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Actinide Carbonate Complexes and Their Importance in Actinide Environmental Chemistry

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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]

Table 1. Oxidation States of Light Actinide Elements[a]

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

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

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,[6−11,53] 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-

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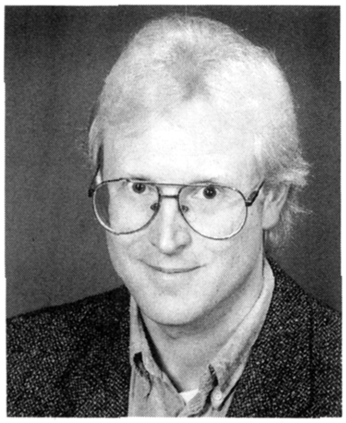

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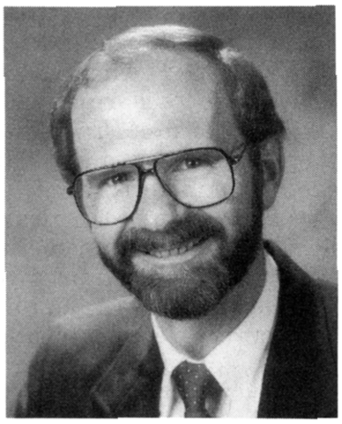

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tinides in aqueous solutions makes this chemistry rather complex. Furthermore, multiple oxidation states of the same element may exist simultaneously; plutonium, for example, may exist in four oxidation states, Pu(III), Pu(IV), Pu(V), and Pu(VI) under 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.

The toxicity of the actinide elements and the long half-lives of their isotopes are cause for concern if 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, $UO_2(CO_3)$,[78] liebigite, $Ca_2[UO_2(CO_3)_3]\cdot 10-11H_2O$,[79] and andersonite, $Na_2Ca[UO_2(CO_3)_3]\cdot 6H_2O$.[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 charge and composition of actinide ions in solution, carbonate complexation may significantly increase actinide solubility, and largely affect actinide sorption. The complexation strength is a measure of how effectively a ligand can compete with water in the coördination sphere of an actinide ion. Actinide ions are "hard" acids and consequently form strong complexes with highly ionic "hard" ligands, such as carbonate and hydroxide.[73] The relative tendency of actinides to form complexes generally follows the trend: An(IV) > An(III) ≈ AnO_2^{2+} > AnO_2^+.[73]

Complexation equilibria can be expressed in a variety of ways. When referencing equilibrium constants it is very important to refer to the primary literature to find out how the original authors define their equilibrium constants. Since measurement of the activities of complex ions is not possible for many systems, most equilibrium constants are determined in terms of concentrations. In this review we will refer to equilibrium constants (K) defined for specific reactions as written, and formation constants (β). The formation constant (β) for any compound $M_mL_lH_h$ is written in the form of eq 1:

$$mM + lL + hH \rightleftharpoons M_mL_lH_h$$

$$\beta_{mlh} = \frac{[M_mL_lH_h]}{[M]^m[L]^l[H]^h} \quad (1)$$

Equilibria involving ionic species are affected by the presence of all ions in solution, which together make up the ionic strength. Thermodynamic data are generally referenced to a standard state, and for solution measurements the standard state of 25 °C and zero ionic strength is generally used.[81] log formation constants (log β's) can be extrapolated to zero ionic strength using an extended Debye-Hückel approach known as the *s*pecific ion *i*nteraction *t*heory (SIT). For more detailed information regarding ionic strength corrections the reader is referred to Appendix B of the recent review on the chemical thermodynamics of uranium and references therein.[81]

A detailed understanding of the chemical equilibria and the formation constants that correspond to actinide species will allow for thermodynamic modeling to predict radionuclide speciation and solubility in differing aqueous environments. The need for accurate thermodynamic data prompted the organization for economic co-operation and development, nuclear energy agency (OECD NEA) to initiate a series of detailed expert reviews of the chemical thermodynamics of key elements in nuclear technology and waste management, and the first volume on the chemical thermodynamics of uranium has been published.[81]

1.2. Hydrolysis

Hydrolysis leads to the formation of ionic species or precipitates by the action of water as illustrated in eq 2 for a tetravalent actinide ion.[35,36] While hydrolysis reactions are often written as in eq 2, for comparison of equilibrium constants it is convenient to express hydrolysis as a complex formation, consistent with the log β notation described in eq 1. In our discussions of actinide ion hydrolysis we use this notation, and have converted literature values for log K into log β format (eq 3).

$$An^{4+} + H_2O \rightleftharpoons An(OH)^{3+} + H^+ \quad (2)$$

$$An^{4+} + OH^- \rightleftharpoons An(OH)^{3+} \quad (3)$$

Actinide hydrolysis yields soluble hydroxide or oxide complexes, as well as precipitates of hydroxides, oxides, or basic salts. Hydrolysis reactions are significant for all of the actinide ions at pH values found in natural waters, with the exception of the pentavalent ion. The actinide (IV) ions have high charge-to-radius ratios and form hydrolysis products even in acidic solutions, as low as pH = 0.[73] Pentavalent actinyl ions, AnO_2^+, do not readily hydrolyze until pH = 9 and the trivalent ions, An^{3+}, and hexavalent actinyl ions, AnO_2^{2+}, do not hydrolyze appreciably below pH 4 at room temperature. For a recent critical review of actinide hydrolysis constants the reader is referred to Fuger,[36] who notes that "the study of the hydrolysis of highly charged ions poses probably one of the most formidable challenges to the solution chemist due to the multiplicity of species that may form simultaneously and which also are a function of the other ions present in the solution."

Thorium Hydrolysis. Thorium(IV) is the largest tetravalent actinide cation with an ionic radius of 0.99 Å (versus 0.93 and 0.90 Å for U(IV) and Pu(IV), respectively),[82] and is the actinide(IV) ion most resistant to hydrolysis. Thorium(IV) hydrolysis has been studied by a number of researchers, and many of these studies indicated stepwise hydrolysis to yield monomeric products of formula $Th(OH)_n^{4-n}$ with n = 1, 2, 3, and 4, in addition to a number of polymeric species.[35,83-91] The most recent emf study by Grenthe and Lagerman indicates that only two of these monomeric species, $Th(OH)^{3+}$ and $Th(OH)_4$ are of any real importance in dilute solutions ($\leq 10^{-3}$ M Th); the corresponding formation constants are log β_{11} = 9.66(±0.09), and log β_{14} = 39.39(±0.04) in 3.0 M $NaClO_4$.[91] However, in a recent ThO_2 solubility study, the best fit to the experimental data required inclusion of the species, $Th(OH)_3^+$.[202] In more concentrated solutions ($\geq 10^{-3}$ M), polynuclear species have been shown to exist. For example the most recent model of Grenthe and Lagerman includes the dimers, $Th_2(OH)_2^{6+}$ and $Th_2(OH)_2^{6+}$, the tetramers, $Th_4(OH)_8^{8+}$ and $Th_4(OH)_{12}^{4+}$, and two hexamers, $Th_6(OH)_{14}^{10+}$ or $Th_6(OH)_{15}^{9+}$.[91] These polynuclear complexes are common in chloride and nitrate solutions.[35,83-90] It is noteworthy that these polynuclear hydrolysis products have only been well-defined for thorium and not for other tetravalent actinide ions. For more detailed information on the hydrolysis of Th(IV) the reader is referred to the works of Moon,[83] Lieser and Hill,[84] Engkvist and Albinsson,[85] Davydov and Toropov,[86] Milic and Suranji,[87] Brown *et al.*,[88] Bruno *et al.*,[89] Ryan and Rai,[90] Grenthe and Lagerman,[91] and references therein.

Uranium Hydrolysis. U(IV) and U(VI) are the oxidation states of uranium expected under environmental conditions. Qualitatively, the hydrolysis of U(IV) is similar to that of Th(IV), although conclusive identification of individual species is lacking.[81] Hydrolysis of U^{4+} has been studied extensively in acidic solutions and begins at acid concentrations less than 0.1 M. There is reasonably good experimental evidence for the formation of $U(OH)^{3+}$ with log β^0_{11} = 13.46(±0.06).[81] There is no direct evidence for other hydrolysis products such as $U(OH)_2^{2+}$, $U(OH)_3^+$, and $U(OH)_4$ (or $UO_2{\cdot}2H_2O$). However, there is a substantial amount of data, particularly from solubility experiments, which is consistent with the neutral species $U(OH)_4$.[81,85] It is unknown whether this species is mono– or polymeric. Solubility studies by Rai *et al.* indicate that the anionic species $U(OH)_5^-$, if it exists, is only of minor importance.[92] There is limited evidence for polymeric species such as $U_6(OH)_{15}^{9+}$.[81] The study of U(IV) hydrolysis is extremely complicated due to the precipitation of insoluble hydroxides or oxides.

The hydrolysis of uranyl(VI) has been studied extensively and begins at about pH = 3. In solutions containing less than 10^{-4} M uranium, the first hydrolysis product is believed to be $UO_2(OH)^+$ with log β^0_{11} = 8.8(±0.3).[81] At higher uranium concentrations, it is accepted that polymeric U(VI) species are predominant in solution. At uranium concentrations above 10^{-4} M, it is generally agreed that the dimer, $(UO_2)_2(OH)_2^{2+}$, is the first hydrolysis product with log β^0_{22} = 22.38(±0.04).[81] Trimeric uranyl hydroxide complexes $(UO_2)_3(OH)_5^+$ and $(UO_2)_3(OH)_4^{2+}$ are also well established with log β^0_{35} = 54.45(±0.12) and log β^0_{34} = 44.1(±0.3), respectively.[81] At higher pH, hydrous uranyl hydroxide precipitate is the stable species.[35] For the most recent discussion and critical review of the hydrolysis literature of uranium, the reader is referred to the NEA review of the thermodynamics of uranium.[81]

Neptunium Hydrolysis. Np(IV) is expected to be the dominant oxidation state under reducing conditions in natural groundwaters.[73] Sullivan and Hindman studied the hydrolysis of Np(IV) spectrophotometrically.[93] They reported the hydrolysis constant of the first hydrolysis product, $Np(OH)^{3+}$, to be log β_{11} = 11.70(±0.03) at room temperature in 2 M $NaClO_4$ solution. Other Np(IV) hydrolysis products are unknown, but Rai and Ryan have established an upper limit for log β_{15} of 45.3 for the formation of $Np(OH)_5^-$.[94]

Np(V), in the form NpO_2^+, is the most common oxidation state in oxygen-rich natural waters and it does not hydrolyze readily below pH = 9. For recent studies concerning the hydrolysis of Np(V) to form $NpO_2(OH)$ and $NpO_2(OH)_2^-$, the reader is referred to the recent works of Sullivan *et al.*,[95] Itagaki *et al.*,[96] and Neck *et al.*[97] Representative valves of Np(V) hydrolysis constants are log β_{11} = 2.44(±0.16) and log β_{12} = 4.10(±0.12) from Neck *et al.*,[97] at 0.1 *m* ionic strength. Hydrolysis of Np(VI) has also been examined, the polymeric products similar to those found for U(VI) have been observed.

In analogy with U(VI), Cassol *et al.* has evidence that the first hydrolysis product is $NpO_2(OH)^+$ with log β_{11} = 8.62(±0.03), recalcualted for a 1 M $NaClO_4$ solution.[98] In a similar fashion, there is evidence for the formation of a dimer $(NpO_2)_2(OH)_2^{2+}$ with log β_{22} = 20.90(±0.02), and a trimer, $(NpO_2)_3(OH)_5^+$ with log β_{35} = 50.70(±0.02), both recalculated for a 1 M $NaClO_4$ solution.[98] Fuger has calculated values at zero ionic strength to be log β^0_{11} = 9.0(±0.3), log β^0_{22} = 21.6(±0.3), log β^0_{35} = 52.5(±0.5).[36]

Plutonium Hydrolysis. Pu(III) hydrolysis is not well known because Pu(III) is readily oxidized to Pu(IV) in anything but strong acid solutions. The first hydrolysis product, $Pu(OH)^{2+}$, was identified by Kraus and Dam who reported log β_{11} = 6.78 in 0.07 M $NaClO_4$.[99]

The hydrolysis of Pu(IV) is extremely complicated. In 0.05 M acid solutions, $Pu(OH)^{3+}$ and $Pu^{4+}_{(aq)}$ are present at about equal concentrations.[32] At lower acid concentrations, further hydrolysis is reported to give the ions $Pu(OH)_2^{2+}$ and $Pu(OH)_3^+$, and the neutral species $Pu(OH)_4$ (equivalent to $PuO_2{\cdot}2H_2O$).[100-102] Formation constants have been estimated for these species, but the majority of literature references report the first hydrolysis product for the formation of $Pu(OH)^{3+}$. The paucity of data for further hydrolysis products is due to the formation of colloidal $PuO_2{\cdot}2H_2O$ under the solution conditions required for existence of these soluble hydrolyzed species. The most recent Pu(IV) hydrolysis experiments have been reported by Lierse,[100] Kim and Kanellakopulos,[101] and by Pazukhin and Kudryavtsev.[102] The hydrolysis constants reported by Lierse[100] and by Pazukhin and Kudryavtsev[102] agree reasonably well. Representative values taken from Pazukhin and Kudryavtsev are log β_{11} = 12.48, log β_{12} = 24.28, log β_{13} = 35.53, and log β_{14} = 46.43 at an ionic strength of 3.0 M.[102]

Pu(V) in the form of PuO_2^+ does not hydrolyze below pH = 9, where $PuO_2(OH)$ forms with log β_{11} = 4.05(±0.1) in 0.1 M $NaClO_4$.[103]

Pu(VI) exists mainly as the free PuO_2^{2+} ion at low plutonium concentrations in acidic solutions. At higher pH, $PuO_2(OH)^+$, $PuO_2(OH)_2$, $PuO_2(OH)_3^+$, $(PuO_2)_2(OH)_2^{2+}$, and $(PuO_2)_3(OH)_5^+$ have been proposed, with log β_{11} = 8.26, log β_{12} = 14.91, log β_{13} = 16.90, log β_{22} = 21.98, and log β_{35} = 56.28 in 0.1 M $NaClO_4$.[104] There are still multiple questions regarding the identity of many of the hydrolyzed plutonium species for the oxidation states of environmental interest. More detailed information is available in the recent works of Pazukhin and Kudryavtsev,[102] Kim *et al.*,[104] Pashilidas *et al.*,[105] Okajima *et al.*,[106,107] and Madic *et al.*[108]

Americium Hydrolysis. Am(III) is expected to be the dominant oxidation state of americium in natural waters. Hydrolysis reactions of Am(III) are not significant even at near-neutral pH values. Stadler and Kim investigated the hydrolysis of Am(III) in aqueous perchlorate media and in carbonate-free saline solutions using solubility.[25] They were able to derive hydrolysis constants for $Am(OH)^{2+}$, $Am(OH)_2^+$, and $Am(OH)_3$ of log β_{11} = 6.3(±0.3), log β_{12} = 12.2(±0.4), and log β_{13} = 14.4(±0.5).[23] These constants seem very reasonable when compared to those found for Pu(III) and Am(III). An interesting aspect of this work is that in concentrated NaCl solutions ($I_m > 3$, pH > 7), α radiolysis generates substantial amounts of oxidized chlorine species, which subsequently oxidize Am(III) to Am(V). These researchers provide a thorough review of published americium hydrolysis studies.[23]

Curium Hydrolysis. Cm(III) is the only oxidation state of curium that can exist in environmental waters. The hydrolysis constants for formation of $Cm(OH)^{2+}$ and $Cm(OH)_2^+$ have been determined.

Recently Wimmer *et al.* performed speciation studies using time-resolved fluorescence spectroscopy, and calculated $\log \beta_{11} = 6.67(\pm 0.18)$ and $\log \beta_{12} = 12.06(\pm 0.28)$ in 0.1 M $NaClO_4$.[109]

1.3. The Carbonate–Bicarbonate Ligand System

The aqueous carbonate system is important in the environment because of the high abundance of carbon dioxide and carbonate-containing minerals, such as calcite ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$) (which are estimated to contain more than 80% of the carbon on earth).[110] The fundamental equilibrium reactions of the aqueous carbonate system, and their equilibrium constants at 25 °C and zero ionic strength are given in eqs 4–7.[111,112] Dissolution of carbon dioxide gas in water will result in some hydrolyses to form carbonic acid, H_2CO_3 as indicated in eqs 4 and 5. The carbonic acid equilibrium shown in eq 5 lies far to the left, as indicated by the magnitude of $\log K_{eq}$.

$$CO_2(g) \rightleftharpoons CO_2(aq) \quad \log K^0{}_H = -1.47 \quad (4)$$

$$CO_2(aq) + H_2O \rightleftharpoons H_2CO_3 \quad \log K_{eq} = -2.70 \quad (5)$$

$$CO_2(aq) + H_2O \rightleftharpoons H^+ + HCO_3{}^- \quad \log K^0{}_1 = -6.35 \quad (6)$$

$$HCO_3{}^- \rightleftharpoons H^+ + CO_3{}^{2-} \quad \log K^0{}_2 = -10.33 \quad (7)$$

Experimentally, it can be extremely difficult to distinguish between $CO_2(aq)$ and H_2CO_3, and hence it is a common practice to define carbonic acid as the sum of H_2CO_3 and $CO_2(aq)$. In closed aqueous carbonate systems such as the depths of the oceans and deep groundwaters, the exchange of CO_2 with the surrounding environment is very slow, so the total carbonate concentration can be expressed as $[CO_2(aq)] + [HCO_3{}^-] + [CO_3{}^{2-}]$. In an open system in which the carbonate solution is in contact with the atmosphere, the total carbonate concentration will vary with the amount of atmospheric CO_2 that dissolves into solution. With a constant CO_2 pressure (P_{CO_2}) the equilibrium in eq 4 is maintained (Henry's Law) where K_H is the Henry's Law constant. Thus the concentrations of $HCO_3{}^-$ and $CO_3{}^{2-}$ in natural waters depend on the ambient P_{CO_2} to which the solutions are exposed. In studying carbonate systems, it is necessary to control the carbon source and the partial pressure of $CO_2(g)$. Hence equations expressed in terms of gaseous CO_2 are more useful. These eqs, 8 and 9, with the relevant equilibrium constants at 25 °C and zero ionic strength were obtained by rearranging the equations given above.

$$CO_2(g) + H_2O \rightleftharpoons 2H^+ + CO_3{}^{2-} \quad \log K^0 = -18.15 \quad (8)$$

$$CO_2(g) + H_2O \rightleftharpoons H^+ + HCO_3{}^- \quad \log K^0 = -7.82 \quad (9)$$

An additional complication of the carbonate ligand system is that hydroxide is also present, and there are always three possible ligands available in carbonate solutions; OH^-, $HCO_3{}^-$, and $CO_3{}^{2-}$. None of these individual ligand concentrations can be varied independently. Because hydrolysis and carbonate equilibria are intimately connected, one cannot study carbonate complexation without a fundamental understanding of the metal ion hydrolysis chemistry. Consideration of the above factors has lead some authors to formally consider the actinide carbonate system as a three-component system of metal, hydroxide, and carbonate.

2. Carbonate Complexes of the Actinide Elements

Actinide carbonate complexes are of interest not only because of their fundamental chemistry and environmental behavior, but also because of extensive industrial applications, primarily in uranium and thorium recovery from ores and nuclear fuel reprocessing.[73] The alkali leaching process for the recovery of uranium utilizes the high stability of the soluble uranyl carbonate complex, $UO_2(CO_3)_3{}^{4-}$, as a means of selectively separating uranium from ore.[73] Recovery of the uranium from the leach liquor can be achieved by addition of hydroxide to precipitate $Na_2U_2O_7$, or by acidification to liberate carbon dioxide.[113] Here we will discuss the carbonate complexes of actinides by oxidation state, presenting the structural types, the established and proposed solution species, their thermodynamic formation constants, and finally, a brief description of their expected species distributions in some natural waters.

2.1. Hexavalent Actinide Carbonate Complexes

2.1.1. Solid State and Structural Studies

Compounds containing the actinyl ($AnO_2{}^{n+}$, $n = 1, 2$) group were among the first actinide complexes to be studied by X-ray diffraction techniques. The linearity of the O=U=O unit was determined from the space group symmetry of sodium uranyl acetate in 1935.[114] Tomes have been written since then concerning structures containing actinyl ions, and rarely has a significant deviation from linearity been observed,[115] other than in organometallic complexes with bulky ligands. While the most precise studies have dealt with complexes of uranium, a few single-crystal structures and many powder diffraction studies have been performed on transuranic actinyl compounds.[116] A general feature seen in all actinyl carbonate structures is that the linear triatomic AnO_2 unit forms the axis of a hexagonal bipyramidal coordination polyhedron in which the oxygen atoms of the carbonate ligand are arrayed about the equator. The known actinide(VI) carbonate solids of empirical formulas, $AnO_2(CO_3)$, $M_2AnO_2(CO_3)_2$, and $M_4AnO_2(CO_3)_3$, will be described.

$AnO_2(CO_3)$. The neutral actinyl carbonate, $UO_2(CO_3)$, occurs in nature as the mineral rutherfordine. It is usually prepared by reacting carbon dioxide with uranium oxides [UO_3, $Na_2U_2O_7$, $(NH_4)_2U_2O_7$, etc.] in an autoclave at high CO_2 pressures and temperatures.[117,118] It can also be prepared in solution by reaction of an aqueous slurry of $UO_3{\cdot}2H_2O$ with CO_2 as outlined in eq 10, or by passing CO_2 through a $UO_2{}^{2+}$ solution.[105] There are also some reports of hydrated forms $UO_2(CO_3){\cdot}nH_2O$ $(0.2 \le n \le 2.5)$.[119–122] For a detailed list of preparations of rutherfordine, the reader is referred to Bagnall's review in the

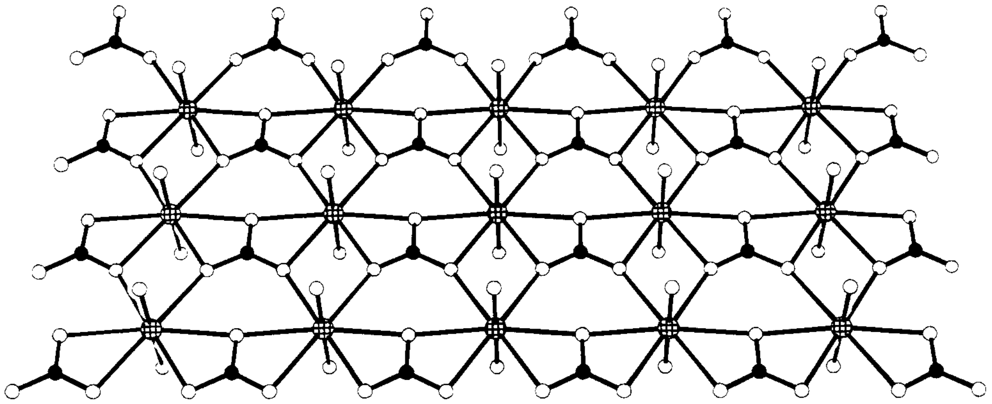


Figure 1. A ball-and-stick drawing of a single $UO_2(CO_3)$ layer in rutherfordine. The drawing was prepared from the fractional coordinates and unit cell parameters reported in ref 78. Hatched atoms = U; black = C; white = O.

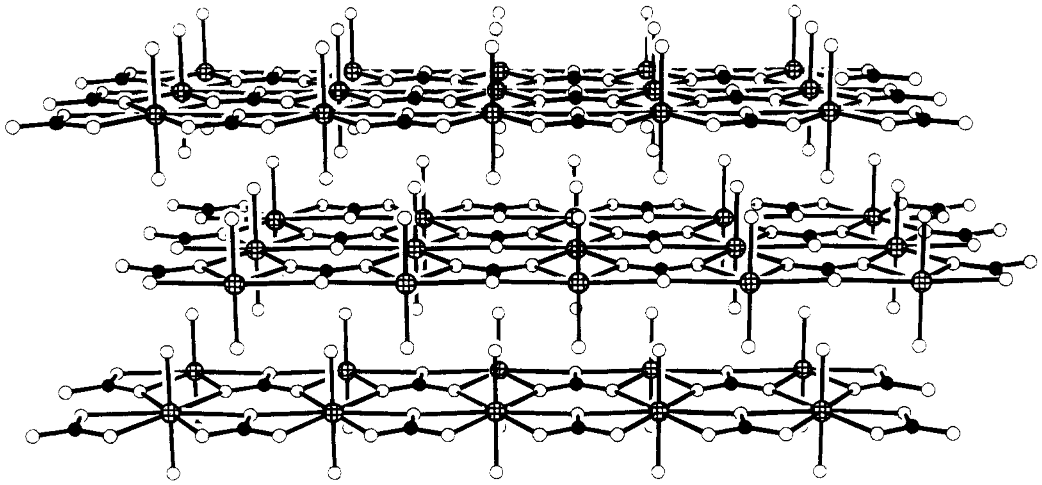


Figure 2. A ball-and-stick drawing illustrating the three-dimensional stacking of $UO_2(CO_3)$ layers in the solid state structure of rutherfordine. The drawing was prepared from the fractional coordinates and unit cell parameters reported in ref 78. Hatched atoms = U; black = C; white = O.

Gmelin Handbook.[113]

$$UO_3{\cdot}2H_2O + CO_2 \rightarrow UO_2(CO_3) + 2H_2O \quad (10)$$

The solid state structure of $UO_2(CO_3)$ has been determined from crystals of both the natural mineral and synthetic samples. Rutherfordine forms green-yellow crystals which crystallize in the orthorhombic space group $Pm2_1n$ or $Pmmm$ with two $UO_2(CO_3)$ moieties in the unit cell. The uranyl unit was assumed to have a linear structure with a U=O distance of 1.93 Å, and this assumption allowed for the remainder of the structure to be determined without more precise measurements.[78] The U=O distance of the UO_2 unit was later measured by Cromer and Harper to be 1.67(9) Å,[123] which is *ca.* 0.1 Å shorter than the average seen in other uranyl compounds. $UO_2(CO_3)$ displays a layered structure in the solid state. The local coordination environment of the uranyl ion is a hexagonal bipyramidal arrangement of oxygen atoms with the uranyl units perpendicular to the orthorhombic plane. Each uranium atom forms six equatorial bonds with the oxygen atoms of four carbonate ligands, two in a bidentate manner and two in a monodentate manner. U−O distances to the carbonate ligands are 2.43 Å for monodentate and 2.52 Å for bidentate linkages, respectively. The orthorhombic plane of hexagonal bipyramidal uranyl units forms infinite, two-dimensional layers. A ball-and-stick view of the solid state structure, emphasizing the local coordination of the uranyl ion in a single $UO_2(CO_3)$ layer, is shown in Figure 1. The $UO_2(CO_3)$ layers are staggered with respect to the layer above or below, such that uranyl units lie above and below a carbonate carbon atom in adjacent layers. The layers are separated by a distance of 4.60 Å. Figure 2 is an illustration of how multiple $UO_2(CO_3)$ layers are staggered with respect to the position of the O=U=O units in the three-dimensional solid.

Solids of $NpO_2(CO_3)$ and $PuO_2(CO_3)$ have been reported, but to the best of our knowledge, $AmO_2(CO_3)$ has never been observed. The $NpO_2(CO_3)$ solid forms as a red-brown precipitate upon lowering the HCO_3^- concentration in $NpO_2(CO_3)_3^{4-}$ solutions.[127] The $PuO_2(CO_3)$ compound has been prepared as a pink or brown solid from the thermal decomposition of $(NH_4)_4PuO_2(CO_3)_3$ according to the stoichiometry of eq 11.[125,126] Navratil and Bramlet have also prepared this compound by adding alkali carbonate to a PuO_2^{2+} nitrate solution and adjusting the pH to between 4 and 7.[126] $PuO_2(CO_3)$ has also been prepared as a white, crystalline precipitate by passing CO_2 through a PuO_2^{2+} solution, analogous to the synthesis of $UO_2(CO_3)$.[105] Powder X-ray diffraction

$$(NH_4)_4PuO_2(CO_3)_3 \rightarrow PuO_2(CO_3) + 2CO_2 + 2H_2O + 4NH_3 \quad (11)$$

studies revealed orthorhombic unit cells with lattice parameters similar to that seen for rutherfordine, but no analysis of the data to yield a refined structure was given.[105,126,127] It seems likely that $NpO_2(CO_3)$ and $PuO_2(CO_3)$ would have solid state structures similar to rutherfordine, but until more data are analyzed, the accurate three-dimensional structures remain uncertain.

$M_2AnO_2(CO_3)_2$. Biscarbonato complexes of uranium(VI) are well established in solution,[81] and there are many reports dating from the late 1940's through the 1960's of solid phases with the general stoichiometry $M_2UO_2(CO_3)_2$ where M is a monovalent cation (Na^+, K^+, Rb^+, Cs^+, NH_4^+, etc.). A summary of the preparative details is given by Chernyaev,[128] and a listing of the compounds is given by Bagnall.[113] As an illustrative example, the anhydrous rubidium and cesium salts, $Rb_2UO_2(CO_3)_2$ and $Cs_2UO_2(CO_3)_2$, are reportedly obtained by treating a concentrated aqueous solution of $M_4UO_2(CO_3)_3$ ($M = Rb^+, Cs^+$) with carbon dioxide.[128] This reaction is now known to be reversible and the empirical formula of the solid is consistent with the rather large body of solution thermodynamic information that has been amassed. A compound of the formula $Na_2UO_2(CO_3)_2$ is reportedly formed in solution by saturating $Na_4UO_2(CO_3)_3$ with UO_3 in a stream of CO_2, or by dissolving $UO_3 \cdot 0.5H_2O$ in aqueous $NaHCO_3$.[129] After standing for 12 h, followed by evaporation of the solvent at 40 °C, the solution yields the product $Na_2UO_2(CO_3)_2$. This solid is reported to be very soluble in water and can be recrystallized from it. Wiegel lists unit cell parameters for $CaUO_2(CO_3)_2$ in his compilation, suggesting that a structure was determined, and refers the reader to Chernyaev for details.[130] However, we can find no reference to structural studies of this complex in Chernyaev's compendium.[128] A careful examination of the more recent literature and our detailed understanding of the solution chemistry suggests that the claims of some of these early reports on solid $M_2UO_2(CO_3)_2$ compounds should be reinterpreted. It is now known that solids of general composition $M_2UO_2(CO_3)_2$ form trimetallic clusters of molecular formula $M_6(UO_2)_3(CO_3)_6$.[131] The trimetallic cluster forms in solution when the metal ion is present in relatively high concentration, and this complex is relatively unstable unless the pH is kept near 6 and a CO_2 atmosphere is maintained over the solution.[81] Concentrated solutions, however, appear to be strongly buffered. Solution X-ray diffraction, potentiometric titration, ^{13}C and ^{17}O NMR, and EXAFS studies are all consistent with maintenance of a trinuclear cluster in solution.[131-135] These trimetallic clusters can rapidly and spontaneously convert back to the starting $UO_2(CO_3)_3^{4-}$ upon exposure of dilute solutions to air because of a shift in the equilibrium shown in eq 12. A recent single-crystal X-ray diffraction study by Bucher *et al.* of $[C(NH_2)_3]_6[(UO_2)_3(CO_3)_6] \cdot 6.5H_2O$ confirms the presence of the trimetallic cluster in the solid state.[131] Figure 3 shows the molecular structure of the $(UO_2)_3(CO_3)_6^{6-}$ anion. As originally proposed by Åberg *et al.*,[132] the molecule consists of a D_{3h} planar structure in which all six carbonate ligands and the three uranium atoms lie within the molecular plane. The six uranyl oxygen atoms are perpendicular to the plane, with three above, and three below the plane. The local coordination geometry about each uranium is hexagonal bipyramidal. Uranyl U=O distances average 1.78 Å, while U−O distances to the carbonate oxygens in the plane average 2.46 Å. The U−U distance within the trimetallic unit averages 4.97 Å, and compares favorably with the value of 4.95 Å determined by solution X-ray diffraction.[132] To the best of our knowledge, there are no reports of the corresponding Np(VI), Pu(VI), or Am(VI) carbonato solids with a 2:1 ligand to metal stoichiometry.

$$3UO_2(CO_3)_3^{4-} + 3H^+ \rightleftharpoons (UO_2)_3(CO_3)_6^{6-} + 3HCO_3^- \quad (12)$$

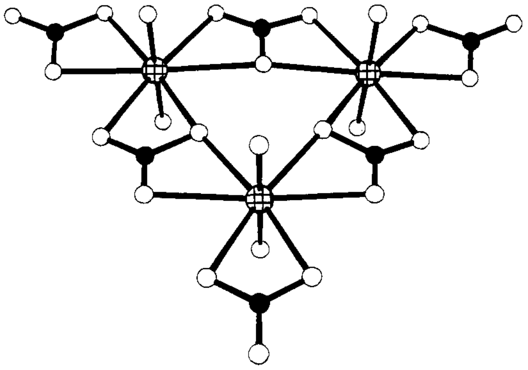


Figure 3. A ball-and-stick drawing illustrating the D_{3h} trimetallic $(UO_2)_3(CO_3)_6^{6-}$ molecular unit found in the solid state structure of $[C(NH_2)_3]_6[(UO_2)_3(CO_3)_6] \cdot 6.5H_2O$. The drawing was prepared from the fractional coordinates and unit cell parameters of $[C(NH_2)_3]_6[(UO_2)_3(CO_3)_6] \cdot 6.5H_2O$ reported in ref 131. Hatched atoms = U; black = C; white = O.

$M_4AnO_2(CO_3)_3$. Without question, the tricarbonato solids of general formula $M_4AnO_2(CO_3)_3$ (An = U, Np, Pu; M = monovalent cation) are the most thoroughly studied actinyl(VI) carbonate solids. These solid phases are generally prepared by evaporation of an aqueous solution of the components, or by precipitation of the corresponding AnO_2^{2+} ion with an excess of carbonate anion as indicated in eq 13. Some of these salts can be further purified by dissolution in water and recrystallized by evaporation. Single-crystal X-ray diffraction studies have been reported for a large number of uranyl complexes and a few of the neptunyl analogs. The unit cell parameters have been reported for a variety of plutonyl analogs, but to the best of our knowledge, no refinement of the structural models to give metrical parameters has been performed. Complexes that have been characterized by X-ray diffraction are summarized by Bagnall and Weigel.[113,130]

Several uranyl salts of formula $M_4UO_2(CO_3)_3 \cdot nH_2O$ occur naturally in minerals with varying amounts of hydrated water such as andersonite ($Na_2CaUO_2(CO_3)_3 \cdot nH_2O$),[136,137] bayleyite ($Mg_2UO_2(CO_3)_3 \cdot nH_2O$),[138] grimselite ($K_3NaUO_2(CO_3)_3 \cdot H_2O$),[139] liebigite ($Ca_2UO_2(CO_3)_3 \cdot 10H_2O$),[79] swartzite ($MgCaUO_2(CO_3)_3 \cdot nH_2O$),[137] and widenmannite ($Pb_2UO_2(CO_3)_3$).[122] Musikas and Burns have reported the X-ray crystal structure for $K_4NpO_2(CO_3)_3$.[116] In the solid state, all monomeric $M_4AnO_2(CO_3)_3$ complexes show the same basic structural features. The molecular structure of the anionic $AnO_2(CO_3)_3^{4-}$ unit from these structures is shown in Figure 4. All actinyl triscarbonato

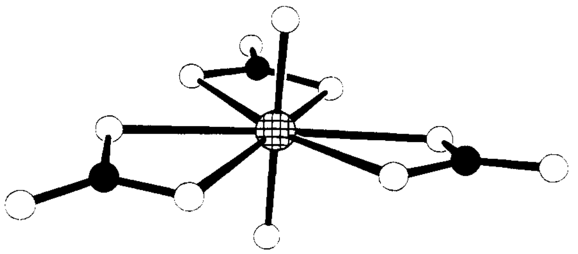
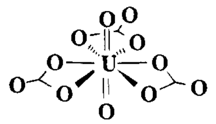


Figure 4. A ball-and-stick drawing illustrating the hexagonal bipyramidal coordination geometry found in the solid state structure of $AnO_2(CO_3)_3^{4-}$ complexes. The drawing was prepared from the fractional coordinates and unit cell parameters of synthetic andersonite, $Na_2CaUO_2(CO_3)_3{\cdot}6H_2O$, 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



I

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.

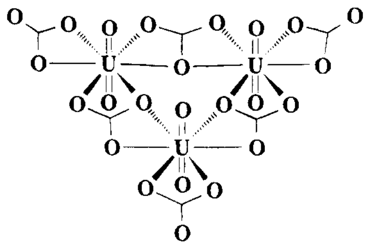
$$AnO_2X_2 + 3M_2CO_3 \rightarrow M_4AnO_2(CO_3)_3 + 2MX$$
$$(An = U, Np, Pu; X = Cl^-, Br^-, NO_3^-, ClO_4^-, etc.) \quad (13)$$

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 $UO_2(CO_3)$, $UO_2(CO_3)_2^{2-}$, and $UO_2(CO_3)_3^{4-}$ 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 $(UO_2)_3(CO_3)_6^{6-}$, $(UO_2)_2(CO_3)(OH)_3^-$, $(UO_2)_3O(OH)_2(HCO_3)^+$, and $(UO_2)_{11}(CO_3)_6(OH)_{12}^{2-}$ 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, $UO_2(CO_3)_3^{4-}$, is complicated because this species is in equilibrium with the hexakiscarbonato uranyl trimer, $(UO_2)_3(CO_3)_6^{6-}$. 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 $UO_2(CO_3)_2^{2-}$ to form $UO_2(CO_3)_3^{4-}$, 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 $(UO_2)_3(CO_3)_6^{6-}$ 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 $AnO_2(CO_3)$ layers in the solid state structures of $KAnO_2(CO_3)$ (An = Pu, Am),[146] which is a simple structural modification of the rutherfordine structure.[78]



II

Ciavatta *et al.* were the first to propose the $(UO_2)_3(CO_3)_6^{6-}$ 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 $(UO_2)_3(CO_3)_6^{6-}$ 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 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 $[C(NH_2)_3]_6[(UO_2)_3(CO_3)_6]$, solid $K_4[UO_2(CO_3)_3]$, and a solution of $(UO_2)_3(CO_3)_6^{6-}$ gave further support of a trimeric structure for the $(UO_2)_3(CO_3)_6^{6-}$ ion.[131] Figure 5 shows the EXAFS Fourier transforms for solid $K_4[UO_2(CO_3)_4]$ (top) and $[C(NH_2)_3]_6[(UO_2)_3(CO_3)_6]$ (bottom).[130] The EXAFS Fourier transform of $[C(NH_2)_3]_6[(UO_2)_3(CO_3)_6]$ 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

Table 2. Representative Values for the Equilibrium Constants of the Carbonate Complexes of Hexavalent Actinides at Selected Ionic Strengths and Room Temperature

reaction	*I*	log *K*	ref
Uranyl			
$UO_2^{2+} + CO_3^{2-} \rightleftharpoons UO_2(CO_3)$	0	9.68(±0.04)	81
	0.5	8.54(±0.05)	140
	3.0	8.89(±0.01)	141
$UO_2^{2+} + 2CO_3^{2-} \rightleftharpoons UO_2(CO_3)_2^{2-}$	0	16.94(±0.12)	81
	0.1	16.15(±0.29)	142
	0.5	14.93(±0.30)	140
	3.0	16.20(±0.15)	141
$UO_2^{2+} + 3CO_3^{2-} \rightleftharpoons UO_2(CO_3)_3^{4-}$	0	21.60(±0.05)	81
	0.1	21.80(±0.10)	142
	0.5	22.30(±0.11)	140
	3.0	22.61(±0.15)	141
$3UO_2(CO_3)_3^{4-} \rightleftharpoons (UO_2)_3(CO_3)_6^{6-} + 3CO_3^{2-}$	3.0	−11.3(±0.1)	124
$3UO_2^{2+} + 6CO_3^{2-} \rightleftharpoons (UO_2)_3(CO_3)_6^{6-}$	0	54.00(±1.0)	81
	0.5	53.82(±0.17)	140
	3.0	56.23(±0.3)	81
$UO_2(CO_3)_2^{2-} + CO_3^{2-} \rightleftharpoons UO_2(CO_3)_3^{4-}$	0.5	6.35(±0.05)	143
$2UO_2^{2+} + CO_2(g) + 4H_2O(l) \rightleftharpoons (UO_2)_2CO_3(OH)_3^- + 5H^+$	0	−19.01(±0.50)	140
	0.1	−18.63(±0.08)	142
	0.5	−19.40(±0.11)	140
$11UO_2^{2+} + 6CO_2(g) + 18H_2O(l) \rightleftharpoons (UO_2)_{11}(CO_3)_6(OH)_{12}^{2-} + 24H^+$	0	−72.5(±2.0)	81
	0.5	−72.48(±0.3)	140
$3UO_2^{2+} + CO_2(g) + 4H_2O(l) \rightleftharpoons (UO_2)_3O(OH)_2(HCO_3)^+ + 5H^+$	0	−17.5(±0.5)	140
	3.0	−16.6(±0.2)	140
Neptunyl			
$NpO_2^{2+} + 2CO_3^{2-} \rightleftharpoons NpO_2(CO_3)_2^{2-}$	1.0	16.51	150
	3.0	17.9	127
$NpO_2^{2+} + 3CO_3^{2-} \rightleftharpoons NpO_2(CO_3)_3^{4-}$	1.0	21.15	150
	3.0	22.1	127
$3NpO_2^{2+} + 6CO_3^{2-} \rightleftharpoons (NpO_2)_3(CO_3)_6^{6-}$	3.0	56.2	127
$3NpO_2(CO_3)_3^{4-} \rightleftharpoons (NpO_2)_3(CO_3)_6^{6-} + 3CO_3^{2-}$	3.0	−10.0(±0.1)	124
Plutonyl			
$PuO_2^{2+} + CO_3^{2-} \rightleftharpoons PuO_2(CO_3)$	3.5	8.6(±0.3)	151
$PuO_2(OH)_2 + 2HCO_3^- \rightleftharpoons PuO_2(CO_3)_2^{2-} + 2H_2O$	0.1	4.4	152
$PuO_2^{2+} + 2CO_3^{2-} \rightleftharpoons PuO_2(CO_3)_2^{2-}$	0[a]	15.1	149
	0.1	13.1(±0.1)	152
	3.5	13.6(±0.7)	151
$PuO_2^{2+} + 3CO_3^{2-} \rightleftharpoons PuO_2(CO_3)_3^{4-}$	0	18.5	149
	3.5	18.2(±0.4)	151
$3PuO_2(CO_3)_3^{4-} \rightleftharpoons (PuO_2)_3(CO_3)_6^{6-} + 3CO_3^{2-}$	3.0	−7.4(±0.2)	124

[a] $NaClO_4/Na_2SO_4$ electrolyte, $I = 0$ data calculated; $NaClO_4$ was used to adjust the ionic strength in all other studies.

carbon atoms, respectively. A well-established uranyl ion multiple scattering peak is seen at 3.60 Å in both spectra.[148] The small peak at 4.75 Å, present in $(UO_2)_3(CO_3)_6^{6-}$ and absent in $UO_2(CO_3)_3^{4-}$ is attributed to backscattering from the other uranium atoms of a polymeric unit. Comparison of EXAFS data from solid $[C(NH_2)_3]_6[UO_2(CO_3)_2]_3$ and $(UO_2)_3(CO_3)_6^{6-}$ solutions suggests the same uranium species is present in both systems. The observation of only one peak near 5 Å attributable to a U−U interaction distance by both solution X-ray diffraction[132] and EXAFS experiments,[131] in conjunction with solution NMR and emf experiments, strongly supports a trimetallic structure in solution.

The corresponding neptunyl, plutonyl, and americyl carbonate systems are in need of more detailed study. All of the relevant data on the neptunyl(VI), plutonyl(VI), and americyl(VI) complexes point to the same limiting monomeric species of general formulas $AnO_2(CO_3)$, $AnO_2(CO_3)_2^{2-}$, and $AnO_2(CO_3)_3^{4-}$.[124,127,149−151] Solution Raman spectroscopic data are consistent with the maintenance of a linear O=An=O unit and bidentate carbonate ligands for $AnO_2(CO_3)_3^{4-}$ complexes in aqueous carbonate solutions of U(VI), Np(VI), Pu(VI), and Am(VI).[153−155] Bicarbonate complexes of AnO_2^{2+} have not been demonstrated to exist even in the pH ranges where bicarbonate ions are present at higher concentrations than carbonate.[142]

Maya found spectrophotometric evidence for a hydroxo carbonato dimer of formula $(NpO_2)_2(CO_3)(OH)_3^-$ in addition to the monomeric $NpO_2(CO_3)_2^{2-}$.[150] More recent spectrophotometric and emf studies by Grenthe *et al.* suggest that the numerical values of the equilibrium constants, and the chemical species reported by Maya may be incorrect.[124] Grenthe's work suggests that the trimeric complex, $(NpO_2)_3(CO_3)_6^{6-}$, is the predominant solution species present at high ionic strength and high metal ion concentration, consistent with the results for uranium.[124] The existence of both $NpO_2(CO_3)_3^{4-}$ and $(NpO_2)_3(CO_3)_6^{6-}$ species has been confirmed by ^{13}C and ^{17}O NMR spectroscopy, and a ^{13}C NMR titration of the Np(VI) system between pH 5.76−7.95 is shown in Figure 6.[144,156] The monomeric $NpO_2(CO_3)_3^{4-}$ has only one type of carbonate ligand environment, giving rise to a single ^{13}C NMR resonance ($\delta = 75.5$ ppm) as seen in Figure 6 at pH 8.0. The proposed trimeric structure for $(NpO_2)_3(CO_3)_6^{6-}$ (shown in **II**) is expected to show two equal intensity resonances as observed at $\delta = 7.7$ and -88.6 ppm, shown in Figure 6 at pH 5.7. Variable-temperature studies (Figure 6 insert) reveal

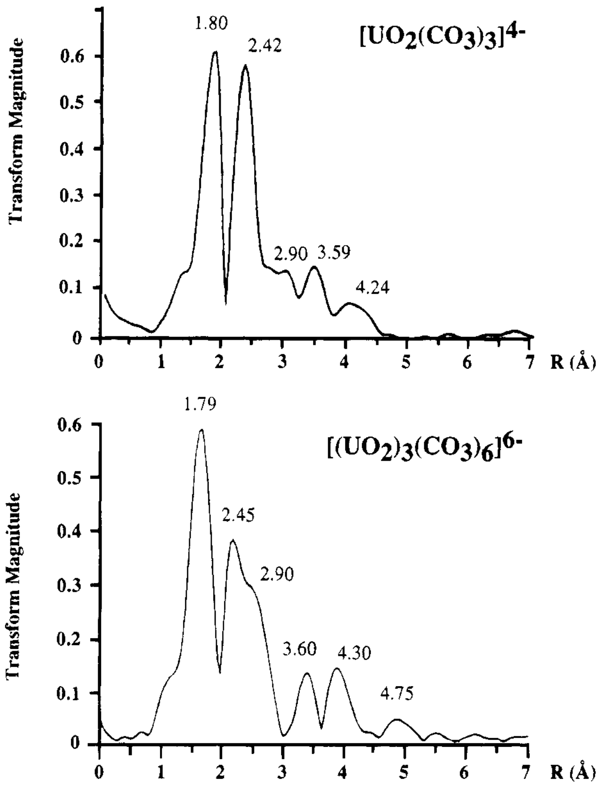


Figure 5. Fourier transform of the EXAFS spectrum of solid $K_4UO_2(CO_3)_3$ (top) and $[C(NH_2)_3]_6[(UO_2)_3(CO_3)_6]$ (bottom) emphasizing the U–U multiple scattering peak at 4.75 Å in the bottom transform (from ref 131).

a temperature-dependent chemical shift and line broadening in the low field resonance, consistent with the assignment of the δ = 7.7 ppm resonance to a terminal carbonate ligand. The higher field resonance at δ = −88.6 ppm does not undergo line broadening with increasing temperature, consistent with the assignment to a bridging carbonate ligand (see Figure 6 insert). Thus the ^{13}C NMR data are consistent with Grenthe's interpretation of spectrophotometric and emf data, supporting trimeric $(NpO_2)_3(CO_3)_6^{6-}$ as the dominant solution species at high ionic strength and metal ion concentration.[124] The consistency between the data for uranium(VI) and neptunium(VI) is very encouraging. Grenthe *et al.* have also reported spectroscopic evidence for the formation of $(PuO_2)_3(CO_3)_6^{6-}$ and of mixed metal $(UO_2)_2(AnO_2)(CO_3)_6^{6-}$ clusters where An = Np and Pu.[124]

In contrast to the many studies of ligand exchange on lanthanide ions, relatively little data have been reported for the ligand substitution kinetics of the actinide ions, with uranyl receiving by far the most attention.[157,158] For these reactions, mostly dissociative (D) or associative interchange (I_a) mechanisms have been proposed for substitutions involving monodentate ligands, but there is no general conclusion in the literature regarding bidentate substitutions, as in the case of carbonate ligands. Along with the limited information concerning the kinetics of bidentate ligand exchange reactions on actinyl(VI) complexes, there is disagreement with regard to the mechanism of carbonate self-exchange in the actinyl triscarbonate system.[159–161] The origin of these discrepancies is apparent from additional experimental data.[160b] Stout *et al.* reported ^{13}C NMR exchange rate data for $UO_2(CO_3)_3^{4-}$ and $NpO_2(CO_3)_3^{4-}$ which suggest an associative transition state,[161] while Brücher *et al.*[159] reported ^{13}C NMR data for $UO_2(CO_3)_3^{4-}$ which support a dissociative transition state. Stout *et al.* used observed rate constants to derive activation parameters, and used the activation entropy as the argument for their assignment of the reaction mechanism.[161] Brücher *et al.* determined

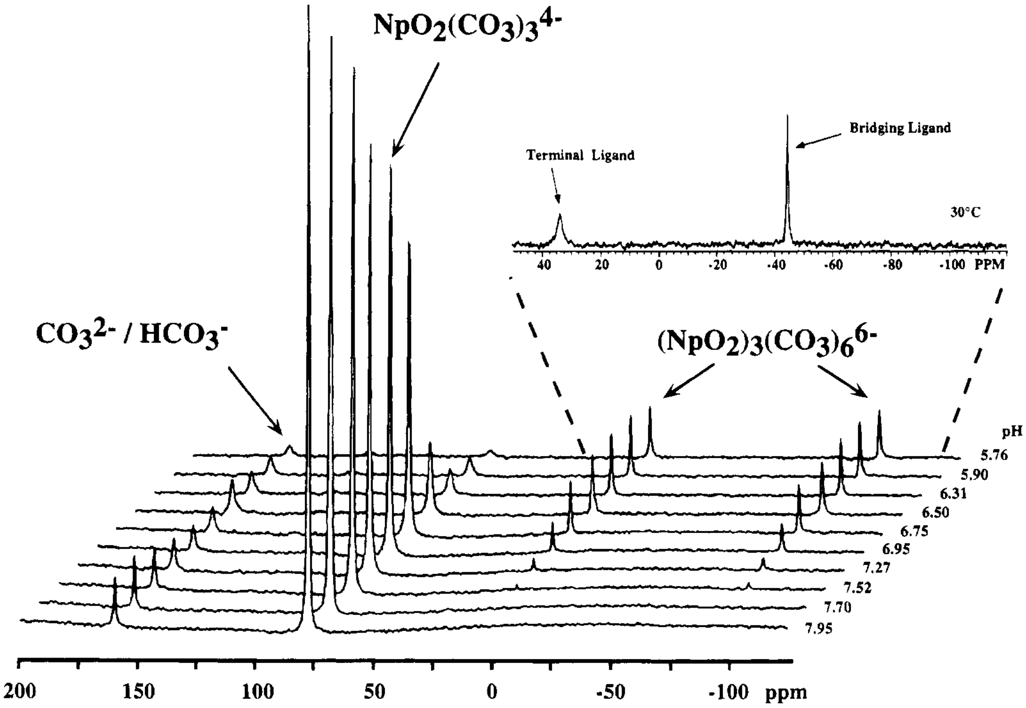


Figure 6. ^{13}C NMR spectra (62.9 MHz) of a 0.05 M neptunyl carbonate solution at 2.5 *m* $NaClO_4$ as a function of pH recorded at 0 °C. Peak assignments are as indicated. The insert is an expansion of the region assignable to trimeric $(NpO_2)_3(CO_3)_6^{6-}$, illustrating the line broadening in the terminal carbonate resonance upon an increase the in temperature to 30 °C.

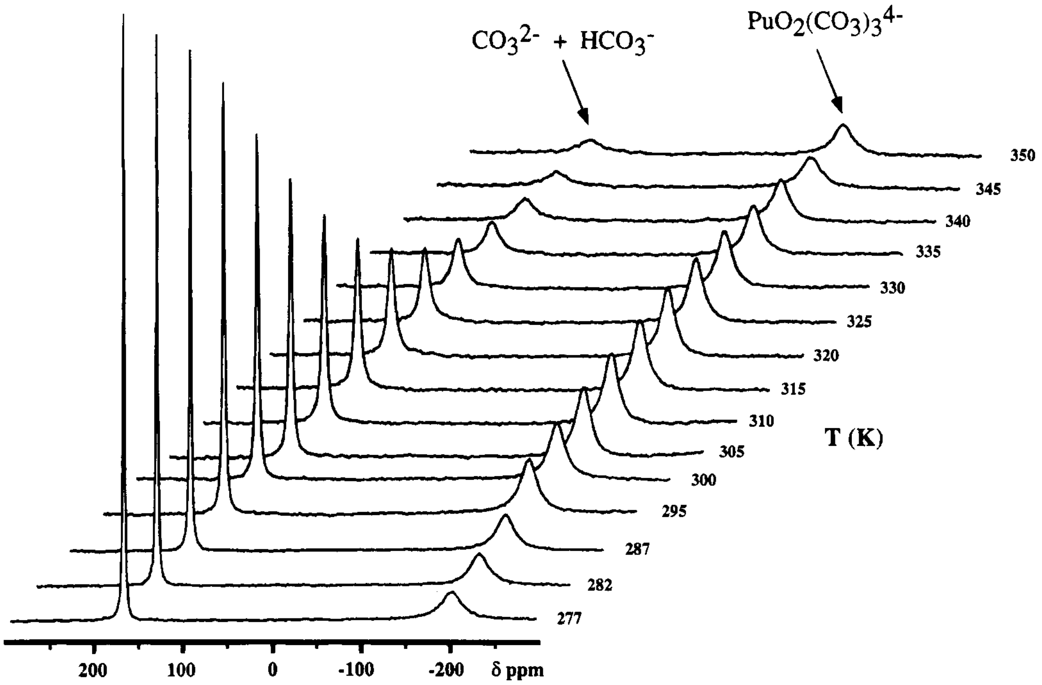


Figure 7. Variable-temperature ^{13}C NMR spectra (62.9 MHz) for a solution containing 0.2 M ^{13}C-enriched $^{242}PuO_2(CO_3)_3^{4-}$ in the presence of 1 M carbonate. The resonance at $\delta = -209$ ppm (295 K) is assignable to the carbonate ligand bound in the $PuO_2(CO_3)_3^{4-}$ complex, and the resonance at $\delta = 166$ ppm is the averaged signal due to free HCO_3^- and CO_3^{2-} in solution. Solution conditions: $[PuO_2^{2+}] = 0.20$ M; $[CO_3^{2-} + HCO_3^-] = 1.00$ M; $[ClO_4^-] = 1.0$ M; pH = 9.5.

the dependence of the observed rate on metal complex and free carbonate concentrations and showed the reaction to be first order in $UO_2(CO_3)_3^{4-}$, hence the reaction must be dissociative.[159] Further insight comes from the examination of carbonate exchange in the corresponding $PuO_2(CO_3)_3^{4-}$ system by Clark *et al.*[160b]

The variable-temperature ^{13}C NMR spectral behavior for aqueous $PuO_2(CO_3)_3^{4-}$ in the presence of excess carbonate is shown in Figure 6.[160] For paramagnetic ions, the chemical shift of the coordinated CO_3^{2-} ligand is strongly influenced by the metal center. In solutions containing $AnO_2(CO_3)_3^{4-}$ (An = U, Np, Pu, Am) and excess carbonate, the observation of two distinct resonances implies that the carbonate exchange reaction (eq 14) is slow on the NMR time scale. For the $PuO_2(CO_3)_3^{4-}$ system shown in Figure 6, the low field resonance at $\delta = 166$ ppm is assigned to the free carbonate ligand, and the high field resonance at $\delta = -210$ ppm is assigned to the carbonate ligand in the $PuO_2(CO_3)_3^{4-}$ complex.[160] The free carbonate resonance at $\delta = 166$ ppm is a singlet indicating the fast exchange between uncomplexed carbonate and bicarbonate ions in solution. Above room temperature, a distinct line broadening is observed in the free carbonate resonance, while little linewidth change is observed in the NMR resonance for the coordinated carbonate ligand because the paramagnetic relaxation dominates the line width for this plutonyl-bound carbonate resonance.

$$AnO_2(CO_3)_3^{4-} + {}^*CO_3^{2-} \rightleftharpoons AnO_2(CO_3)_2({}^*CO_3)^{4-} + CO_3^{2-} \quad (14)$$

If one uses the temperature dependence of the observed rate constants from the line-broadening experiment to calculate activation parameters, then a negative activation entropy is obtained.[160] However, additional experimentation and derivation of the rate law revealed that the $PuO_2(CO_3)_3^{4-}$ exchange is first order in metal complex and zero order in free ligand,[160b] just as in Brücher's results for uranium.[159] Thus the reaction must be dissociative. When the true first-order rate constant is calculated from the observed rate law, and its temperature dependence is used to derive activation parameters, a consistent picture for carbonate ligand exchange emerges. In both the U and Pu system, the rate law is first order and the reaction is dissociative. Activation parameters are $\Delta H^{\ddagger} = 82$ kJ/M for uranium[159] and 34 kJ/M for plutonium,[160b] and $\Delta S^{\ddagger} = +50$ J/MK for uranium[159] and +31 J/MK for plutonium.[160b]

2.1.3. Species Distribution in Aqueous Solutions

Polynuclear actinyl(VI) complexes are not expected to be present in natural water systems due to the low metal ion concentrations and low ionic strengths generally anticipated. The situation may be different in a nuclear waste repository or contaminated site, where the concentration of actinyl ions is expected to be significantly higher, and where radiolysis may provide redox agents in the near field. Grenthe *et al.* have suggested that under such conditions, the uranyl(VI) complexes are capable of acting as a "carrier" for the heavier actinyl ions in the form of mixed $(UO_2)_2(AnO_2)(CO_3)_6^{6-}$ polynuclear complexes, where An = Np and Pu.[124]

Under typical groundwater conditions, monomeric actinyl carbonate complexes are expected to dominate the solution chemistry. As an illustrative example, the thermodynamic binding constants for uranyl(VI) hydrolysis and carbonate complexation can be used to predict species distributions in groundwaters at the proposed Yucca Mountain repository for storage of highly radioactive waste. Chemical analyses have established that the Yucca Mountain groundwaters

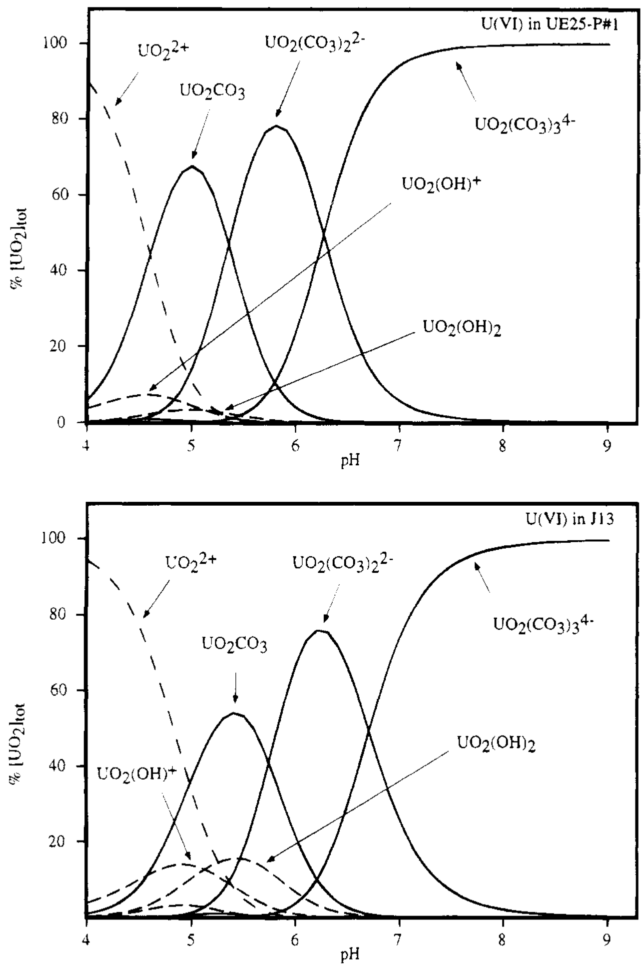


Figure 8. Calculated uranyl species distributions in carbonate solutions modeling Yucca Mountain UE25P#1 (top) and J-13 (bottom) groundwaters at 25 °C using NEA-suggested formation constants[81] corrected to an ionic strength of 0.1 *m* using specific ion interaction theory. Solution conditions: (UE25P#1) $[UO_2^{2-}] = 1 \times 10^{-5}$ 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 $M_{(2n-1)}AnO_2(CO_3)_n$ 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

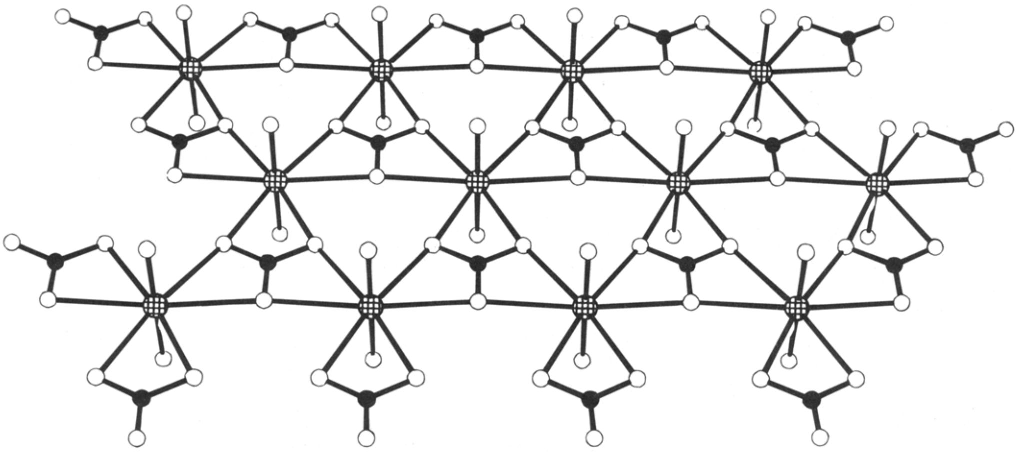


Figure 9. A ball-and-stick drawing illustrating a single $PuO_2(CO_3)$ layer in $KPuO_2(CO_3)$. The drawing was prepared from the fractional coordinates and unit cell parameters reported in ref 146. Hatched atoms = Pu; black = C; white = O.

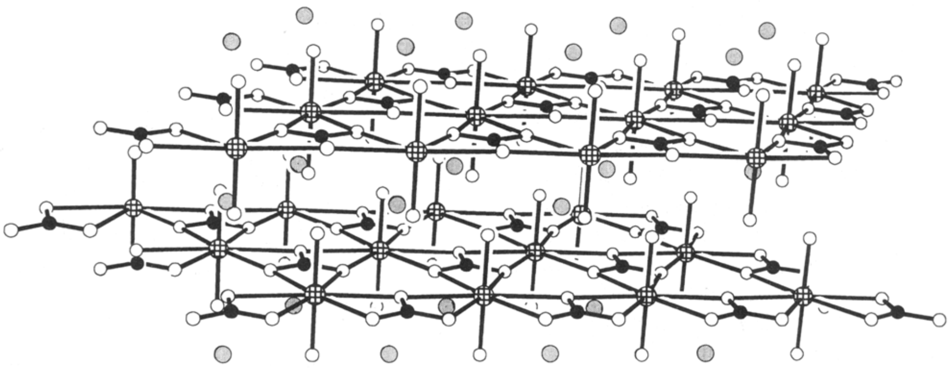


Figure 10. A ball-and-stick drawing illustrating the stacking of alternating $PuO_2(CO_3)^-$ and K^+ layers in the solid state structure of $KPuO_2(CO_3)$. The drawing was prepared from the fractional coordinates and unit cell parameters reported in ref 146. Hatched atoms = Pu; light gray = K; black = 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 $KPuO_2(CO_3)$ or $(NH_4)PuO_2(CO_3)$ precipitated. These have been extremely well characterized.[170] Sodium and potassium americyl(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 $(NH_4)AmO_2(CO_3)$ and $RbAmO_2(CO_3)$, 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 $K_3AmO_2(CO_3)_2$ and $K_5AmO_2(CO_3)_3$ solids.

$MAnO_2(CO_3)$. The actinyl(V) 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[146] 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 $MAnO_2(CO_3)$ 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 *P*6₃/*mmc* with two $KPuO_2(CO_3)$ moieties in the unit cell.[146] 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.[165] That is,

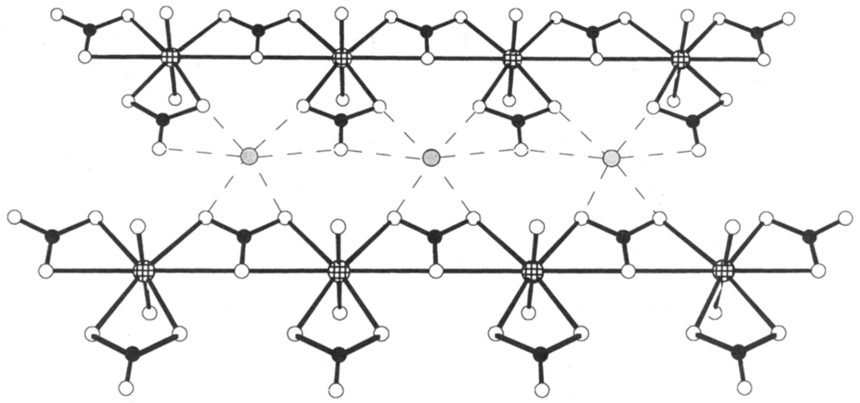
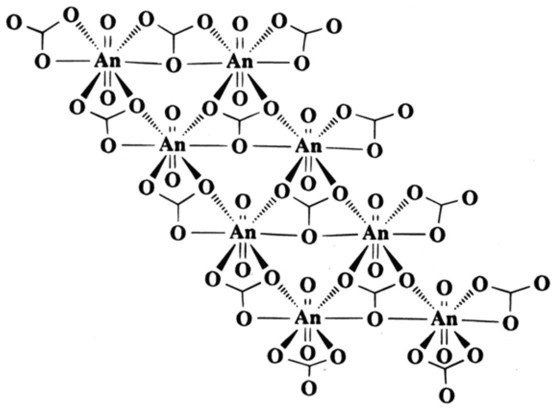
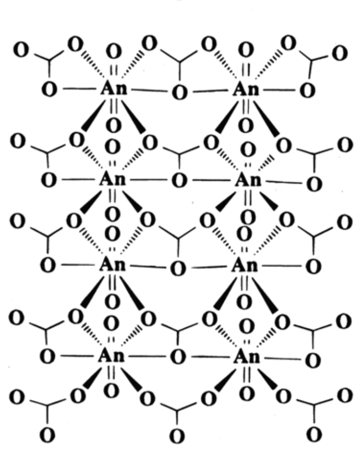


Figure 11. A ball-and-stick drawing illustrating a single $KNpO_2(CO_3)_2$ layer in the solid state structure of $K_3NpO_2(CO_3)_2$. The drawing was prepared from the fractional coordinates and unit cell parameters reported by in ref 166. Hatched atoms = Np; light gray = K; black = C; white = O.

in the series of neptunium(V) monocarbonates $MNpO_2(CO_3)$ with M = Cs^+, Rb^+, NH_4^+, K^+, Na^+, and Li^+, a hexagonal-to-orthorhombic phase change was observed within the $NpO_2(CO_3)$ layer at the potassium–sodium boundary. The solids maintain a layered structure, but the orthorhombic $NpO_2(CO_3)$ 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 is more open than the hexagonal structure which appears to allow for the closer contacts necessary for the smaller sodium and lithium cations.



III
hexagonal



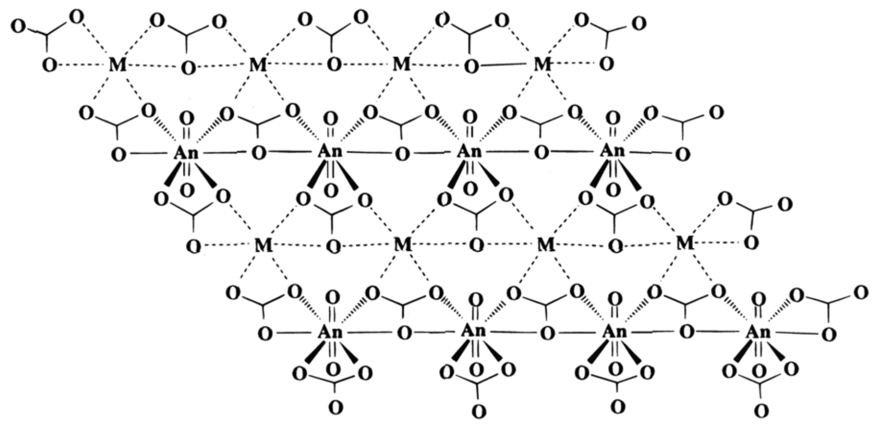
IV
orthorhombic

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 $KAnO_2(CO_3){\cdot}nH_2O$ with intercalated water molecules.

$M_3AnO_2(CO_3)_2$. The actinyl(V) carbonate solids of general formula $M_3AnO_2(CO_3)_2$ (An = Np, Pu, Am, and M = Na, K, 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, $M_3AnO_2(CO_3)_2$ compounds maintain the same orthorhombic layered structure as seen in $MAnO_2(CO_3)$ 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 $[M_{0.5}(AnO_2)_{0.5}(CO_3)]$ 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 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 AnO_2^+ ions allows for a relatively straightfor-

Chart 1



V

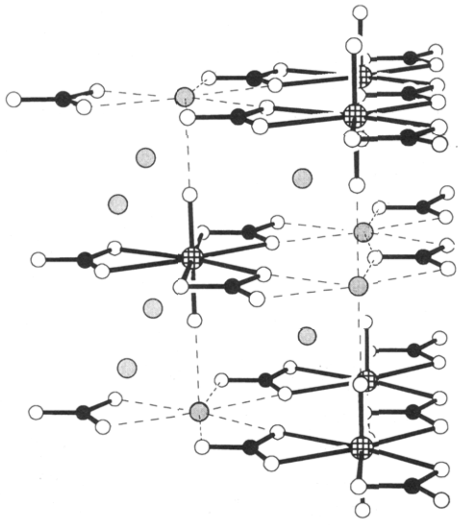


Figure 12. A ball-and-stick drawing illustrating the infinite stacking between $KNpO_2(CO_3)_2$ layers in the solid state structure of $K_3NpO_2(CO_3)_2$. The drawing was prepared from the fractional coordinates and unit cell parameters reported in ref 166. Hatched atoms = Np; light gray = K; black = C; and white = O.

ward explanation for the presence of nonstoichiometric solids such $M_4AnO_2(CO_3)_{2.5}{\cdot}nH_2O$. 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 $M_{(3+2x)}AnO_2(CO_3)_{(2+x)}{\cdot}nH_2O$, 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 $M_5AnO_2(CO_3)_3$.

Diffuse reflectance spectra recorded for $NaNpO_2(CO_3)$ and $Na_3NpO_2(CO_3)_2$ solids are compared in Figure 13.[176] The remarkable differences in the spectra of these solids can be attributed to the significant differences in the solid state structures as noted above (see Figures 9 and 11).

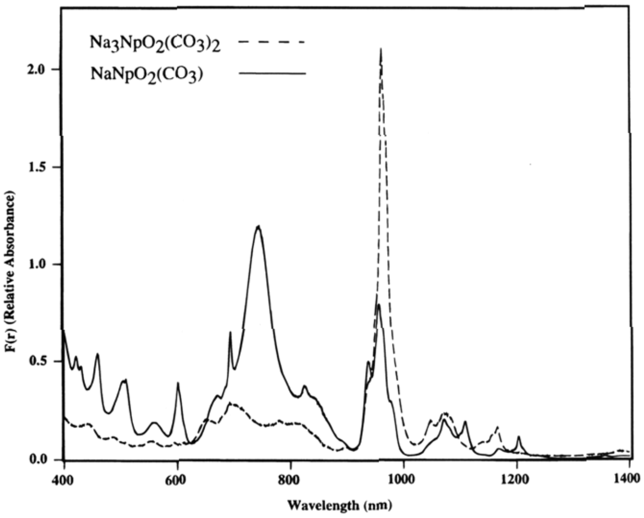


Figure 13. Comparison of the diffuse reflectance spectra of the solids $NaNpO_2(CO_3)$ (solid line) and $Na_3NpO_2(CO_3)_2$ (dashed line).

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. $UO_2(CO_3)_3^{4-}$ reduced to $UO_2(CO_3)_3^{5-}$ 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 $NpO_2(CO_3)_3^{5-}$. Both AmO_2^+ and PuO_2^+ in carbonate solutions have Raman bands at 755 cm^{-1}. In comparison with the 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] Na_2CO_3 electrolyte. [b] NaCl electrolyte; $NaClO_4$ 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 $AnO_2(CO_3)_3^{4-}$ to $AnO_2(CO_3)_3^{5-}$ in 1 M Na_2CO_3 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, $CO_3^{\bullet-}$ can oxidize any of the $AnO_2CO_3)_3^{5-}$ 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.[180-186] There is only one uranyl(V) species for which quantitative thermodynamic information is available, namely $UO_2(CO_3)_3^{5-}$. The formation constant for this species was determined on the basis of the formation constant of $UO_2(CO_3)_3^{4-}$ and the reduction potential of the equilibrium shown in eq 15.[180]

$$UO_2(CO_3)_3^{4-} + e^- \rightarrow UO_2(CO_3)_3^{5-} \qquad (15)$$

There is ample spectrophotometric and solubility data supporting the formation of monomeric complex anions, $NpO_2(CO_3)^-$, $NpO_2(CO_3)_2^{3-}$, and $NpO_2(CO_3)_3^{5-}$ in solution; and these correlate nicely with the known solid phase salts $MNpO_2(CO_3)$, $M_3NpO_2(CO_3)_2$, and $M_5NpO_2(CO_3)_3$ (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 for the first two complex anions are reasonably well understood (Table 3), but those for $NpO_2(CO_3)_3^{5-}$ 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 $PuO_2(CO_3)^-$ using photoacoustic spectroscopy (PAS), then employed the *s*pecific *i*on *i*nteraction *t*heory (SIT) to calculate a formation constant at zero ionic strength (Table 3).[103] This value compares favorably with the corresponding log β_{11} for the $NpO_2(CO_3)^-$ analog (Table 3). No evidence for mixed hydroxy carbonate species was found in this study, in which hydrolysis behavior of the PuO_2^+ ion was also investigated. The formation constant for the triscarbonato species, $PuO_2(CO_3)_3^{5-}$ was determined by Lierse using the formation constant of $PuO_2(CO_3)_3^{4-}$ 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 AmO_2^{2+}/AmO_2^+ redox couple in carbonate media.[180] This reinterpretation indicates that AmO_2^+ forms a limiting carbonate complex $AmO_2(CO_3)_3^{5-}$ with approximately the same formation constant as found for the analogous uranyl(V) species. One problem with extrapolation of the formation constants of $AnO_2(CO_3)_3^{5-}$ 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 $NpO_2(CO_3)^-$, and $NpO_2(CO_3)_2^{3-}$ are expected to dominate above pH = 7, and hydrolysis to form $NpO_2(OH)$ 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 $NpO_2(CO_3)_3^{5-}$ 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, $NpO_2(CO_3)^-$ is predicted to be the dominant species even at pH = 9. There is never enough carbonate present to increase the concentration of the biscarbonato species $NpO_2(CO_3)_2^{3-}$

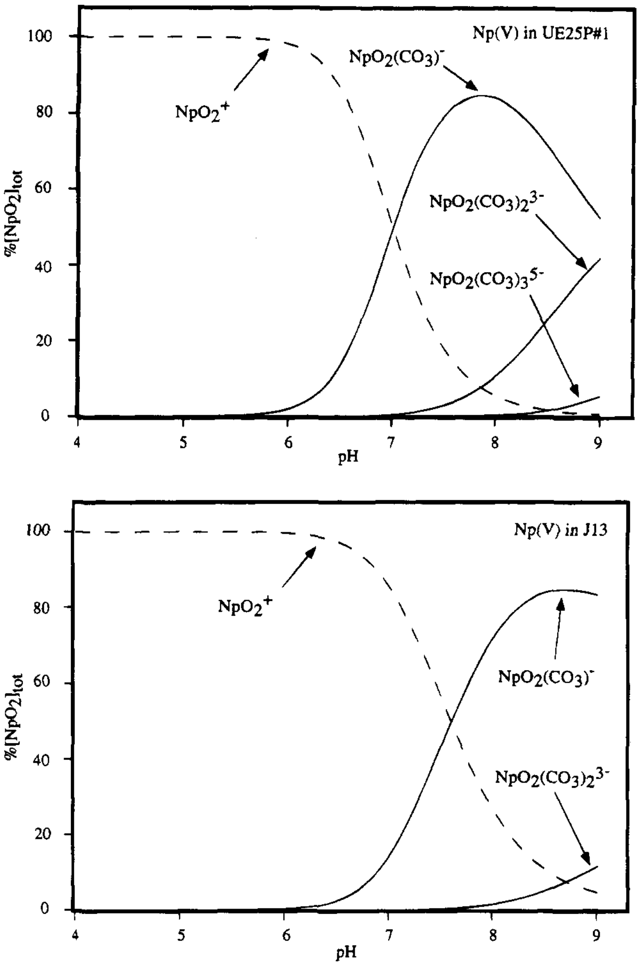


Figure 14. Calculated neptunyl species distributions in carbonate solutions modeling Yucca Mountain UE25P#1 (top) and J-13 (bottom) groundwaters at 25 °C. Np(V) carbonate binding constants were taken from Riglet,[181] (I_m = 0.5 *m*); hydrolysis constants were taken from Neck *et al.*[97] (I_m = 0.1 *m*); and ligand protonation constnats were calculated for I_m = 0.1 *m* using SIT and data from Grenthe *et al.*[81] Solution conditions: (UE25P#1) $[NpO_2^+] = 1 \times 10^{-5}$ M, $[CO_3^{2-} + HCO_3^-] = 0.002$ M. (J-13) $[NpO_2^+] = 1 \times 10^{-5}$ M, $[CO_3^{2-} + HCO_3^-] = 0.0114$ M. Formation constants (log β): ML = 4.3; ML_2 = 6.5; ML_3 = 7.9 (I_m = 0.5 *m*); LH = 9.1; LH_2 = 16.05 (I_m = 0.1 *m*). Hydrolysis constants (log K): MOH = −11.32; $M(OH)_2$ = −23.42 (I_m = 0.1 m), where M = NpO_2 and L = 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 carbonato solids has been given by Bagnall.[187] Simple, neutral binary thorium(IV) carbonates of formula $Th(CO_3)_2$ and $Th(CO_3)_2{\cdot}nH_2O$ (*n* = 0.5 and 3.00−3.57) are claimed to form during the pyrolysis of $Th(C_2O_4)_2$, or by heating thorium hydroxide under CO_2 at 150 °C, respectively.[187] There are literature reports on solids of formula $ThO(CO_3)$ and $Th(OH)_2(CO_3){\cdot}2H_2O$, but these solids are not well characterized.[187] The existence of the guanidinium complexes $[C(NH_2)_3][An(CO_3)_3]$ (An = Th, U) have also been claimed. It has been reported that addition of ethylenediammonium sulfate to uranium(IV) solutions of $(NH_4)_2CO_3$ or $KHCO_3$ results in the precipitation of $[C_2H_4(NH_3)_2][U(CO_3)_3(H_2O)]{\cdot}2H_2O$.[188] Hydrolysis of this complex occurs with dissolution to give $[C_2H_4(NH_3)_2]_2[U_2(OH)_2(CO_3)_5(H_2O)_4]{\cdot}2H_2O$ or $[C_2H_4(NH_3)_2][U(OH)_2(CO_3)_2(H_2O)_2]{\cdot}H_2O$. Tetracarbonato uranium salts of composition $[C(NH_2)_3]_4[U(CO_3)_4]$ and $[C(NH_2)_3]_3(NH_4)[U(CO_3)_4]$ 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 $M_6An(CO_3)_5{\cdot}nH_2O$ (An = Th, U; M_6 = Na_6, K_6, Tl_6, $[Co(NH_3)_6]_2$, $[C(NH_2)_3]_3[(NH_4)]_3$, $[C(NH_2)_3]_6$; *n* = 4−12) have all been reported.[189−191] The sodium salt can be prepared by chemical or electrochemical reduction of $Na_4UO_2(CO_3)_3$, followed by the addition of Na_2CO_3 to form a precipitate. The potassium salt, $K_6U(CO_3)_5{\cdot}6H_2O$ 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 $U(SO_4)_2$ 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 $M_6An(CO_3)_5{\cdot}nH_2O$ 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 $Th(CO_3)_5^{6-}$ and $Th(CO_3)_6^{8-}$.[192−196,200]

Solid plutonium(IV) carbonato complexes of general formula $M_{(2x-4)}Pu(CO_3)_x{\cdot}nH_2O$ have been prepared for a variety of alkali metal cations (M = Na^+, K^+, 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, $K_4Pu(CO_3)_4{\cdot}nH_2O$, $K_6Pu(CO_3)_5{\cdot}nH_2O$, $K_8Pu(CO_3)_6{\cdot}nH_2O$, and $K_{12}Pu(CO_3)_8{\cdot}nH_2O$ have all been reported.[197] These compounds are all reported as green amorphous powders which are water soluble. $K_6[Pu(CO_3)_5]{\cdot}nH_2O$ can be isolated as brownish green crystals where *n* = 3 or 4. Sodium salts of formula $Na_4Pu(CO_3)_4{\cdot}3H_2O$, $Na_6Pu(CO_3)_5{\cdot}2H_2O$, and $Na_6Pu(CO_3)_5{\cdot}4H_2O$ have been claimed as light green crystalline compounds that appear to lose some waters of hydration and crumble upon exposure to air.[198] Similarly, the $(NH_4)_4Pu(CO_3)_4{\cdot}4H_2O$ and $[Co(NH_3)_6]_2Pu(CO_3)_5{\cdot}5H_2O$ 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

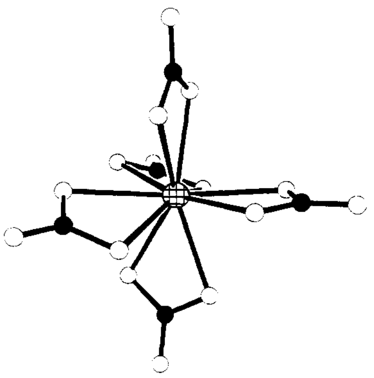


Figure 15. A ball-and-stick drawing illustrating the pseudo hexagonal bipyramidal coordination geometry of the $Th(CO_3)_5^{6-}$ anion in the solid state structure of $[C(NH_2)_3]_6[Th(CO_3)_5]$. The drawing was prepared from the fractional coordinates and unit cell parameters reported in ref 194. Hatched atoms = Th; black = C; and white = O.

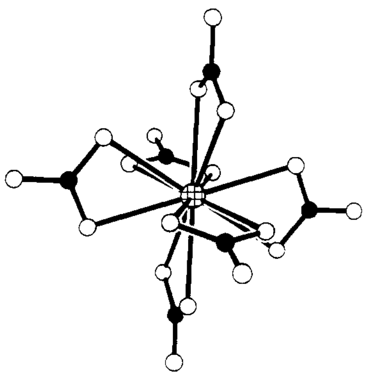
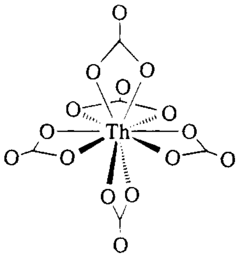


Figure 16. A ball-and-stick drawing illustrating the icosahedral coordination geometry (virtual T_h symmetry) of the $Th(CO_3)_6^{8-}$ anion in the solid state structure of tuliokite $Na_6BaTh(CO_3)_6{\cdot}6H_2O$. The drawing was prepared from the fractional coordinates and unit cell parameters reported in ref 200. Hatched atoms = Th; black = C; and white = O.

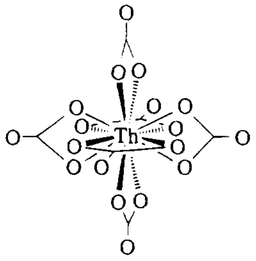
analogous thorium compounds, plutonium(IV) carbonato anions of formula $Pu(CO_3)_4^{4-}$, $Pu(CO_3)_5^{6-}$, and $Pu(CO_3)_6^{8-}$ seem reasonable, but higher-order anions may well be mixtures of the plutonium(IV) carbonato complexes and alkali carbonate.

$M_6An(CO_3)_5$. Single crystals of $Na_6Th(CO_3)_5{\cdot}12H_2O$ 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 $Th(CO_3)_5^{6-}$ anion consists of a central thorium atom coordinated to 10 oxygen atoms of five bidentate carbonato 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 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 $AnO_2(CO_3)_3^{4-}$. Viewed in this way, the $Th(CO_3)_5^{6-}$ 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 $[C(NH_2)_3]_6[Th(CO_3)_5]$,[194] and the correct space group has been subsequently assigned.[196]

$Na_6BaTh(CO_3)_6{\cdot}6H_2O$. The only well-characterized actinide(IV) carbonate solid with six carbonates per metal atom is the recently reported mineral tuliokite $Na_6BaTh(CO_3)_6{\cdot}6H_2O$, 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 $Th(CO_3)_6^{8-}$ anions; the basic structural features of this ion are shown in a ball-and-stick representation in Figure 16. The icosahedral $Th(CO_3)_6^{8-}$ unit is characterized by three mutually 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] Joâo *et al.*,[201] and Östhols *et al.*[202] In the study by Östhols *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 carbonato complex of formula $Th(OH)_3(CO_3)^-$ and the pentacarbonato complex $Th(CO_3)_5^{6-}$; 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 $U(CO_3)_5^{6-}$ 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(VI) redox couple was then used to estimate the valve of log β_{15} for formation of the limiting complex $U(CO_3)_5^{6-}$ in eq 17. Pratopo *et al.* reanalyzed solubility data for uranium in a Swedish groundwater, assumed the presence of 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)			
$Th^{4+} + 5CO_3^{2-} \rightleftharpoons Th(CO_3)_5^{6-}$	1.0[a]	26.2(±0.2)	201
	2.5[a]	26.3(±0.2)	201
	3.0	32.3	202
$ThO_2(s) + 4H^+ + 5CO_3^{2-} \rightleftharpoons Th(CO_3)_5^{6-}$	3.0	39.64(±0.4)	202
$ThO_2(s) + H^+ + H_2O + CO_3^{2-} \rightleftharpoons Th(OH)_3(CO_3)^-$	3.0	6.78(±0.3)	202
Uranium(IV)			
$U^{4+} + 5CO_3^{2-} \rightleftharpoons U(CO_3)_5^{6-}$	0	34.0(±0.9)	81
	3.0	69.86(±0.55)	204
$U(CO_3)_4^{4-} + CO_3^{2-} \rightleftharpoons U(CO_3)_5^{6-}$	0	−1.12(±0.22)	205
Neptunium(IV)			
$Np^{4+} + 3CO_3^{2-} \rightleftharpoons Np(CO_3)_3^{2-}$	0.3	37.1(±1.2)	207
$Np^{4+} + 4CO_3^{2-} \rightleftharpoons Np(CO_3)_4^{4-}$	0.3	41.1(±1.4)	207
$Np^{4+} + 4OH^- + 2CO_3^{2-} \rightleftharpoons Np(OH)_4(CO_3)_2^{4-}$	0.1	53.07(±0.44)	206
Plutonium(IV)			
$Pu^{4+} + CO_3^{2-} \rightleftharpoons Pu(CO_3)^{2+}$	0.3	17.0(±0.7)	100
$Pu^{4+} + 2CO_3^{2-} \rightleftharpoons Pu(CO_3)_2$	0.3	29.9(±0.96)	100
$Pu^{4+} + 3CO_3^{2-} \rightleftharpoons Pu(CO_3)_3^{2-}$	0.3	39.1(±0.82)	100
$Pu^{4+} + 4CO_3^{2-} \rightleftharpoons Pu(CO_3)_4^{4-}$	0.3	42.9(±0.75)	100
$Pu^{4+} + 5CO_3^{2-} \rightleftharpoons Pu(CO_3)_5^{6-}$	0.3	44.5(±0.77)	100
$Pu^{4+} + 2CO_3^{2-} + 4OH^- \rightleftharpoons Pu(OH)_4(CO_3)_2^{4-}$	≈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 $U(OH)_2(CO_3)_2^{2-}$, 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.

$$UO_2(CO_3)_3^{4-} + 2e^- + 2CO_2 \rightleftharpoons U(CO_3)_5^{6-} \tag{16}$$

$$U^{4+} + 5CO_3^{2-} \rightleftharpoons U(CO_3)_5^{6-} \tag{17}$$

Moriyama and co-workers reported complexation constants of Np(IV) in carbonate solutions based on solubility data and suggested the formation of $Np(CO_3)_3^{2-}$ and $Np(CO_3)_4^{4-}$ 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 $Np(OH)_4(CO_3)_2^{4-}$ above pH = 10, and $Np(OH)_2(CO_3)_2^{2-}$ 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 $Pu(CO_3)^{2+}$ 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 $Pu(CO_3)^{2+}$, $Pu(CO_3)_2$, $Pu(CO_3)_3^{2-}$, $Pu(CO_3)_4^{4-}$, and $Pu(CO_3)_5^{6-}$ in analogy with the reported solid phases and these valves 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 Sullivan[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 *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 $Pu(OH)_x(CO_3)_y$ 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 $Pu(OH)_2(CO_3)_2^{2-}$ below pH = 10, and $Pu(OH)_4(CO_3)_2^{4-}$ at pH greater than 10.[210]

Americium(IV) is generally very unstable with respect to reduction or disproportionation in noncomplexing 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 $Am(CO_3)_5^{6-}$ 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 $Th(CO_3)_5^{6-}$ and $U(CO_3)_5^{6-}$; while for Np(IV) $Np(CO_3)_3^{2-}$ and $Np(CO_3)_4^{4-}$ are proposed; while for Pu(IV) the entire series, $Pu(CO_3)_n^{4-2n}$ ($n = 1-5$), has been proposed. Clearly the widely scattered nature of the carbonate formation constants for tetravalent plutonium, and the question of whether mixed hydroxo carbonates $Pu(OH)_n(CO_3)_2^{n-}$ (n = 2 or 4) or $Pu(CO_3)_n^{4-2n}$ (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 carbonato 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 $Th(CO_3)_5^{6-}$ (in the absence of ligands other than hydroxide and carbonate).[202] The most recent data on plutonium indicate that hydroxo carbonato complexes are likely to form; but we believe that these species are, at best, defined only as $Pu(OH)_x(CO_3)_y$, where the values of x and y have yet to be determined satisfactorily. The tendency of Pu(IV) to hydrolyze and form colloidal $PuO_2 \cdot 2H_2O$ 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 $Am_2(CO_3)_3 \cdot 4H_2O$.[211] Treatment of $Am_2(CO_3)_3$ with either 0.5 M $NaHCO_3$ or 1.5 M Na_2CO_3 solutions produces $NaAm(CO_3)_2 \cdot 4H_2O$ and $Na_3Am(CO_3)_3 \cdot 3H_2O$, respectively.[211] Acidified Am(III) solutions maintained under varying partial pressures of CO_2 yield solids which Runde *et al.* characterized as orthorhombic $Am(OH)(CO_3)$ or $Am_2(CO_3)_3$ 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 $Am(OH)(CO_3)$, but an earlier report of a hexagonal form of $Am(OH)(CO_3)$ 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 $Cm_2(CO_3)_3$ by analogy with americium.[214]

2.4.2. Solution Chemistry

Americium(III) carbonate complexation has been studied by spectrophotometry, solubility, potentiometry, and solvent extraction techniques. Nitsche *et al.* used absorption spectrophotometry to determine log β_{11} for formation of $Am(CO_3)^+$ in 0.1 M perchlorate solution.[215] Felmy and co-workers studied the solubility of $Am(OH)(CO_3)$ over a wide range of conditions and proposed the formation of $Am(CO_3)^+$, $Am(CO_3)_2^-$, and $Am(CO_3)_3^{3-}$, 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. $Am_2(CO_3)_3$ 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 $Am(CO_3)^+$ and $Am(CO_3)_2^-$.[216] Meinrath and Kim's value for log β_{11} is in good agreement with that reported by Nitsche. Bernkoff and Kim used a model containing mono-, bis-, 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 ^{241}Am(III) to ^{241}Am(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 $Am(CO_3)_3^{3-}$. 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 carbonato solution species and implies that more data is needed in this area.

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)			
$Am^{3+} + CO_3^{2-} \rightleftharpoons Am(CO_3)^+$	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
$Am^{3+} + 2CO_3^{2-} \rightleftharpoons Am(CO_3)_2^-$	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
$Am^{3+} + 3CO_3^{2-} \rightleftharpoons Am(CO_3)_3^{3-}$	0	15.2	183
	0.1	12.12(±0.85)	218
	5.0[a]	12.9(±0.2)	185
$Am^{3+} + CO_3^{2-} + OH^- \rightleftharpoons Am(OH)(CO_3)$	0.1	12.15(±0.15)	218
$Am^{3+} + 2CO_3^{2-} + OH^- \rightleftharpoons Am(OH)(CO_3)_2^{2-}$	0.1	16.16(±0.14)	218
$Am^{3+} + CO_3^{2-} + 2OH^- \rightleftharpoons Am(OH)_2(CO_3)^-$	0.1	18.29(±0.17)	218

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

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 compositions found at the proposed Yucca Mountain

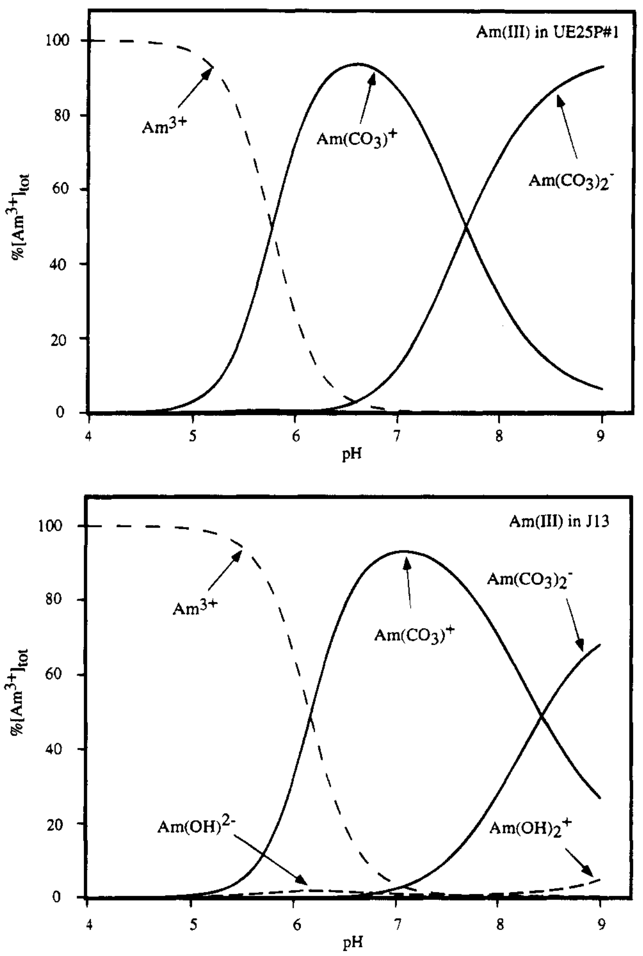


Figure 17. Calculated americium(III) species distributions in carbonate solutions modeling Yucca Mountain UE25P#1 (top) and J-13 (bottom) groundwaters at 25 °C. Am(III) carbonate formation constants were taken from Meinrath and Kim;[216] hydrolysis constants were taken from Stadler and Kim;[23] and ligand 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 β): 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 complexation 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 carbonato 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 biscarbonato 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 carbonato 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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