observed within the \(\text{NpO}_2\)\((\text{CO}_3)_2\) layer at the potassium—sodium boundary. The solids maintain a layered structure, but the orthorhombic \(\text{NpO}_2\)\((\text{CO}_3)_2\) sheets now have the same structure as that found in rutherfordine (Figure 1). The hexagonal and orthorhombic structures are related by displacement of the \((\text{CO}_3)_2\) atoms within the \(\text{MAnO}_2\)\((\text{CO}_3)_2\) sheets. In the general case, the potassium carbonates 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)_2\(n\)\(\text{H}_2\)\(\text{O}\) with intercalated water molecules.

\(\text{M}_3\text{AnO}_2\)\((\text{CO}_3)_2\(n\)\(\text{H}_2\)\(\text{O}\). The actinyl(V) carbonate solids of general formula \(\text{M}_3\text{AnO}_2\)\((\text{CO}_3)_2\(n\)\(\text{H}_2\)\(\text{O}\) (An = Np, Pu, Am, and \(M =\) Na, K, Rb) have been studied extensively by Volkov and co-workers.\(^{166,171,172}\) 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\(n\)\(\text{H}_2\)\(\text{O}\) compounds maintain the same orthorhombic layered structure as seen in \(\text{MAnO}_2\)\((\text{CO}_3)_2\) except that one half of the \(\text{AnO}_2\)\(^+\) 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 \(\text{AnO}_2\)\(^+\) cations form alternating chains within the familiar hexagonal sheet and give rise to the approximate composition \([\text{M}_0.5\text{(AnO}_2\text{)}0.5\text{(CO}_3\text{)}]\) 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 \(\text{AnO}_2\)\(^+\) 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 \(M-O-An\) interaction between layers. In this way, a second infinite chain of \(O-An-O-M-O-An-O\) 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 \(\text{AnO}_2\)\(^+\) ions allows for a relatively straightforward explanation of the observed structural variations.

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

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The octahedral anions form a tightly packed infinite layer which is more open than the hexagonal structure which is 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, the orthorhombic structure

\[\text{M}_3\text{AnO}_2\)\((\text{CO}_3)_2\(n\)\(\text{H}_2\)\(\text{O}\) compounds maintain the same orthorhombic layered structure as seen in \(\text{MAnO}_2\)\((\text{CO}_3)_2\) except that one half of the \(\text{AnO}_2\)\(^+\) 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 \(\text{AnO}_2\)\(^+\) cations form alternating chains within the familiar hexagonal sheet and give rise to the approximate composition \([\text{M}_0.5\text{(AnO}_2\text{)}0.5\text{(CO}_3\text{)}]\) 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 \(\text{AnO}_2\)\(^+\) 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 \(M-O-An\) interaction between layers. In this way, a second infinite chain of \(O-An-O-M-O-An-O\) 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.

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ward explanation for the presence of nonstoichiometric solids such as $M_xAnO_2(CO_3)_{2x+y}nH_2O$. 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 $M_{x+2y}AnO_2(CO_3)_{2x+y}nH_2O$, 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 $H_2O-M^+-OH_2$ 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 $M_xAnO_2(CO_3)$.  

Diffuse reflectance spectra recorded for $NaNPo_2(CO_3)$ and $Na_xNPo_2(CO_3)_{2x+y}$ solids are compared in Figure 13. The remarkable differences in the spectra of these solids can be attributed to the

**Figure 12.** A ball-and-stick drawing illustrating the infinite stacking between $KNpO_2(CO_3)$ layers in the solid state structure of $K_2NPo_2(CO_3)$. 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.

**Figure 13.** Comparison of the diffuse reflectance spectra of the solids $NaNPo_2(CO_3)$ (solid line) and $Na_xNPo_2(CO_3)$ (dashed line).

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

**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. The Raman-active $v_1$ 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. $UO_2(CO_3)_{3}^{4-}$ reduced to $UO_2(CO_3)_{3}^{6-}$ has a $v_1$ Raman band at 759 cm$^{-1}$, and the $NpO_2^+$ ion in 2 M carbonate solution has a $v_1$ Raman band at 755 cm$^{-1}$. The species present is thought to be $NpO_2(CO_3)_{3}^{5-}$. Both $AmO_2^+$ and $PuO_2^+$ in carbonate solutions have Raman bands at 755 cm$^{-1}$. In comparison with the $v_1$ frequencies measured in acidic solutions, those in carbonate solutions show a small negative shift for $v_1$ of $Np(V)$ and a positive shift for $v_1$ of $Am(V)$. Madic et al. suggested that the differences between frequencies in noncomplexing media and in carbonate media may
be related to hydrogen bonding between the oxygen of the actinyl ions and water molecules.\textsuperscript{134}

Wester and Sullivan measured the formal potentials for the reduction of AnO\textsubscript{2}(CO\textsubscript{3})\textsuperscript{4-} to AnO\textsubscript{2}(CO\textsubscript{3})\textsuperscript{5-} in 1 M Na\textsubscript{2}CO\textsubscript{3} to be \(-0.538, +0.445, +0.334\) V for An = U,\textsuperscript{177} Np,\textsuperscript{178} and Pu,\textsuperscript{179} respectively. They observed that the carbonate radical, CO\textsubscript{3}\textsuperscript{2-} can oxidize any of the AnO\textsubscript{2}(CO\textsubscript{3})\textsuperscript{5-} 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.\textsuperscript{180-186}

There is only one uranyl(V) species for which quantitative thermodynamic information is available, namely UO\textsubscript{2}(CO\textsubscript{3})\textsuperscript{5-}. The formation constant for this species was determined on the basis of the formation constant of UO\textsubscript{2}(CO\textsubscript{3})\textsuperscript{4-} and the reduction potential of the equilibrium shown in eq \textsuperscript{180}

\[ \text{UO}_2^{2+} + 3C_2 = \text{UO}_2(CO_3)^{3-} \quad (15) \]

There is ample spectrophotometric and solubility data supporting the formation of monomeric complex ions, NpO\textsubscript{2}(CO\textsubscript{3})\textsuperscript{5-}, NpO\textsubscript{2}(CO\textsubscript{3})\textsuperscript{4-}, and NpO\textsubscript{2}(CO\textsubscript{3})\textsuperscript{3-} in solution; and these correlate nicely with the known solid phase salts MNpO\textsubscript{2}(CO\textsubscript{3}), M\textsubscript{2}NpO\textsubscript{2}(CO\textsubscript{3})\textsubscript{2}, and M\textsubscript{3}NpO\textsubscript{2}(CO\textsubscript{3})\textsubscript{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 constants of the carbonate complexes of pentavalent actinides at selected ionic strengths and 25°C are given in Table 3.\textsuperscript{181}

Bennett and co-workers determined the formation constant for PuO\textsubscript{2}(CO\textsubscript{3})\textsuperscript{4-} using photoacoustic spectroscopy (PAS), then employed the specific ion interaction theory (SIT) to calculate a formation constant at zero ionic strength (Table 3).\textsuperscript{183} This value compares favorably with the corresponding log \(A_{11}\) for the NpO\textsubscript{2}(CO\textsubscript{3})\textsuperscript{5-} analog (Table 3). No evidence for mixed hydroxy carbonate species was found in this study, in which hydrolysis behavior of the PuO\textsubscript{2}\textsuperscript{3+} ion was also investigated. The formation constant for the triscarbonate species, PuO\textsubscript{2}(CO\textsubscript{3})\textsuperscript{5-}, was determined by Lierse using the formation constant of PuO\textsubscript{2}(CO\textsubscript{3})\textsuperscript{4-} and the one electron reduction potential between the two species in analogy to eq \textsuperscript{15}.\textsuperscript{100}

Ferri, Grenthe, and Salvatore recalculated previous redox data of Bourges et al.\textsuperscript{182} for the AmO\textsubscript{2}\textsuperscript{5+}/AmO\textsubscript{2}\textsuperscript{4+} redox couple in carbonate media.\textsuperscript{180} This reinterpretation indicates that AmO\textsubscript{2}\textsuperscript{5+} forms a limiting carbonate complex AmO\textsubscript{2}(CO\textsubscript{3})\textsubscript{5-} with approximately the same formation constant as found for the analogous uranyl(V) species. One problem with extrapolation of the formation constants of AmO\textsubscript{2}(CO\textsubscript{3})\textsubscript{5-} to zero ionic strength arises from the strong ion-pairing between cations such as Na\textsuperscript{+} and the pentactinian.

### 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 groundwater found at the proposed Yucca Mountain repository. Calculated neptunyl species distributions under carbonate complexation conditions representative of those found in UE25P#1 and J-13 groundwater 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 NpO\textsubscript{2}(CO\textsubscript{3})\textsuperscript{4-} and NpO\textsubscript{2}(CO\textsubscript{3})\textsuperscript{3-} are expected to dominate above pH = 7, and hydrolysis to form NpO\textsubscript{2}(OH)\textsubscript{2} 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 NpO\textsubscript{2}(CO\textsubscript{3})\textsubscript{5-} 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, NpO\textsubscript{2}(CO\textsubscript{3})\textsubscript{5-} is predicted to be the dominant species even at pH = 9. There is some enough carbonate present to form up to the monoisotopic NpO\textsubscript{2}(CO\textsubscript{3})\textsubscript{5-} complex, but there is not enough carbonate present to form the tris complex even at pH = 9.

### 2.3. Trivalent Actinides

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23. Tetravalent Actinide Carbonate Complexes

23.1. Solid State and Structural Studies

A discussion of thorium carbonate and carbonate solids has been given by Bagnall. Simple, neutral binary thorium(IV) carbonates of formula Th(CO₃)₂ and Th(CO₃)₂·nH₂O (n = 0.5 and 3.00–3.57) are claimed to form during the pyrolysis of Th₂O₃, or by heating thorium hydroxide under CO₂ at 150 °C, respectively. There are literature reports on solids of formula Th(CO₃)₂ and Th(OH)₂(CO₃)₂·2H₂O, but these solids are not well characterized. The existence of the guanidinium complexes [C(NH₄)₃][An-(CO₃)₃] (An = Th, U) have also been claimed. It has been reported that addition of ethylenediammonium sulfate to uranium(IV) solutions of (NH₄)₂CO₃ or KHCO₃ results in the precipitation of [Co₂(H₂O)₆]⁺⁺(NH₄)₂CO₃ or [Co₂(H₂O)₆]⁺⁺(CO₃)₂·H₂O or [Co₂(H₂O)₆]⁺⁺(CO₃)₂·(H₂O)₂H₂O. Tetracarbonato uranium(IV) complexes of composition [C(NH₄)₃][U(CO₃)₄] and [C(NH₄)₃][U(CO₃)₄] have been reported. 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 M₂⁺An(CO₃)₅·nH₂O (An = Th, U; M₂⁺ = Na⁺, K⁺, Th⁴⁺, CO₃) have been prepared by chemical or electrochemical reduction of Na₄UO₂(CO₃)₃, followed by the addition of Na₂CO₃ to form a precipitate. The potassium salt, K₃(U(CO₃)₅·6H₂O, can be prepared by dissolution of freshly prepared U(IV) hydroxide in K₂CO₃ solution in the presence of CO₂; and the guanidinium salt can be prepared by addition of guanidinium carbonate to a warm U(SO₄)₂ solution, followed by cooling. 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 M₂⁺An(CO₃)₅·nH₂O 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 Th(CO₃)₄²⁻ and Th(CO₃)₃⁺.

Solid plutonium(IV) carbonate complexes of general formula M₂x⁺Pu(CO₃)₅·nH₂O have been prepared for a variety of alkali metal cations (M = Na⁺, K⁺, NH₄⁺; 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, K₃Pu(CO₃)₅·7H₂O, K₄Pu(CO₃)₅·9H₂O, K₅Pu(CO₃)₅·7H₂O, and K₆Pu(CO₃)₅·7H₂O have all been reported. These compounds are all reported as green amorphous powders which are water soluble. K₃Pu(CO₃)₅·7H₂O can be isolated as brownish green crystals where n = 3 or 4. Sodium salts of formula Na₄Pu(CO₃)₅·3H₂O, Na₅Pu(CO₃)₅·2H₂O, and Na₆Pu(CO₃)₅·4H₂O have been claimed as light green crystalline compounds that appear to lose some waters of hydration and crumble upon exposure to air. Similarly, the (NH₄)₅Pu(CO₃)₅·4H₂O and [Co(NH₃)₆]₃⁺Pu(CO₃)₅·5H₂O salts have been prepared. 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
analogous thorium compounds, plutonium(IV) carbonato anions of formula Pu(CO\(_3\))\(_{5}^{2-}\), Pu(CO\(_3\))\(_{6}^{3-}\), and Pu(CO\(_3\))\(_{8}^{8-}\) seem reasonable, but higher-order anions may well be mixtures of the plutonium(IV) carbonato complexes and alkali carbonate.

\[ \text{M}_2\text{An(CO}_3\text{)}_3\text{.} \]  
Single crystals of Na\(_2\)Th(CO\(_3\))\(_6\)12H\(_2\)O were originally reported to possess monoclinic symmetry.\(^{182}\) Two forms of this solid have since been shown to have triclinic crystal symmetry.\(^{183} - 186\) The solid state structure has been determined from single-crystal X-ray diffraction data. In the solid state, the Th(CO\(_3\))\(_6^{6-}\) 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 decahexahedron. A ball-and-stick drawing of the solid state structure of the thorium hexaion 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 AnO\(_2\)(CO\(_3\))\(_3^{3-}\). Viewed in this way, the Th(CO\(_3\))\(_6^{6-}\)-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 [C(NH\(_2\))\(_3\)]\(_2\)-[Th(CO\(_3\))\(_6\)],\(^{194}\) and the correct space group has been subsequently assigned.\(^{186}\)

\[ \text{Na}_2\text{BaTh(CO}_3\text{)}_6\text{H}_2\text{O}. \]  
The only well-characterized actinide(IV) carbonate solid with six carbonates per metal atom is the recently reported mineral tuliokite Na\(_2\)BaTh(CO\(_3\))\(_6\)H\(_2\)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 Th(CO\(_3\))\(_6^{6-}\) anions; the basic structural features of this ion are shown in a ball-and-stick representation in Figure 16. The icosahedral coordination geometry (virtual T\(_6\) symmetry) of the Th(CO\(_3\))\(_6^{6-}\) anion in the solid state structure of tuliokite Na\(_2\)BaTh(CO\(_3\))\(_6\)H\(_2\)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.

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.,\(^{199}\) Grenthe et al.,\(^{21}\) Joao et al.,\(^{201}\) and Ostholz et al.\(^{202}\) In the study by Ostholz 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 hydroxocarbonate complex of formula Th(OH)(CO\(_3\))\(_3^{3-}\) and the pentacarbonato complex Th(CO\(_3\))\(_6^{6-}\); the formation constants were determined for both species.\(^{202}\) The observation of a mixed hydroxocarbonate 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 U(CO\(_3\))\(_5^{5-}\) and U(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(III) redox couple was then used to estimate the value of log f\(_{\text{U}}\) for formation of the limiting complex U(CO\(_3\))\(_5^{5-}\) in eq 17. Pratopo et al. reanalyzed solubility data for uranium in a
mixed hydroxo carbonato complex of formula $\text{U(OH)}_2\text{(CO}_3)_3^{2-}$, and proposed a value for the formation constant,\textsuperscript{205} 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.

\begin{equation}
\text{UO}_2\text{(CO}_3)_3^{4-} + 2e^- + 2\text{CO}_2 \rightleftharpoons \text{U(CO}_3)_5^{6-} \tag{16}
\end{equation}

\begin{equation}
\text{U}^{4+} + 5\text{CO}_2^{2-} \rightleftharpoons \text{U(CO}_3)_6^{6-} \tag{17}
\end{equation}

Moriyama and co-workers reported complexation constants of Np(IV) in carbonate solutions based on solubility data and suggested the formation of Np(IV) complexes. More recently, Pratop et al. reported a solubility study of the Np(VO) complex system and concluded that the formation of mixed hydroxo carbonato complexes was required to explain the data. Pratop et al. proposed the formation of Np(IV) complexes in solution.\textsuperscript{207} They determined that mixed hydroxo carbonato compounds of general formula $\text{Pu(OH)}_2\text{(CO}_3)_3^{4-}$ must be present, but the values for x and y could not be determined from the data.\textsuperscript{208} The equilibria were quite complicated and multiple mixed ligand complexes were detected. Yamaguchi \textit{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.\textsuperscript{210} They interpreted their results in terms of the formation of $\text{Pu(OH)}_2\text{(CO}_3)_3^{4-}$ at pH = 10, and $\text{Pu(OH)}_2\text{(CO}_3)_3^{6-}$ at pH greater than 10.\textsuperscript{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.\textsuperscript{182} This observation prompted Grein et al. to propose the formation of Am(IV)$\text{CO}_3^{6-}$ 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 $\text{Th(CO}_3)_3^{6-}$ and $\text{U(CO}_3)_3^{6-}$; while for Np(IV) $\text{Np(CO}_3)_3^{2-}$ and $\text{Np(CO}_3)_4^{4-}$ are proposed; while for Pu(IV) the entire series, $\text{Pu(CO}_3)_n^{2-}$ ($n = 1$–5), has been proposed. Clearly the widely scattered nature lower than the original values discussed by Newton and Sullivan\textsuperscript{2} 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 \textit{et al.} attempted to use a complex-competition method to determine the carbonate complexation of Pu(IV) using the citrate ion.\textsuperscript{209} They determined that mixed hydroxo carbonato compounds of general formula $\text{Pu(OH)}_2\text{(CO}_3)_3^{4-}$ must be present, but the values for x and y could not be determined from the data.\textsuperscript{209} The equilibria were quite complicated and multiple mixed ligand complexes were detected. Yamaguchi \textit{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.\textsuperscript{210} They interpreted their results in terms of the formation of $\text{Pu(OH)}_2\text{(CO}_3)_3^{4-}$ at pH = 10, and $\text{Pu(OH)}_2\text{(CO}_3)_3^{6-}$ at pH greater than 10.\textsuperscript{210}

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

<table>
<thead>
<tr>
<th>reaction</th>
<th>$K$</th>
<th>ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Th$^{4+} + 5\text{CO}_2^{2-} \rightleftharpoons \text{Th(CO}_3)_3^{6-}$</td>
<td>$1.0^*$</td>
<td>201</td>
</tr>
<tr>
<td>$\text{ThO}_2\text{(CO}_3)_3^{4-} + 2\text{H}^+ + 3\text{CO}_2^{2-} \rightleftharpoons \text{Th(OH)_2(CO}_3)_3^{4-}$</td>
<td>$3.0$</td>
<td>202</td>
</tr>
<tr>
<td>$\text{ThO}_2\text{(CO}_3)_3^{4-} + \text{H}_2\text{O} + \text{CO}_2^{2-} \rightleftharpoons \text{Th(OH)_2(CO}_3)_3^{4-}$</td>
<td>$3.0$</td>
<td>202</td>
</tr>
<tr>
<td>$\text{U}^{4+} + 5\text{CO}_2^{2-} \rightleftharpoons \text{U(CO}_3)_5^{6-}$</td>
<td>$0.0$</td>
<td>81</td>
</tr>
<tr>
<td>$\text{UO}_2\text{(CO}_3)_3^{4-} + 2\text{e}^- + 2\text{CO}_2 \rightleftharpoons \text{U(CO}_3)_5^{6-}$</td>
<td>$0.3$</td>
<td>204</td>
</tr>
<tr>
<td>$\text{Np}^{4+} + 3\text{CO}_2^{2-} \rightleftharpoons \text{Np(CO}_3)_3^{3-}$</td>
<td>$0.3$</td>
<td>207</td>
</tr>
<tr>
<td>$\text{Np}^{4+} + 4\text{CO}_2^{2-} \rightleftharpoons \text{Np(CO}_3)_4^{2-}$</td>
<td>$0.3$</td>
<td>207</td>
</tr>
<tr>
<td>$\text{Np}^{4+} + 4\text{OH}^- + 2\text{CO}_2^{2-} \rightleftharpoons \text{Np(OH)}_2\text{(CO}_3)_3^{4-}$</td>
<td>$0.1$</td>
<td>206</td>
</tr>
<tr>
<td>$\text{Pu}^{4+} + \text{CO}_2^{2-} \rightleftharpoons \text{Pu(CO}_3)^{2+}$</td>
<td>$0.3$</td>
<td>100</td>
</tr>
<tr>
<td>$\text{Pu}^{4+} + 2\text{CO}_2^{2-} \rightleftharpoons \text{Pu(CO}_3)_2^{2+}$</td>
<td>$0.3$</td>
<td>100</td>
</tr>
<tr>
<td>$\text{Pu}^{4+} + 3\text{CO}_2^{2-} \rightleftharpoons \text{Pu(CO}_3)_3^{5-}$</td>
<td>$0.3$</td>
<td>100</td>
</tr>
<tr>
<td>$\text{Pu}^{4+} + 4\text{CO}_2^{2-} \rightleftharpoons \text{Pu(CO}_3)_4^{4-}$</td>
<td>$0.3$</td>
<td>100</td>
</tr>
<tr>
<td>$\text{Pu}^{4+} + 5\text{CO}_2^{2-} \rightleftharpoons \text{Pu(CO}_3)_5^{6-}$</td>
<td>$0.3$</td>
<td>100</td>
</tr>
<tr>
<td>$\text{Pu}^{4+} + 2\text{CO}_2^{2-} + 4\text{OH}^- \rightleftharpoons \text{Pu(OH)}_2\text{(CO}_3)_3^{4-}$</td>
<td>$0.1$</td>
<td>210</td>
</tr>
</tbody>
</table>

$^*\text{NH}_4\text{NO}_3$ electrolyte. $^*\text{K}_2\text{CO}_3$ electrolyte, 20 °C; NaClO$_4$ was used to adjust the ionic strength in all other studies.
of the carbonate formation constants for tetravalent plutonium, and the question of whether mixed hydroxocarbonates Pu(OH)₃(CO₃)₂⁻ (n = 2 or 4) or Pu(CO₃)₄²⁻ (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 hydroxocarbonato 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 tetravalent 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 Th(CO₃)₆⁶⁻ (in the absence of ligands other than hydroxide and carbonate). The most recent data on plutonium indicate that hydroxocarbonato complexes are likely to form; but from what we have measured in these complexes we believe that these species are, at best, defined only as Pu(OH)₃(CO₃)₃, where the values of x and y have yet to be determined satisfactorily. The tendency of Pu(IV) to hydrolyze and form colloidal PuO₂H₂O 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 CO₂-saturated solution of NaHCO₃ to aqueous solutions of Am(III). The resulting pink precipitate was washed with a CO₂-saturated solution. Thermogravimetric data are consistent with the formulation of Am₃(CO₃)₄H₂O. Treatment of Am₃(CO₃)₄ with either 0.5 M NaHCO₃ or 1.5 M Na₂CO₃ solutions produces Na₃Am(CO₃)₂H₂O and Na₃Am(CO₃)₃.²¹¹ Acidified Am(III) solutions maintained under varying partial pressures of CO₂ yield solids which Runde et al. characterized as orthorhombic Am(OH)(CO₃)₂ or Am₂(CO₃)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 Am(OH)(CO₃)₂, but an earlier report of a hexagonal form of Am(OH)(CO₃)₂ 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 Cm₂(CO₃)₃ by analogy with americium.²¹⁴

2.4.2. Solution Chemistry

Americium(III) carbonate complexation has been studied by spectrophotometry, solubility, potential, and isotope dilution analysis. Am(III) hydroxide and carbonate complexes are important in describing the aqueous solution behavior. Plutonium(III) complexation has not been studied as extensively as Am(III), and the lack of thermodynamic data results in considerable uncertainty in the description of Pu(III) carbonate species. Plutonium(III) carbonate complexes are important in describing the aqueous solution behavior.

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

<table>
<thead>
<tr>
<th>reaction</th>
<th>I</th>
<th>log K</th>
<th>ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Am³⁺ + CO₃⁻ → Am(CO₃)²⁻</td>
<td>0</td>
<td>7.6</td>
<td>183</td>
</tr>
<tr>
<td>Am³⁺ + 2CO₃⁻ → Am(CO₃)₃⁻</td>
<td>0</td>
<td>12.3</td>
<td>183</td>
</tr>
<tr>
<td>Am³⁺ + 3CO₃⁻ → Am(CO₃)₄⁻</td>
<td>0</td>
<td>15.2</td>
<td>183</td>
</tr>
</tbody>
</table>

NaCl electrolyte; NaClO₃ was used to adjust the ionic strength in all other studies.

Clark et al. used absorption spectrophotometry to determine log β₁ for formation of Am(CO₃)⁺ in 0.1 M perchlorate solution.²¹⁵ Felmy and coworkers studied the solubility of Am(OH)(CO₃) over a wide range of conditions and proposed the formation of Am(CO₃)⁺, Am(CO₃)₂⁻, and Am(CO₃)₃⁻, consistent with the known solids.²¹⁶ Meinrath and Kim examined the absorption and photoacoustic spectroscopy of Am(III) species under a 1% CO₂ atmosphere. Am₂(CO₃)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 Am(CO₃)⁺ and Am(CO₃)₂⁻.²¹⁷ Meinrath and Kim's value for log β₁ is in good agreement with that reported by Nitsche. Bernkoff and Kim used a model containing mono-, bi-, and triscarbonato complexes as well as mixed hydroxo carbonato complexes to fit americium carbonate solubility data.²¹⁸ Giffaut and Vitorge reported evidence for radiolytic oxidation of ²⁴⁵Am(III) to ²⁴⁵Am(V) under CO₂ atmospheres and indicated that the slow kinetics of precipitation can induce experimental uncertainties in solubility measurements for these intense radioactive isotopes.²¹⁹ 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 Am(CO₃)⁴⁻. When the carbonate complex formation constants for Am(III) carbonates are compared with the hydrolysis constants, it becomes clear that hydrolysis is competitive with carbonate complexation in the trivalent americium system. This raises the question of mixed hydroxocarbonato 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 systems. We also used the isotope dilution and solubility data to further refine our understanding of americium(III) hydrolysis and carbonate complexation.
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. 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) spectroscopies224,225,226 extended X-ray absorption fine structure (EXAFS),131 laser resonance ionization mass spectroscopy,233 improved trace analyses,234 combined extraction methods,183,226 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 hydroxylated species. In the solid state, An(II) are well characterized for uranium, while the analogous neptunium and plutonium solids are not as well defined, and the actinide solids are unknown. In aqueous solution there is little doubt that the important species are AnO(2)(CO(3))&, AnO(2)(CO(3))&-1, AnO(2)(CO(3))&, and (AnO(2))(CO(3))& preparand for An = U, Np, and Pu. For uranyl there is also a great deal of evidence for additional polymeric species (UO(2))(CO(3))(OH(3)), (UO(2)O(OH))&HC03&), and (UO(2))&1(CO(3))(OH(1))&-; the corresponding neptunyl, plutoanyl, and americ履约 carbonate systems need further study.

Pentavalent actinide carbonate solids of general formula M(2n-1)AnO(2)CO(3) (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))&1/2 or MAnO(2)(CO(3))& (n = 1, 2, or 3, An = Np, Pu, or Am) have been observed. Consistent quantitative data are available for all three monocarbonate complexes and for the biscarbonato neptunyl complex.

Tetravalent actinide carbonate solids have only been well studied for thorium and uranium. Only pentacarbonyl and hexacarbonyl salts of formula M(5)AnO(2)CO(3) and M(5)AnO(2)CO(3) 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 carbonate complexes An(OH)m(CO(3))&m (n = 2 or 4) or An(CO(3))&4-R (n = 1-5) are the predominant solution species. There are recent data which support the formation of Th(OH)3(CO3)2- and Th(CO3)42- as the
only important solution species, and also data which suggest that complexes of formula \( \text{An(OH)}_{x}^{-}\cdot\text{(CO}_3^{2-} \cdot \text{(H}_2\text{O})_{n-x} \cdot \text{U}_{n} \cdot \text{P}_{m} \cdot \text{Pu}_{p} \) 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 \( \text{An(OH)}_{x}^{-}\cdot\text{(CO}_3^{2-} \cdot \text{(H}_2\text{O})_{n-x} \cdot \text{Pu}^{3+} \cdot \text{An(OH)}_{x}^{-} \cdot\text{(CO}_3^{2-} \cdot \text{(H}_2\text{O})_{n-x} \cdot \text{Pu}^{3+} \) for \( \text{An} = \text{Am} \) and \( \text{Cm} \), 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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5. References

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