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### Evaluation of Possible Physical-Chemical Processes That Might Lead to Separations of Actinides in ORNL Waste Tanks

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Chemical Technology Division

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Separations of Actinides in ORNL Waste Tanks**

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## SUMMARY

The concern that there might be some physical-chemical process which would lead to a separation of the poisoning actinides ( $^{232}\text{Th}$ ,  $^{238}\text{U}$ ) from the fissionable ones ( $^{239}\text{Pu}$ ,  $^{235}\text{U}$ ) has led to a study of potential separation processes involving these elements. We find that there is no problem with the waste tank chemistry as the storage tanks are presently being maintained. However, because such separations are achieved through chemical processing, it is reasonable to assume that some chemistry could occur that would lead to separations of these actinides.

We have evaluated various chemistries and have identified the carbonate complexation reaction as the most plausible means of achieving the separation of these actinides. The particular chemistry is dependent on the equilibration of atmospheric carbon dioxide ( $\text{CO}_2$ ) with the aqueous solution, which is maintained at pH 8–12 to form carbonate ions ( $\text{CO}_3^{=}$ ) in solution. Under normal conditions without  $\text{CO}_2$ , the actinides exist in the sludge as hydroxy or oxide precipitates that have undergone a significant amount of aging, resulting in further stabilization of the solids.

The occurrence of soluble  $\text{CO}_3^{=}$  can selectively dissolve the solid actinides through the formation of soluble carbonate complexes. Uranium(VI), as uranyl ion, is most readily dissolved, followed by thorium(IV), and finally plutonium(IV). These soluble species are strongly dependent on the pH, the temperature, and the presence of other ions. Therefore, changes in any one or more of these parameters over a period of time, especially cyclic changes, could cause a selective dissolution and redeposition of the more soluble species away from the less soluble ones. Detailed calculations on the stability constants for the carbonates have shown that the most likely range for this process to occur is pH 10–11. While temperature gradients in the waste tanks are the most probable source of such cyclic changes, temperature data for these species are not readily available. Nevertheless, it is certain that there will be measurable effects on the solubility and these will provide the driving force for the dissolution/deposition process.

This carbonate complexation chemistry is presently not occurring in the Melton Valley Storage Tanks (MVSTs) because the carbonate concentration in solution is extremely low due to the precipitation of insoluble calcium carbonate. Consequently, several events would have to occur before this process could become a problem: (1) air sparging of the solutions, with associated  $\text{CO}_2$ , continues to such a degree that

the calcium content of the solution is consumed; (2) analysis of the liquid layer becomes so infrequent that the increase in soluble carbonate goes undetected; (3) a sufficient period of time passes that the slow, unstirred equilibration of the aqueous carbonate liquid is able to dissolve uranyl compounds in the sludge and saturate the solution (correction for a high soluble carbonate situation would be a simple matter of adding calcium ions through either calcium oxide or nitrate); and (4) a sufficient temperature gradient exists that the saturated actinide carbonate precipitates and the process cycles continuously across the gradient.

While this is the most plausible series of events that could lead to a separation of the actinides, other processes were considered as well. These included extraction processes in separate organic phases or onto adsorbing media and other complexation reactions. None of these were regarded as possible under the present operating and storage conditions for the MVSTs. The details of this study are given in this report.

It must be emphasized that these findings are not a cause for alarm with regard to the present procedures regarding the MVSTs. They should be used only to increase awareness of potential problems that, although unlikely, could possibly result under certain chemical conditions.

## ABSTRACT

The concern that there might be some physical-chemical process which would lead to a separation of the poisoning actinides ( $^{232}\text{Th}$ ,  $^{238}\text{U}$ ) from the fissionable ones ( $^{239}\text{Pu}$ ,  $^{235}\text{U}$ ) in waste storage tanks at Oak Ridge National Laboratory has led to a paper study of potential separations processes involving these elements. At the relatively high pH values ( $>8$ ), the actinides are normally present as precipitated hydroxides. Mechanisms that might then selectively dissolve and reprecipitate the actinides through thermal processes or additions of reagents were addressed. Although redox reactions, pH changes, and complexation reactions were all considered, only the last type was regarded as having any significant probability. Furthermore, only carbonate accumulation, through continual unmonitored air sparging of the tank contents, could credibly account for gross transport and separation of the actinide components. From the large amount of equilibrium data in the literature, concentration differences in Th, U, and Pu due to carbonate complexation as a function of pH have been presented to demonstrate this phenomenon. While the carbonate effect does represent a potential separations process, control of long-term air sparging and solution pH, accompanied by routine determinations of soluble carbonate concentration, should ensure that this separations process does not occur.



## 1. INTRODUCTION

Low-level liquid waste (LLLW) at the Oak Ridge National Laboratory (ORNL) consists of various concentrates from evaporators and from elution of ion-exchange columns, as well as solutions from laboratories and chemical processing operations for radioisotope and actinide element production. This LLLW is ultimately stored in tanks such as the Melton Valley Storage Tanks (MVST). A detailed description of the MVST facilities is provided in ORNL/TM-10218,<sup>1</sup> which traces a history that began with the facilities being used to temporarily hold LLLW concentrate between hydrofracture injections and then to serve as feed tanks for the hydrofracture facility. Upon cessation of the hydrofracture operations, the MVST have become a terminal storage point until an alternate disposal technology is placed in operation. Current plans are directed towards ultimate disposal at the Waste Isolation Pilot Plant (WIPP).

In the meantime, numerous reports<sup>2-7</sup> on the status and chemical analyses of the tanks have been generated. These reports, including the most recent<sup>7</sup> on the analysis of representative MVST contents, indicate that the composition typically consists of a wide variety of chemical components which have been listed in such groups as the Resource Conservation and Recovery Act (RCRA) metals (principally Ba, Cd, Cr, Ni, and Pb), process metals (Al, K, Na, P, Si, Th, U, and Zn), semiquantitative metals, anions, beta-gamma emitters, alpha emitters, and uranium isotopes. Also identified in these analyses are alkalinity, carbon (organic and inorganic) content, densities, and physical properties such as total solids.

Isotopic analysis of the fissile elements have also been reported<sup>3</sup> to establish the denature ratio. The denature ratio is the ratio of chemically similar nonfissile isotopes to fissile isotopes. The ratio for uranium is  $^{238}\text{U}/[(1.35 \times ^{233}\text{U}) + ^{235}\text{U}]$ , whereas the ratio for plutonium is  $^{232}\text{Th}/(^{239}\text{Pu} + ^{241}\text{Pu})$ . The denature ratio for uranium and plutonium (typically >100, but recently increased<sup>8</sup> to >200) is in accordance with the waste acceptance criteria for wastes discharged into the LLLW system.

A recent communication<sup>8</sup> described concerns for nuclear criticality safety and the need for an evaluation to support the assumption that thorium will remain fixed with plutonium and uranium under conditions likely to be encountered in the active LLLW system. The ORNL Criticality Review Committee had previously recommended that a formal investigation be conducted to determine whether thorium that had been admixed with plutonium would be sufficiently chemically similar to ensure that chemical separation would not occur. The investigation should consider the processes that produced the material currently in



the LLLW tanks, the tank chemistry as it is today, and what processes are expected to be discharged into the LLLW system in the future. It was also suggested by the committee that the scope of the study be expanded to include separations other than just thorium from uranium and uranium from plutonium. A memorandum<sup>9</sup> has already been issued in response to the committee request. The current report provides details of the study leading to the conclusions stated in the memorandum.

## 2. SCOPE

The approach to this study was to consider the chemistry in light of the contents of the tanks and possible additions that might be made in the future. The goal was to identify possible chemical mechanisms that might result in separation of the actinides Th, U, and Pu. Chemical reactions of the tank contents causing changes in the oxidation states, hydrolysis or complexation, possible extraction into immiscible phases, and reactions with atmospheric components were all considered. These actinide elements can, in fact, be separated, and schemes within the laboratory can be devised to accomplish this. Based on this understanding, the tank chemistry was considered with regard to determining the necessary separations routes.

Standard separation mechanisms typically involve extraction, precipitation, or volatilization. The latter is not possible in the case of the aqueous actinide systems and was not considered as part of this study. Extraction would depend on a separate phase of sufficient concentration to selectively remove one of the actinide components from the others. While used extensively for laboratory separations processes, the release of significant amounts of immiscible organic components into the LLLW system is carefully controlled. No separate organic phase (solid or liquid) is expected to occur, and thus extraction is considered to be highly unlikely. These processes are generally quite sensitive to changes in redox potentials. The oxidation states considered here were Th(IV), U(VI), Pu(IV), and Pu(VI). The U(IV) and Pu(III) species were not considered because they would be formed only under highly reductive conditions not present in the tanks. The Pu(V) species, while typically occurring in the environment under extremely dilute conditions, would not be expected to occur in the waste tanks at the concentrations present and, therefore, was also not considered here.

Dissolution-precipitation processes are by far the most likely routes for actinides to "auto-separate" within the waste tanks given the existing chemical composition. Dissolution processes would most

readily be driven by complexants that might have been added during treatment and disposal processes or by contact with the environment. The most probable complexant, carbonate ion ( $\text{CO}_3^{=}$ ), can be introduced in an unnoticeable fashion through contact with air, where carbon dioxide,  $\text{CO}_2$ , dissolves in the aqueous supernate phase. Continuous air sparging would only accelerate the dissolution of  $\text{CO}_2$ , with a resultant  $\text{CO}_3^{=}$  formation (as described later in the text).

Dissolution alone is not enough to effect a separation of actinides. Reprecipitation must follow in sequence. Temperature gradients provide the most probable driver for reprecipitation because solubilities will certainly be temperature dependent, allowing dissolution to take place at one temperature and reprecipitation at another (usually lower) temperature, with the resulting slow transport of the more soluble actinide away from the less soluble one. While considerable data exist for carbonate complexation, almost no data are available for the effects of temperature on the solubility. These values have to be estimated in order to assess the magnitude of this cyclic process.

Therefore, the focus of this study was on complexation equilibria of carbonates, with the three actinides showing the differences in solubility of the various carbonates at different pH values. This would serve to show just how a separation could occur in a waste tank system where an aqueous phase was in contact with a precipitated solid phase and the pH was maintained at values  $>7.0$ . Temperature effects on the solubility were estimated to determine the extent to which reprecipitation could occur. In addition, dissolution by reaction with other complexants was also considered since the possibility existed that some of these could be discharged into the LLLW system.

To illustrate the solubility behavior of the Th, U, and Pu hydroxides in the presence of soluble carbonate at high pH values, calculations were performed using a fixed 1.0 M concentration of total carbonate species (TC).<sup>‡</sup> The uncomplexed carbonate can be distributed among three species,  $\text{CO}_2'(\text{aq})$ ,<sup>‡‡</sup>  $\text{HCO}_3^-$ , and  $\text{CO}_3^{=}$ , according to the pH of the solution. The equilibria used, with their associated equilibrium constants,<sup>10</sup> were the following:

---

<sup>‡</sup>TC as used here for total carbonate concentration should not be confused with a similar notation used by other authors to represent *total carbon* (which includes organic carbon, as well).

<sup>‡‡</sup>Where, according to the notation used by Palmer,<sup>10</sup>  $\text{CO}_2'(\text{aq})$  is the total dissolved  $\text{CO}_2$ , which is the sum of  $\text{CO}_2(\text{aq})$  and  $\text{H}_2\text{CO}_3$  but does not include the ionized forms  $\text{HCO}_3^-$  and  $\text{CO}_3^{=}$ .



Calculated solubilities of Th, U, and Pu hydroxides and of Th-U-Pu mixed hydroxides at a 1.0 MTC over a pH range of 8-14 are presented in the following section. Values of all equilibrium species at 1.0 MTC and estimated metal hydroxide solubilities at ambient CO<sub>2</sub> pressure (0.00033 atm) are presented in the appendix.

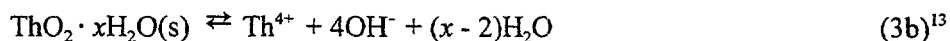
### 3. COMPLEXATION WITH CARBONATE IONS

#### 3.1 INCREASED SOLUBILITY OF Th(IV) BY COMPLEXATION WITH CO<sub>3</sub><sup>=</sup>

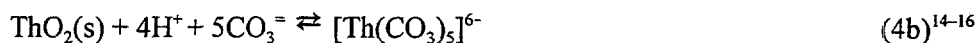
The Th(IV) hydroxy-carbonato species and equilibria considered for the calculations were the following:



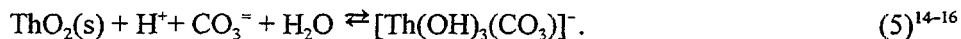
or



or



and



Some of the reported values<sup>11,12</sup> for the solubility product ( $K_{sp}$ ) for Th(OH)<sub>4</sub>(s) at 25°C were 10<sup>-39</sup> and 10<sup>-42</sup>; the calculated<sup>13</sup>  $K_{sp}$  for ThO<sub>2</sub> was 4.0 × 10<sup>-50</sup>. The wide range of reported values for the  $K_{sp}$  is probably due to the varied characteristics of the hydroxide materials, ranging from almost completely amorphous to more crystalline materials. The more representative  $K_{sp}$  number for the actual solubilities will depend on the conditions used during the hydroxide formation and on aging.

Calculations were made using three different values of  $K_{sp}$  ( $10^{-39}$ ,  $10^{-42}$ , and  $4.0 \times 10^{-50}$ ) to illustrate the quantitative uncertainty of the solubility predictions. The qualitative conclusions are, nevertheless, the same. The concentration expressions used for the computations are given in Table 1. Expression (d) was used in conjunction with the  $K_{sp}$  values for  $\text{Th}(\text{OH})_4$  ( $10^{-39}$  and  $10^{-42}$ ), while Expression (e) ( $K_{sp}$  independent) was used for the  $\text{ThO}_2(\text{s})$  equilibria ( $K_{sp} = 4.0 \times 10^{-50}$ ). In addition, the TC chosen was 1.0 M.

These expressions were used in simultaneous equations to solve the solubility behavior of Th(IV) as a function of the solution pH. Figure 1 depicts the calculated solubility of Th(IV) in the presence of 1.0 M TC [as defined in expression (g) of Table 1] using the three  $K_{sp}$  values as a function of the pH.

Figures 2a and 2b show the calculated species distribution as a function of pH for 1.0 M TC using (a)  $\log K_{sp} = -49.4$  and (b)  $\log K_{sp} = -42$  in Eq. (3a). The curve labeled Sol-Th(IV) represents the total concentration of Th(IV) in solution. At relatively high concentrations of Th(IV) in solution, the main species present is  $[\text{Th}(\text{CO}_3)_5]^{6-}$  (Fig. 2b). At low concentrations of Th(IV), the main species is  $[\text{Th}(\text{OH})_3\text{CO}_3]^-$ .

### 3.2 INCREASED SOLUBILITY OF U(VI) BY COMPLEXATION WITH $\text{CO}_3^{2-}$

Carbonate complexation has a much more dramatic effect on the solubility of the uranyl ion. To illustrate this, a similar analysis was performed to determine the increased solubility (due to carbonate complexation) of uranyl(VI) as a function of pH. The U(VI) hydroxy and carbonato equilibria considered for the calculations were the following:



**Table 1. Expressions for the molar concentrations, [ ], of various species used in the determination of Th(IV) solubility, based on the equilibrium equations given in the text**

- 
- (a)  $[\text{CO}_3^{=}] = 4.69 \times 10^{-11} [\text{HCO}_3^-]/[\text{H}^+]$
- (b)  $[\text{HCO}_3^-] = 4.48 \times 10^{-7} [\text{CO}_2'(\text{aq})]/[\text{H}^+]$
- (c)  $[\text{Th}^{4+}] = K_{\text{sp}}/[\text{OH}^-]^4$
- (d)<sup>14-16</sup>  $[\text{Th}(\text{CO}_3)_5]^{6-} = 2.00 \times 10^{32} [\text{Th}^{4+}][\text{CO}_3^{=}]^5$
- (e)<sup>14-16</sup>  $[\text{Th}(\text{CO}_3)_5]^{6-} = 4.37 \times 10^{39} [\text{CO}_3^{=}]^5[\text{H}^+]^4$
- (f)  $[\text{Th}(\text{OH})_3(\text{CO}_3)]^- = 3.35 \times 10^8 [\text{CO}_3^{=}][\text{H}^+]$
- (g)  $\text{TC} = [\text{CO}_2'(\text{aq})] + [\text{HCO}_3^-] + [\text{CO}_3^{=}] + 5[\text{Th}(\text{CO}_3)_5]^{6-} + [\text{Th}(\text{OH})_3(\text{CO}_3)]^-$
-



Some of the reported<sup>13,17</sup> values for solubility product,  $K_{sp}$ , for  $\text{UO}_2(\text{OH})_2(\text{s})$  at 25°C were  $10^{-22}$  and  $10^{-23.74}$ . Calculations were made using both  $10^{-22}$  and  $10^{-23.74}$  to illustrate, as with the Th(IV) case, the quantitative variance due to these two values. The concentration expressions derived from the above equilibria and used for the computations are given in Table 2. As before, these were used in simultaneous equations to solve for the solubility dependence of U(VI) as a function of pH.

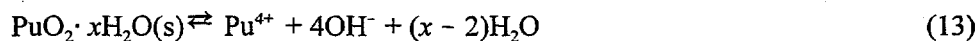
Figure 3 depicts the calculated solubility of U(VI) in the presence of a 1.0 M TC solution as a function of pH for the two different  $K_{sp}$  values. The solubilities calculated using  $\log K_{sp} = -22$  are very high at high pH values because of the predominance of  $[\text{UO}_2(\text{OH})]^-$  as defined in Eq. (f) of Table 2. Figure 4 shows the distribution of U(VI) species and total U(VI) in a 1.0 M TC solution as a function of pH using  $\log K_{sp} = -23.74$ . The main species present in solution is  $[\text{UO}_2(\text{CO}_3)_3]^{4-}$ .

### 3.3 INCREASED SOLUBILITY OF Pu(IV) BY COMPLEXATION WITH $\text{CO}_3^{2-}$

The Pu(IV) hydroxy and carbonato species and their respective equilibria were as follows:

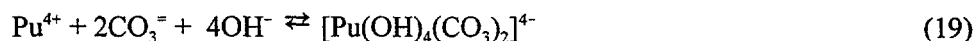


or

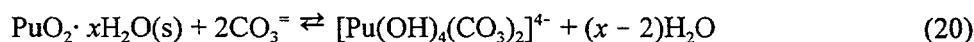


**Table 2. Expressions for the molar concentrations, [ ], of various species used in the determination of uranyl(VI) solubility, based on the equilibrium equations given in the text**

- 
- (a)  $K_{sp} = [\text{UO}_2^{2+}][\text{OH}^-]^2$
- (b)<sup>14</sup>  $[\text{UO}_2\text{CO}_3] = 7.76 \times 10^8 [\text{UO}_2^{2+}][\text{CO}_3^{=}]$
- (c)<sup>14</sup>  $[\text{UO}_2(\text{CO}_3)]^{2-} = 1.584 \times 10^{16} [\text{UO}_2^{2+}][\text{CO}_3^{=}]^2$
- (d)<sup>14</sup>  $[\text{UO}_2(\text{CO}_3)_3]^{4-} = 4.07 \times 10^{22} [\text{UO}_2^{2+}][\text{CO}_3^{=}]^3$
- (e)<sup>14</sup>  $[(\text{UO}_2)_3(\text{CO}_3)_6]^{6-} = 1.698 \times 10^{56} [\text{UO}_2^{2+}][\text{CO}_3^{=}]^6$
- (f)<sup>18</sup>  $[\text{UO}_2(\text{OH}_3)]^- = 6.31 \times 10^{-20} [\text{UO}_2^{2+}]/[\text{H}^+]^3$
- (g)  $\text{TC} = [\text{CO}_2(\text{aq})] + [\text{HCO}_3^-] + [\text{CO}_3^{=}] + [\text{UO}_2\text{CO}_3]$   
 $+ 2[\text{UO}_2(\text{CO}_3)_2]^{2-} + 3[\text{UO}_2(\text{CO}_3)_3]^{4-}$   
 $+ 6[(\text{UO}_2)_3(\text{CO}_3)_6]^{6-}$
-



or

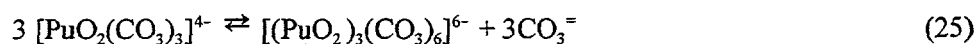
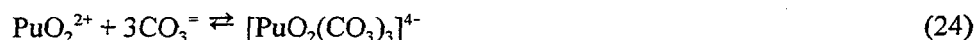


Some of the reported  $K_{\text{sp}}$  values<sup>19</sup> for  $\text{Pu}(\text{OH})_4(\text{s})$  at 25°C were  $10^{-52}$ ,  $10^{-56}$ , and  $7 \times 10^{-56}$ ; the calculated<sup>13</sup>  $K_{\text{sp}}$  for  $\text{PuO}_2$  was  $10^{-63}$ . Again, the wide range of reported values for the  $K_{\text{sp}}$  is probably due to the varied characteristics of the hydroxide materials, from almost completely amorphous to very crystalline forms. The  $K_{\text{sp}}$  values for the actual solubilities will depend on the state of the Pu(IV) hydroxide product and on aging conditions in the storage tanks. Calculations were made using  $K_{\text{sp}}$  = values of  $10^{-56}$  and  $10^{-63}$  to illustrate the quantitative variance that could result. The concentration expressions<sup>5</sup> used for the computations are given in Table 3. Equation (h) of Table 3 used a  $K_{\text{sp}}$  value of  $10^{-56}$  for  $\text{Pu}(\text{OH})_4$ , while Eq.(i) ( $K_{\text{sp}}$  independent)<sup>20</sup> used a  $K_{\text{sp}}$  of  $10^{-63}$  for  $\text{PuO}_2(\text{s})$ .

Figure 5 depicts the calculated solubility of Pu(IV) as a function of pH in the presence of a 1.0 M TC using the different  $K_{\text{sp}}$  values. Figure 6 shows the distribution of major Pu(IV) species and total soluble Pu(IV) in a 1.0 M TC solution as a function of pH using  $\log K_{\text{sp}} = -56$ . The main species present in solution are  $[\text{Pu}(\text{CO}_3)_4]^{4-}$  and  $[\text{Pu}(\text{CO}_3)_5]^{6-}$ .

### 3.4 INCREASED SOLUBILITY OF Pu(VI) BY COMPLEXATION WITH $\text{CO}_3^{=}$

The Pu(VI) hydroxy and carbonato species and their respective equilibria were the following:





**Table 3. Expressions for the molar concentration, [ ], of various Pu(IV) species used in the determination of Pu(IV) solubility, based on the equilibria given in Eqs. (12-20)**

---

(a)	$K_{sp} = [\text{Pu}^{4+}][\text{OH}^-]^4$
(b)	$[\text{Pu}(\text{OH})_4(\text{CO}_3)_2]^{4-} = 1.995 \times 10^{-3} [\text{HCO}_3^-]^2$
(c)	$[\text{PuCO}_3]^{2-} = 10^{17} [\text{Pu}^{4+}][\text{CO}_3^{=}]$
(d)	$[\text{Pu}(\text{CO}_3)_2] = 7.94 \times 10^{29} [\text{Pu}^{4+}][\text{CO}_3^{=}]^2$
(e)	$[\text{Pu}(\text{CO}_3)_3]^{2-} = 1.259 \times 10^{39} [\text{Pu}^{4+}][\text{CO}_3^{=}]^3$
(f)	$[\text{Pu}(\text{CO}_3)_4]^{4-} = 7.94 \times 10^{42} [\text{Pu}^{4+}][\text{CO}_3^{=}]^4$
(g)	$[\text{Pu}(\text{CO}_3)_5]^{6-} = 3.16 \times 10^{44} [\text{Pu}^{4+}][\text{CO}_3^{=}]^5$
(h)	$[\text{Pu}(\text{OH})_4(\text{CO}_3)_2]^{4-} = 2.51 \times 10^{46} [\text{Pu}^{4+}][\text{OH}^-]^4[\text{CO}_3^{=}]^2$
(i)	$[\text{Pu}(\text{OH})_4(\text{CO}_3)_2]^{4-} = 1.047 \times 10^{-5} [\text{CO}_3^{=}]^2$
(j)	$\begin{aligned} \text{TC} = & [\text{CO}_2'(\text{aq})] + [\text{CO}_3^{=}] + [\text{HCO}_3^-]^2 + 2[\text{Pu}(\text{CO}_3)]^{2+} \\ & + 2[\text{Pu}(\text{CO}_3)_2] + 3[\text{Pu}(\text{CO}_3)_3]^{2-} \\ & + 4[\text{Pu}(\text{CO}_3)_4]^{4-} + 5[\text{Pu}(\text{CO}_3)_5]^{6-} \\ & + 2[\text{Pu}(\text{OH})_4(\text{CO}_3)_2]^{4-} + 2[\text{Pu}(\text{OH})_2(\text{CO}_3)_2]^{2-} \end{aligned}$

---

Some of the reported  $K_{sp}$  values<sup>13,17</sup> for the  $\text{PuO}_2(\text{OH})_2(\text{s})$  at 25°C were  $10^{-22.7}$  and  $10^{-24.5}$ . Calculations were made using  $K_{sp} = 10^{-22.7}$  and  $10^{-24.5}$  to illustrate the quantitative variance attributed to the two values. The concentration expressions used for the computations in Eqs. (21) to (25) are given in Table 4.

Figure 7 depicts the calculated solubility of Pu(VI) as a function of pH in the presence of a 1.0 M TC solution using the two different  $K_{sp}$  values. The calculated solubilities show that the predominant species in carbonate solutions is  $[\text{PuO}_2(\text{CO}_3)_3]^{4-}$ , with only very minor amounts of  $[(\text{PuO}_2)_3(\text{CO}_3)_6]^{6-}$  at pH  $\approx$  8.

### 3.5 COMBINED SOLUBILITY EFFECTS ON Th(IV), Pu(IV), AND U(VI)

The precipitation of metal ions as hydroxides is not a selective process. Many ions that might be present in a waste solution will coprecipitate, including Th(IV), Pu(IV), Pu(VI), U(VI), Fe(III), etc. The actual solubility of the precipitate will be a strong function of the degree of order in the structure (amorphous being significantly more soluble than crystalline). In general the solubility decreases significantly as the precipitate ages because the growth of the crystal lattice produces forces that enhance the stability of the precipitate. For this reason, calculations of actual and relative solubilities will depend on the particular solubility products chosen (which are, in turn, related to the degree of precipitate aging). It is possible, therefore, to estimate tendencies and display generic trends that will help investigators better understand the general behavior of these complicated systems.

Figures 8 and 9 display the result of a solubility calculation for one combination of Th(IV), Pu(IV), and U(VI) in a 1.0 M TC solution. Figure 8 shows the calculated absolute solubilities, while Fig. 9 shows the relative values. The  $K_{sp}$  values used were  $10^{-42}$  for  $\text{Th}(\text{OH})_4(\text{s})$ ,  $10^{-56}$  for  $\text{Pu}(\text{OH})_4(\text{s})$ , and  $10^{-23.74}$  for  $\text{UO}_2(\text{OH})_2(\text{s})$ . [It should be noted that the Pu(IV) plot lies under the Th(IV) along the abscissa in Fig. 9 even though the solubility of Pu(IV) is considerably less than that of Th(IV).]

This set of  $K_{sp}$  values tends to represent the highest possible solubility for Pu(IV) and Th(IV) and the lowest for U(VI). In spite of this biased selection, Figs. 8 and 9 show that U(VI) is very intensely solubilized by carbonate relative to Pu(IV) and Th(IV). If any other  $K_{sp}$  values had been chosen, the differences in solubility between that of U(VI) and either Pu(IV) or Th(IV) would have been even greater.

**Table 4. Expression for the molar concentration, [ ], of various Pu(VI) species used in the determination of Pu(VI) solubility, based on the equilibria given in Eqs. (21-25)**

- 
- (a)  $K_{sp} = [\text{PuO}_2]^{2+}[\text{OH}^-]^2$
- (b)  $[\text{PuO}_2(\text{CO}_3)] = 3.98 \times 10^8 [\text{PuO}_2^{2+}][\text{CO}_3^{=}]$
- (c)  $[\text{PuO}_2(\text{CO}_3)_2]^{2-} = 3.98 \times 10^{13} [\text{PuO}_2^{2+}][\text{CO}_3^{=}]^2$
- (d)  $[\text{PuO}_2(\text{CO}_3)_3]^{4-} = 1.585 \times 10^{18} [\text{PuO}_2^{2+}][\text{CO}_3^{=}]^3$
- (e)  $[(\text{PuO}_2)_3(\text{CO}_3)_6]^{6-} = 3.98 \times 10^{-8} [\text{PuO}_2(\text{CO}_3)_3]^{4-}^3 / [\text{CO}_3^{=}]^3$
- (f)  $\text{TC} = [\text{CO}_2'(\text{aq})] + [\text{HCO}_3^-] + [\text{CO}_3^{=}] + [\text{PuO}_2(\text{CO}_3)]$   
 $+ 2[\text{PuO}_2(\text{CO}_3)_2]^{2-} + 3[\text{PuO}_2(\text{CO}_3)_3]^{4-}$   
 $+ 6[(\text{PuO}_2)_3(\text{CO}_3)_6]^{6-}$
-

### 3.6 COMBINED SOLUBILITY OF Th(IV) AND Pu(IV)

As shown in Sects. 3.1 and 3.3, the Th(IV) hydroxide is generally more soluble than the Pu(IV) hydroxide. However, the carbonate complexes of Pu(IV) are generally more stable than the thorium ones. As a result, the solubilities of Th(IV) and Pu(IV) in a carbonate solution are comparable.

Again, the calculated solubilities will largely depend on the  $K_{sp}$  values selected. For example, Figs. 10 and 11 depict the calculated solubilities for Pu(IV) and Th(IV) for two combinations of  $K_{sp}$  values in the presence of 1.0 M TC. The calculated Th-to-Pu ratio in solution will depend on the  $K_{sp}$  values used, the TC, and the pH; however, the Th-to-Pu denaturing ratio in the solid phase will be unchanged. Figure 12 gives the Th-to-Pu ratio for the corresponding systems shown in Figs. 10 and 11.

### 3.7 COMBINED SOLUBILITY OF Th(IV) AND Pu(VI)

Just as in the previous case of Th(IV) and Pu(IV), we can compare the relative solubilities of Th(IV) and Pu(VI) when they occur simultaneously in solution. By comparing the results described in Sects. 3.1 and 3.4, Th(IV) is seen to be less soluble ( $\log K_{sp} = -39$  to  $-49.4$ ) than Pu(VI) hydroxide ( $\log K_{sp} = -22.7$  to  $-24.5$ ). However, the Th(IV) carbonate complexes are generally more stable than the corresponding carbonate complexes of Pu(VI), as shown in Tables 1 and 4. As a result, the solubilities of Pu(VI) and Th(IV) are comparable and any estimate of the Pu(VI)-to-Th(IV) ratio in solution will depend on the set of values chosen. To illustrate the range over which this ratio can vary, Figs. 13 and 14 give the results of the combined calculated solubilities for Th(IV) and Pu(VI) in a 1.0 M TC solution for two different sets of  $K_{sp}$  values.

As shown in Sect. 3.1, Eq. (d) of Table 1 was used in conjunction with  $\log K_{sp} = -42$  for  $\text{Th}(\text{OH})_4$ , while Eq. (e) was used with  $\log K_{sp} = -49.4$  for the  $\text{ThO}_2$  equilibria ( $K_{sp}$  independent). The calculated Pu(VI)-to-Th(IV) ratios shown in Fig. 15, therefore, depend on the particular  $K_{sp}$  values, the TC, and the pH of the solution. They do not, however, depend on the Th-to-Pu denaturing ratio in the sludge.

### 3.8 EFFECT OF TEMPERATURE ON THE CARBONATE COMPLEXATION AND ULTIMATE SOLUBILITIES

It is possible that a temperature gradient due to local, daily, or seasonal ambient temperature differences

could provide a means for the transportation and separation of radionuclides (in this particular study, actinides) by repeated cycles of dissolution, complexation—enhanced by carbonate—and reprecipitation.

The characteristics of the precipitated hydroxide materials, particularly the degree of crystallinity, will significantly change the expected solubility. For this reason, one of the most important temperature effects will be in altering the nature of the precipitates and their solubility. The concentration and distribution of the different carbonate and hydroxide complexes will also be affected by the temperature since all the solution equilibria are a function of the temperature. The accurate prediction of all the actinide transport phenomena caused by temperature gradients occurring in the storage tanks would require a significant research effort beyond the scope of this present work.<sup>21</sup>

However, assuming a given precipitate,  $K_{sp}$  value, and stability constants for the complexes in solution, it is possible to estimate the temperature effects by solving the multiple equilibrium expressions using the appropriate set of constants for the different temperatures. These calculations are not intended to predict the exact behavior in the tanks but, instead, to demonstrate the expected magnitude of the temperature effects. The data available in the literature for estimating temperature effects are scarce. However, a relatively good set of thermodynamic properties is available for U(VI) species from which such temperature effects can be estimated.

The following section describes a calculation similar to the one shown in Sect. 4 for a temperature ( $T$ ) = 25°C but conducted at  $T = 0$  and 40°C. Because most of the equilibrium constants ( $K$ ) are measured at 25°C, the integrated van't Hoff equation is used to calculate the values at different temperatures, where  $\Delta H$  is the enthalpy change for the particular reaction (dissolution, hydrolysis, complexation),  $R$  is the molar gas constant, and  $T$  is the Kelvin temperature.

$$\ln \frac{K_2}{K_1} = -\frac{\Delta H}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \quad (26)$$

Table 5 gives the set of equilibrium values at 25°C and the calculated sets for 0 and 40°C. The ionization constants for water ( $K_w$ ) at different temperatures were taken directly from ref. 22, while the temperature dependence of the  $\text{CO}_2\text{-H}_2\text{O}$  equilibria was calculated using the following equations:<sup>29</sup>

$$\log K_1 = -356.3094 - 0.06091964 \times T + \frac{21834.37}{T} + 126.8339 \times \log T - \frac{1684915}{T^2} \quad (27)$$

$$\log K_2 = -107.8871 - 0.03252849 \times T + \frac{5151.79}{T} + 38.92561 \times \log T - \frac{563713.9}{T^2} \quad (28)$$

Table 5. Calculated temperature effects on uranyl hydroxy and carbonato equilibria

Reaction	log K			$\Delta H$ (KJ/mol)	Ref.
	0°C	25°C	40°C		
$H_2O \rightleftharpoons H^+ + OH^-$	-14.9435	-13.9965	-13.5348		22
$UO_2(OH)_2(s) \rightleftharpoons UO_2^{2+} + 2 OH^-$	-24.86	-23.74	-23.15	70	23-25
$UO_2^{2+} + CO_3^{2-} \rightleftharpoons UO_2CO_3$	8.82	8.89	8.93	4.6	18, 26-28
$UO_2^{2+} + 2CO_3^{2-} \rightleftharpoons [UO_2(CO_3)_2]^{2-}$	16.6	16.2	16.0	-23	18, 26-28
$UO_2^{2+} + 3 CO_3^{2-} \rightleftharpoons [UO_2(CO_3)_3]^{4-}$	23.25	22.61	22.27	-40	18, 26-28
$3UO_2^{2+} + 6CO_3^{2-} \rightleftharpoons [(UO_2)_3(CO_3)_6]^{6-}$	57.24	56.23	55.70	-63	18, 26-28
$UO_2^{2+} + 3H_2O \rightleftharpoons [UO_2(OH)_3]^- + 3H^+$	-19.5	-19.2	-19.0	18	18
$HCO_3^- \rightleftharpoons CO_3^{2-} + H^+$	-10.22	-10.33	-10.63		29
$CO_2'(aq) \rightleftharpoons HCO_3^- + H^+$	-6.30	-6.35	-6.57		29

Figure 16 shows the calculated solubility of U(VI) for all the species considered in Sect. 4 at three different temperatures (0, 25, and 40°C) using the equilibria constants from Table 5 as a function of pOH.<sup>‡</sup> Figure 17 shows the calculated increased solubility of U(VI) at 0°C with respect to the solubility

<sup>‡</sup>Normally, the pH  $\approx$  14 - pOH for  $T \neq 25^\circ C$  would be given here, but to be exact, we use pOH.

at 40°C as a function of pOH. The main factors are the decreased stability of the carbonate complexes and relatively lower free carbonate versus an increased solubility of the hydroxide at higher temperatures. As shown in Fig. 17, the calculated solubility is slightly higher at lower temperatures. The real expected behavior can be significantly more complicated and beyond the scope of this report.

These calculations serve to demonstrate the magnitude of the temperature effect that can lead to the separation and transport of the actinides. Similar calculations could be performed for Th(IV), Pu(IV)/Pu(VI), and for the simultaneous equilibria involving all species if sufficient thermodynamic data were available. We can expect that the magnitude of the temperature effects on these species will be similar and, therefore, transport due to temperature gradients to be a very probable actinide separation route.

#### 4. EDTA COMPLEXATION

The presence of significant quantities of some strong complexant agent in the storage tanks could also selectively solubilize and separate the actinides present in the sludge in a manner similar to that described for carbonate ion complexation. As an example, the effect of having the EDTA, ethylenediaminetetraacetic acid, was considered. The uncomplexed EDTA species distribution was calculated using the following set of equilibria:



The equations used were as follows:

$$\alpha = [H^+]^6 + K[H^+]^5 + KK'[H^+]^4 + KK'K_1[H^+]^3 + KK'K_1K_2[H^+]^2 + KK'K_1K_2K_3[H^+] + KK'K_1K_2K_3K_4 \quad (35)$$

where  $\alpha$  is the fraction of EDTA that is undissociated, that is,  $H_4EDTA$ . If  $FEDTA$  is the concentration of EDTA not complexed with the metal ions, the concentrations of the uncomplexed EDTA species are given by

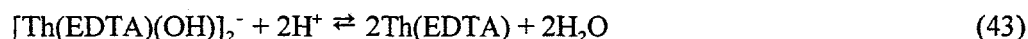
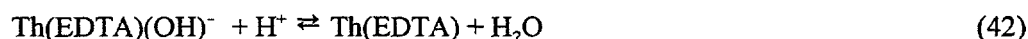
$$[EDTA]^{4-} = \frac{KK'K_1K_2K_3K_4}{\alpha} \cdot FEDTA \quad (36)$$

$$[H(EDTA)]^{3-} = \frac{KK'K_1K_2K_3[H^+]}{\alpha} \cdot FEDTA \quad (37)$$

$$[H_2(EDTA)]^{2-} = \frac{KK'K_1K_2[H^+]^2}{\alpha} \cdot FEDTA \quad (38)$$

#### 4.1 INCREASED SOLUBILITY OF Th(IV) BY EDTA COMPLEXATION

Only the alkaline pH range is of interest in this report; nevertheless, an extended range from pH = 4 was considered for these calculations. Again, the calculated solubilities and speciation depend greatly on the solubility product used for the Th(IV) hydroxide. The equilibria considered were as follows, with the respective concentration expressions used in the calculations given in Table 6:





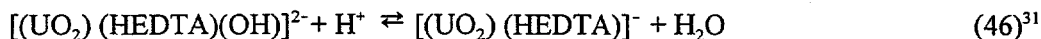
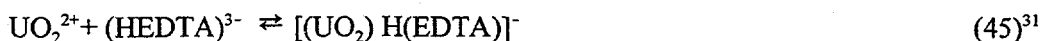
**Table 6. Expressions for the molar concentrations, [ ], of various species used in the determination of Th(IV) solubility due to complexation with EDTA, based on the equilibrium equations given in the text**

- 
- (a)  $K_{sp} = [\text{Th}^{4+}][\text{OH}^-]$
- (b)<sup>30</sup>  $[\text{Th}(\text{EDTA})] = 1.585 \times 10^{23} [\text{Th}^{4+}] [\text{EDTA}^{4-}]$
- (c)  $[\text{Th}(\text{EDTA})\text{H}]^+ = 95.5[\text{Th}(\text{EDTA})] [\text{H}^+]$
- (d)  $[\text{Th}(\text{EDTA})(\text{OH})^-] = [\text{Th}(\text{EDTA})]/\{1.096 \times 10^7 [\text{H}^+]\}$
- (e)  $[\{\text{Th}(\text{EDTA})(\text{OH})\}_2^{2-}] = [\text{Th}(\text{EDTA})]^2/\{6.61 \times 10^9 [\text{H}^+]^2\}$
-

Two  $K_{sp}$  values selected for these calculations were  $10^{-42}$  and  $4.0 \times 10^{-50}$  to demonstrate the quantitative variance in the concentration due to the range of reported values. The calculations were made using both  $\log K_{sp} [\text{Th(IV)}] = -42$  and  $-49.4$ . As shown in Fig. 18, a lower  $K_{sp}$  value moves the EDTA-Th(IV) solubility zone toward lower pH values. According to these results, EDTA could not dissolve an aged thorium hydroxide under alkaline conditions. Figure 19 displays the main Th(IV) species distribution as a function of pH in equilibrium with a solution having a 1.0 M total EDTA concentration. All relevant equilibrium species are shown in Appendix A-2, Table A-2.1, for the lower  $K_{sp}$  value.

#### 4.2 INCREASED SOLUBILITY OF U(VI) BY EDTA COMPLEXATION

As in the cases before, the calculated solubilities and species distributions are very dependent on the solubility product used for the U(VI) hydroxide. The equilibria considered were as follows with the respective concentration expressions used in the calculations given in Table 7:



Two  $K_{sp}$  values selected for these calculations were  $10^{-22}$  and  $10^{-23.74}$ . According to these calculations as shown in Fig. 20, EDTA could significantly increase the solubility of uranyl hydroxide through complexation under alkaline conditions. The U(VI)-EDTA complexes are significantly less stable than the EDTA complexes of Th(IV) and Pu(IV).<sup>32</sup> However, the solubility product of the uranyl hydroxide is relatively high when compared with the Th(IV) and Pu(IV) hydroxides (or hydrated oxides). As a result, the calculated U(VI) solubilities due to EDTA complexation are significant, even in the alkaline range. Figure 21 displays the U(VI) main species distribution as a function of pH in equilibrium with a solution having a 1.0 M total EDTA concentration.

**Table 7. Expressions for the molar concentrations, [ ], of various species used in the determination of U(VI) solubility due to complexation with EDTA, based on the equilibrium equations given in the text**

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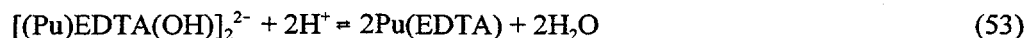
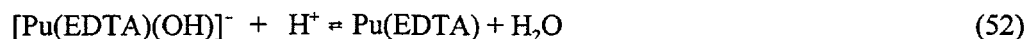
(a)	$K_{sp} [U(VI)] = [UO_2^{2+}] [OH^-]^2$
(b)	$[(UO_2)H(EDTA)]^- = 2.24 \times 10^7 [UO_2^{2+}] \cdot [H(EDTA)^{3-}]$
(c)	$[(UO_2)H(EDTA)(OH)^-] = [(UO_2)H(EDTA)^-]/(4.17 \times 10^5 [H^+]^2)$
(d)	$[(UO_2)EDTA(OH)^{3-}] = [(UO_2)H(EDTA)^-]/(8.32 \times 10^{11} [H^+]^2)$
(e)	$[(UO_2)_2EDTA] = 5.89 \times 10^{17} [EDTA^{4-}] [UO_2^{2+}]^2$
(f)	$[\{(UO_2)H(EDTA)(OH)\}_2^{2-}] =$ $1.862 \times 10^3 [\{(UO_2)H(EDTA)(OH)\}^-]^2$

---

#### 4.3 INCREASED SOLUBILITY OF Pu(IV) BY EDTA COMPLEXATION

The equilibria data for the Pu(IV)-EDTA system is scarce. The reported values for log K of the 1:1 complex range from 24.2 to 26.1.<sup>33-39</sup> A qualitative description of the hydrolysis and polymerization of the 1:1 complex has been reported<sup>39</sup>; however, there are no reported values for the respective equilibria.

The stability constant for the U(IV)-EDTA 1:1 complex,<sup>30</sup> log K = 25.8, is about the same as the reported value for the Pu(IV)-EDTA 1:1 complex. Additionally, the U(IV) and Pu(IV) ions are quite similar, and all the hydrolysis and polymerization equilibria for the EDTA complexes should also be quite similar. Accordingly, the U(IV) set of reported equilibrium values<sup>30</sup> was used in this report to estimate the Pu(IV) speciation for a system containing a 1.0 M total EDTA concentration. The equilibria considered were as follows, with the respective concentration expressions used in the calculations given in Table 8:



Two  $K_{\text{sp}}$  values selected for these calculations were  $10^{-56}$  and  $4.0 \times 10^{-63}$  to demonstrate the quantitative variance in concentration due to the range of reported values. As shown in Fig. 22, a lower  $K_{\text{sp}}$  value moves the Pu(IV)-EDTA solubility zone toward lower pH values. According to these calculations, EDTA could not dissolve plutonium hydroxide under alkaline conditions. Figure 23 illustrates the Pu(IV) species distribution as a function of pH in equilibrium with a solution having a 1.0 M total EDTA concentration. All relevant equilibrium species are shown in Table A-10 in the appendix for the lower  $K_{\text{sp}}$  value.

#### 4.4 COMBINED SOLUBILITY OF Th(IV), Pu(IV), AND U(VI) BY EDTA COMPLEXATION

As mentioned in Sect. 4.2, the EDTA complexes with U(VI) are significantly less stable than the ones formed with Th(IV) and Pu(IV). However, the solubility of uranyl hydroxide is relatively high when

**Table 8. Expressions for the molar concentrations, [ ], of various species used in the determination of Pu(IV) solubility due to complexation with EDTA, based on the equilibrium equations given in the text**

- 
- (a)  $K_{sp}(\text{Pu(IV)}) = [\text{Pu}^{4+}][\text{OH}^-]^4$
- (b)  $[\text{Pu(EDTA)}] = 1.259 \times 10^{26} [\text{Pu}^{4+}][(\text{EDTA})^{4-}]$
- (c)  $[\text{Pu(EDTA)(OH)}^-] = [\text{Pu(EDTA)}]/(5.25 \times 10^4 [\text{H}^+])$
- (d)  $[\{\text{Pu(EDTA)(OH)}\}_2^{2-}] = [\text{Pu(EDTA)}]^2/(3.39 \times 10^6 [\text{H}^+]^2)$
-

compared with Th(IV) and Pu(IV) hydroxides. The Pu(IV) complexes with EDTA are slightly more stable than the Th(IV) equivalents, but the Pu(IV) hydroxide is significantly less soluble than the Th(IV) hydroxide. As in the previous calculations, the calculated combined solubilities will depend greatly on the values chosen for the solubility products.

Figures 24-26 show the results for three sets of  $K_{sp}$  values that represent a wide range of conditions. As can be seen, U(VI) is preferentially solubilized by complexation with EDTA in the alkaline range, while Th(IV) complexation is prevalent at lower pHs. The calculated solubilities for Pu(IV) complexed with EDTA are always insignificant (Fig. 22) and are not shown in these combined figures. We can conclude from these results that the three actinides, having widely different solubilities of their respective EDTA complexes, could autoseparate in a manner similar to that which takes place during carbonate complexation.

## 5. CONCLUSIONS

The concern that there might be some physical-chemical process which would lead to a separation of the poisoning actinides ( $^{232}\text{Th}$ ,  $^{238}\text{U}$ ) from the fissionable ones ( $^{239}\text{Pu}$ ,  $^{235}\text{U}$ ) has led to a study of potential separation processes involving these elements. We find that there is no problem whatsoever with the waste tank chemistry as the storage tanks are presently maintained. However, recognizing that it is through chemical processing that such separations are achieved, it is reasonable to assume that some chemistry could occur which would lead to separations of these actinides.

We have evaluated various chemistries and have identified the carbonate complexation reaction as the most plausible means of achieving the separation of these actinides. The particular chemistry is dependent on the equilibration of atmospheric carbon dioxide,  $\text{CO}_2$ , with the aqueous solution which is maintained at a pH of 8-12 to form carbonate ions,  $\text{CO}_3^{2-}$ , in solution. Under normal conditions without  $\text{CO}_2$ , the actinides exist in the sludge as hydroxy or oxide precipitates which have undergone a significant amount of aging, resulting in further stabilization of the solids.

Carbonate ions (formed by the dissolution and hydrolysis of atmospheric  $\text{CO}_2$ ) can selectively dissolve the solid actinides through the formation of soluble carbonate complexes. Uranyl(VI) is most readily dissolved, followed by Th(IV) and finally Pu(IV). These soluble carbonate species are greatly dependent on the pH, temperature, and other ions and, therefore, changes in any one or more of these parameters

over a period of time, especially cyclic changes, could cause a selective dissolution and redeposition of the more soluble species away from the less soluble ones. Detailed calculations using the stability constants for the carbonates have shown that the most likely pH range for this process to occur is pH = 10-11. While temperature gradients in the waste tanks are the most probable source of such cyclic changes, temperature data for these species are not readily available. Regardless, the temperature effects on uranyl(VI) solubility shown here demonstrate that the solubility of these cations has a significant temperature dependence which can provide the driving force in a separation process that is based on dissolution/deposition through solubility differences.

This carbonate complexation chemistry is presently not occurring in the MVSTs because the carbonate concentration in solution is extremely low due to the precipitation of insoluble calcium carbonate. Consequently, several events must occur before the carbonate complexation process becomes a problem: (1) air sparging of the solutions, with associated CO<sub>2</sub>, must continue to such a degree that the calcium content of the solution is consumed; (2) analyses of the liquid layer becomes so infrequent that the soluble carbonate increase goes undetected; (3) a long enough period of time passes that the slow, unstirred, equilibration of the aqueous carbonate liquid is able to dissolve uranyl compounds in the sludge and saturate the solution. (Correction for a high soluble carbonate situation would be a simple matter of adding calcium ions through either calcium oxide or nitrate.); and (4) there exists enough of a temperature gradient that the saturated actinide carbonate precipitates and the process cycles continuously across this gradient.

While this is the most plausible series of events which could lead to a separation of the actinides, other process were considered as well. Increased solubility through reaction with organic complexants such as EDTA was also considered; and while it presents a situation similar to carbonate complexation and similar potential for auto-separations of the actinides in the waste tanks, it would require first the uncontrolled dumping of large amounts of such a complexant into the drain tank system.....a situation of unlikely probability with the numerous administrative controls on the effluents entering the waste system.

Other processes such as extraction processes in separate (organic) phases or onto adsorbing media were considered improbable for reasons similar to those which limit the probability of organic complexants. Therefore, none of these were regarded as possible under the present operating/storage conditions of the MVSTs.

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## FIGURES



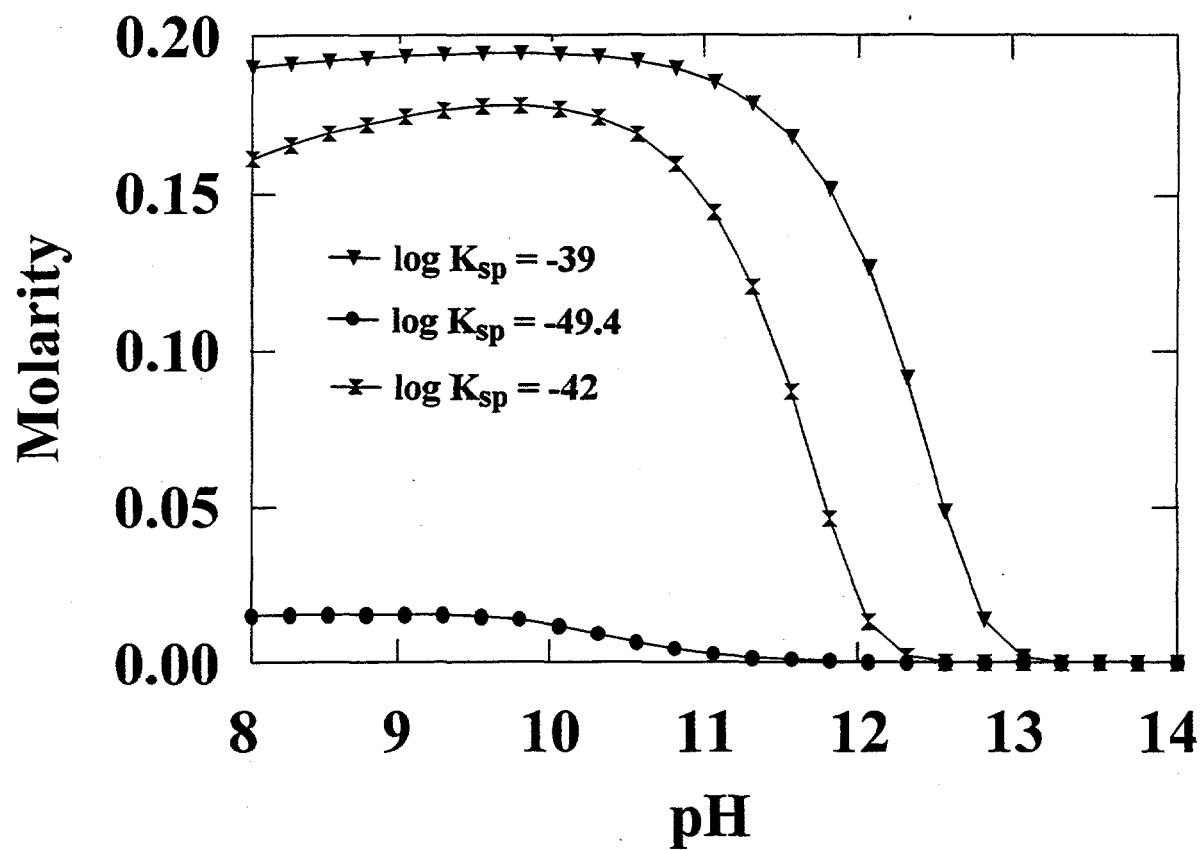


Fig. 1. Calculated solubility of Th(IV) using three different  $K_{sp}$  values in a 1.0 M TC solution as a function of pH.

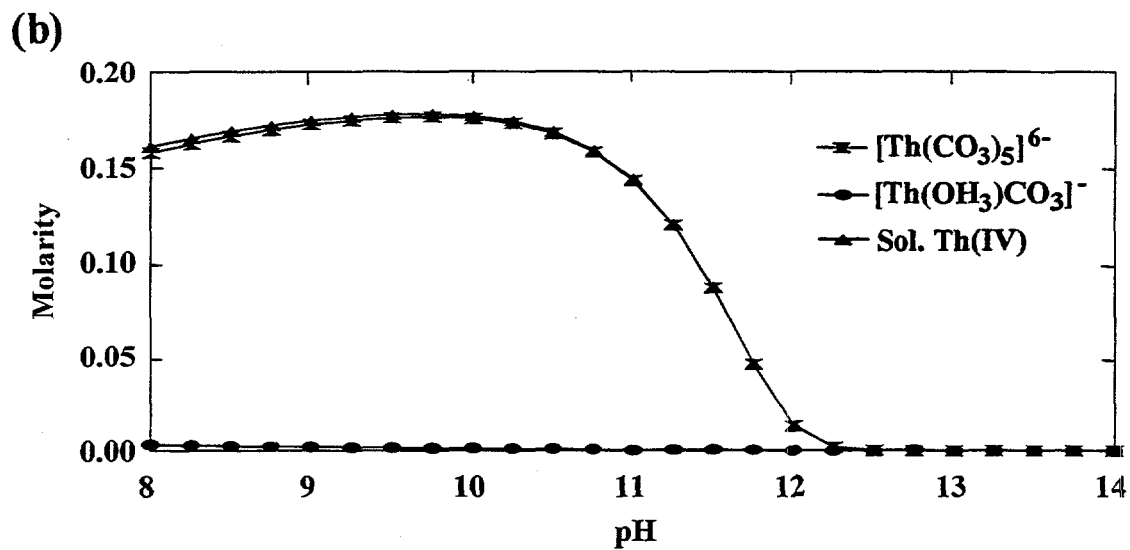
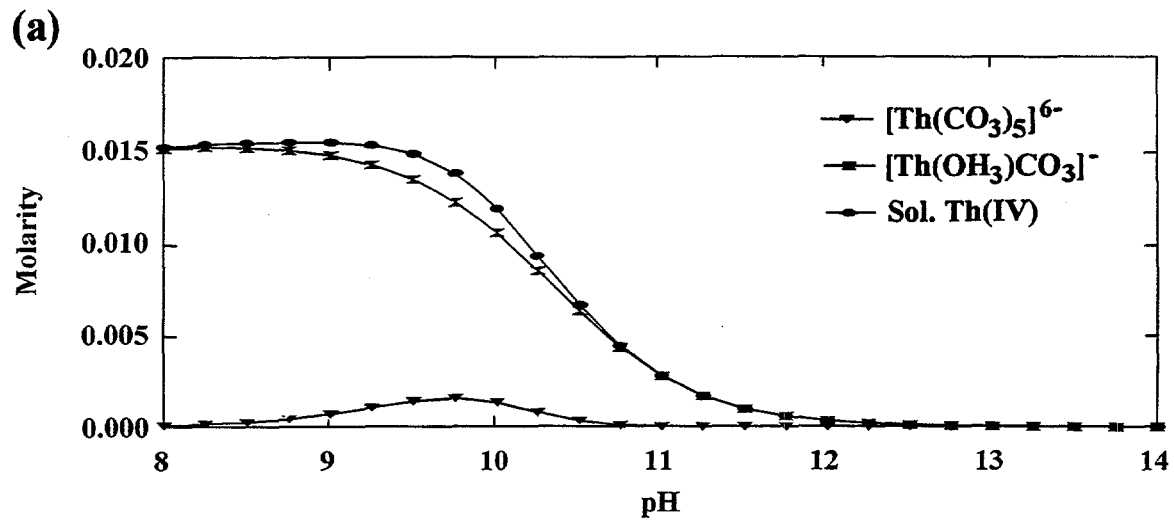


Fig. 2. Solubility of the two major species and total Th(IV) in a 1.0 M TCC solution as a function of pH using (a)  $\log K_{sp} = -49.4$  in Eq. (3a) and (b)  $K_{sp} = -42$  in Eq. (3a).

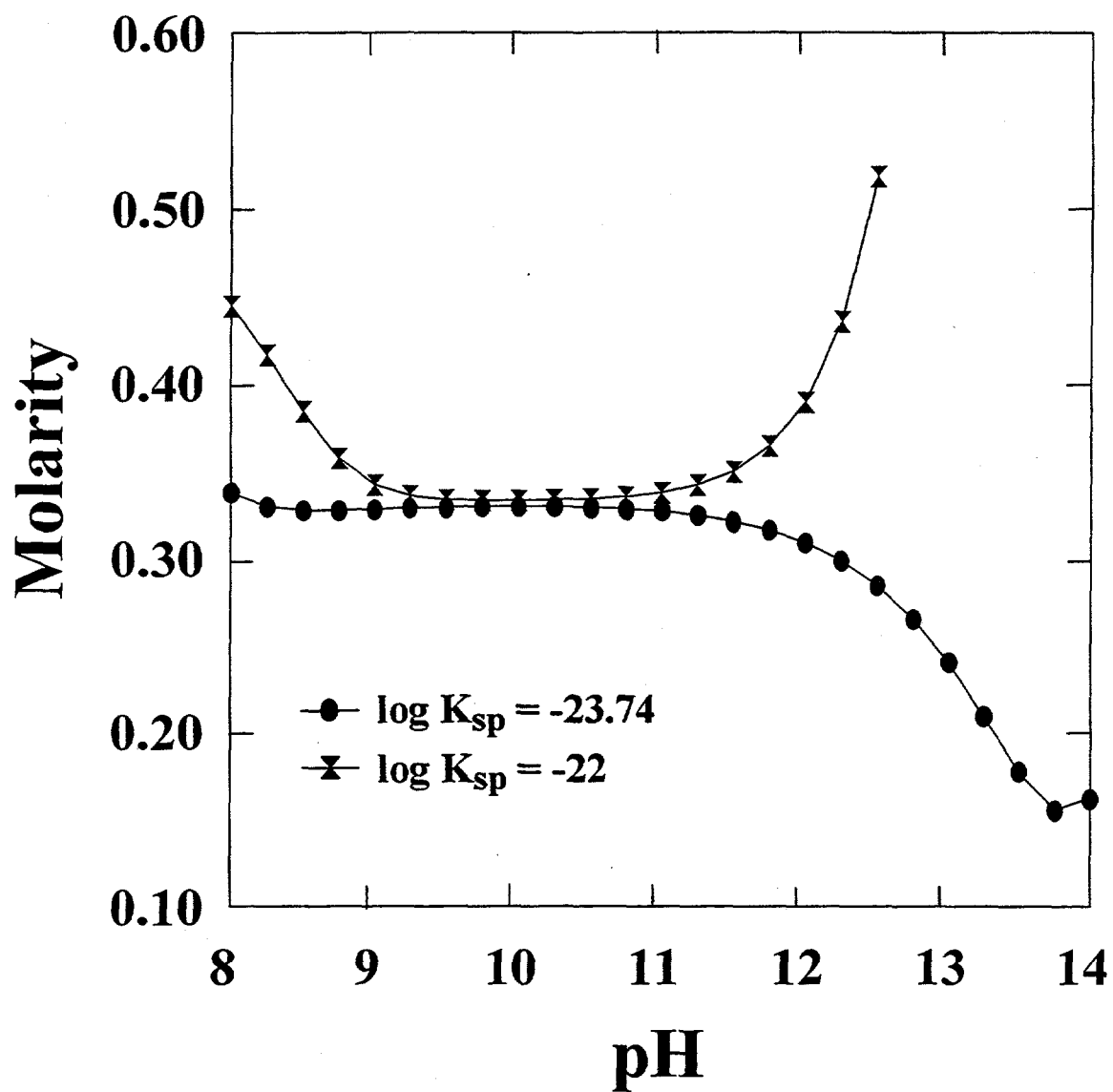


Fig. 3. Calculated solubility of U(VI) in a 1.0 M TCl<sub>4</sub> solution as a function of pH using  $\log K_{sp} = -23.74$  and  $-22$ .



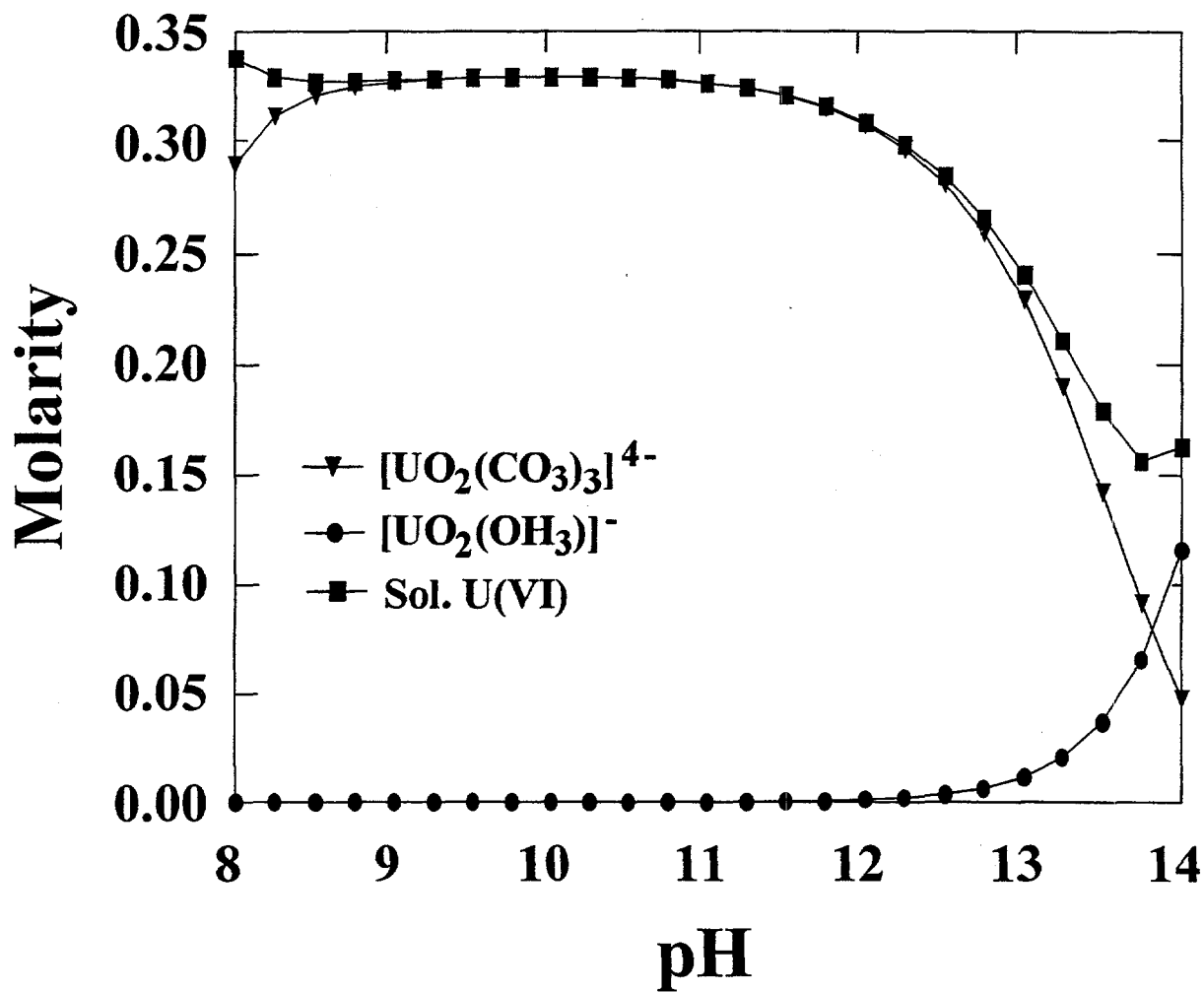


Fig. 4. Distribution of U(VI) species and total soluble U(VI) in a 1.0 M TC solution as a function of pH using  $\log K_{sp} = -23.74$ .

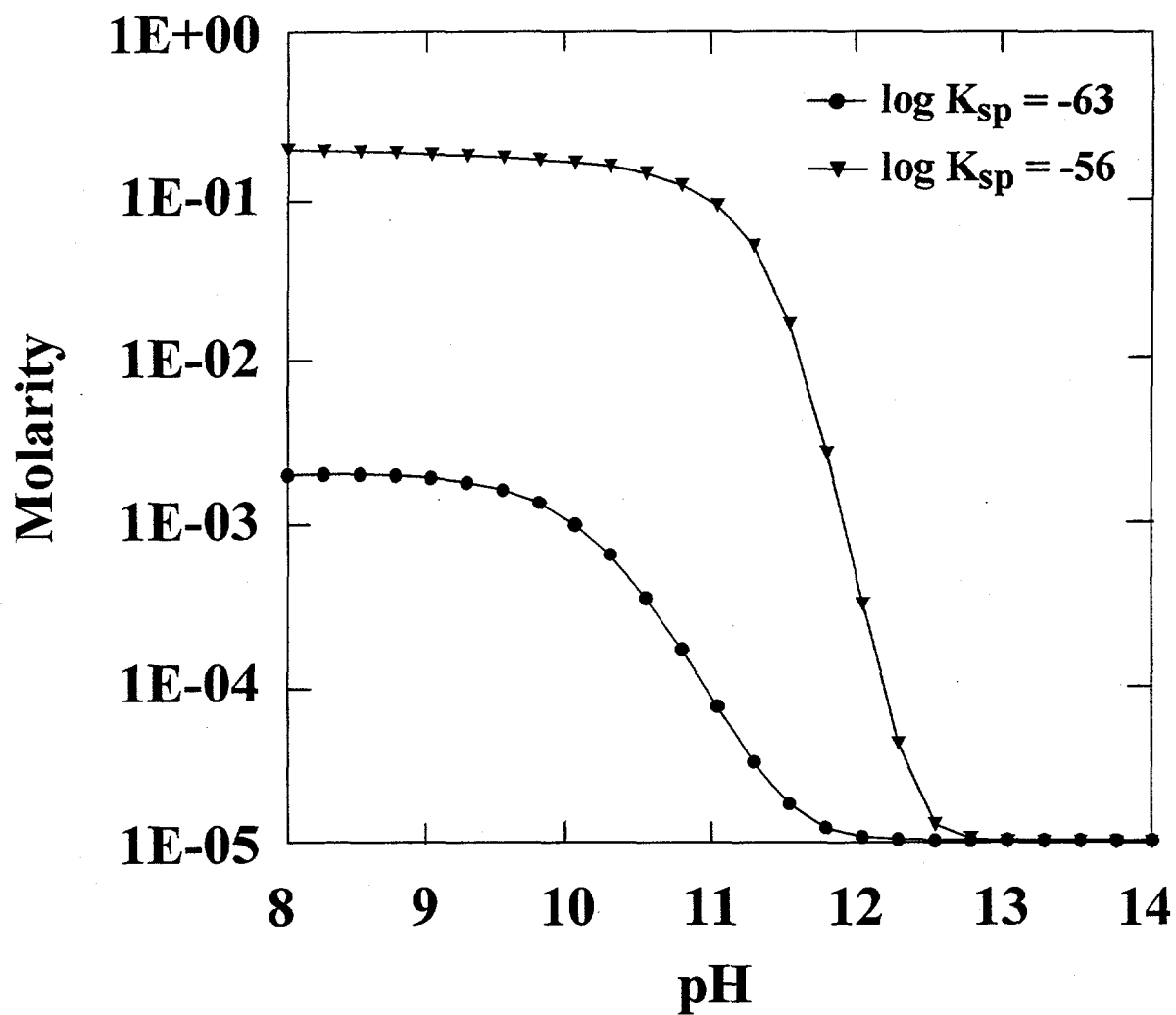


Fig. 5. Calculated solubility of Pu(IV) in a 1.0 M TC solution as a function of pH using  $\log K_{sp} = -63$  and  $-56$ .

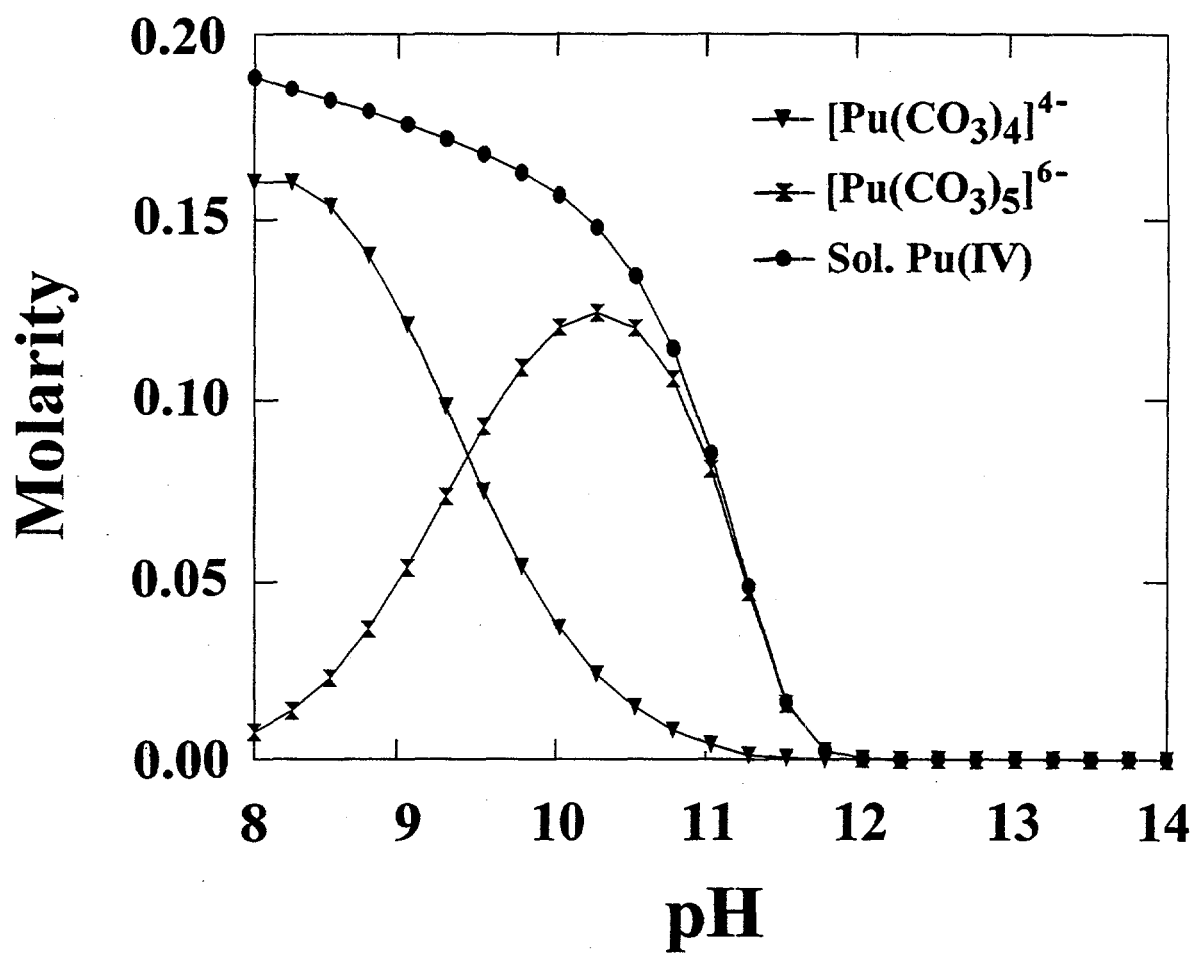


Fig. 6. Distribution of Pu(IV) species and total soluble Pu(IV) in a 1.0 M TC solution as a function of pH using  $\log K_{sp} = -56$ .

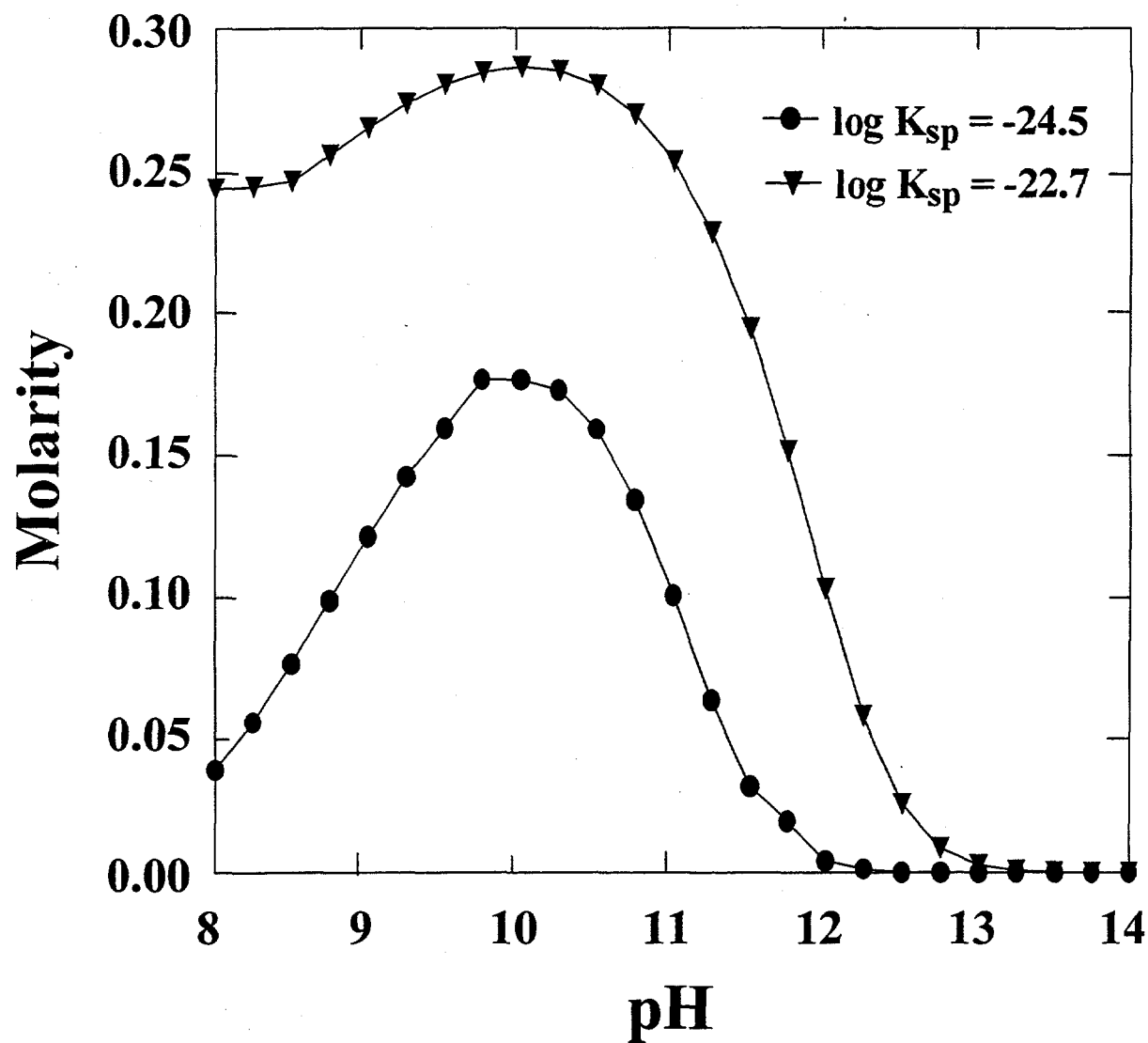


Fig. 7. Calculated solubility of Pu(VI) in a 1.0 M TC solution as a function of pH using  $\log K_{sp} = -24.5$  and  $-22.7$ .

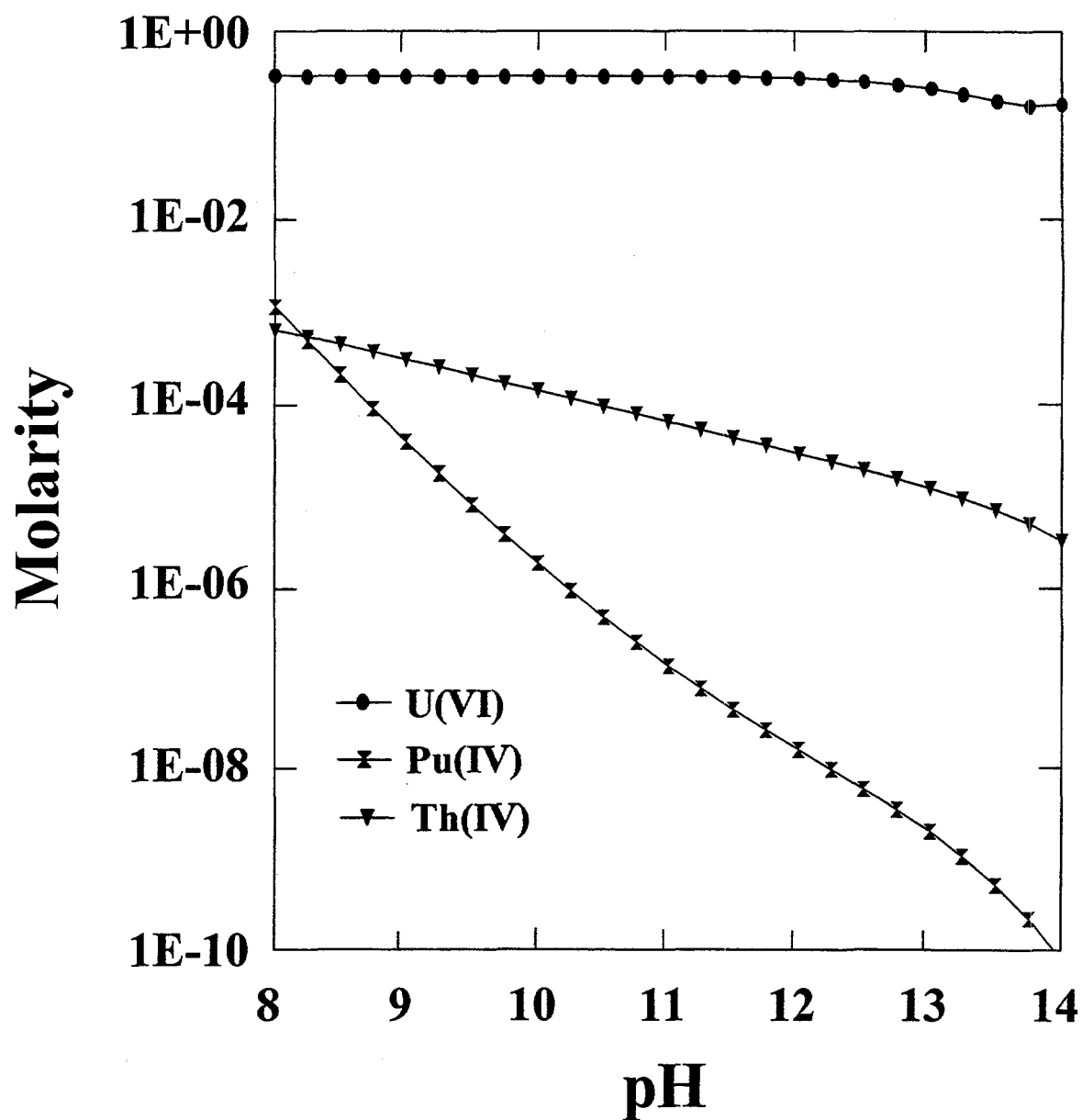


Fig. 8. Solubility of total U(VI) compared with total soluble Pu(IV) and Th(IV) in a 1.0 M TC solution as a function of pH using  $\log K_{sp} [\text{U(VI)}] = -23.74$ ,  $\log K_{sp} [\text{Pu(IV)}] = -56$ , and  $\log K_{sp} [\text{Th(IV)}] = -42$ .

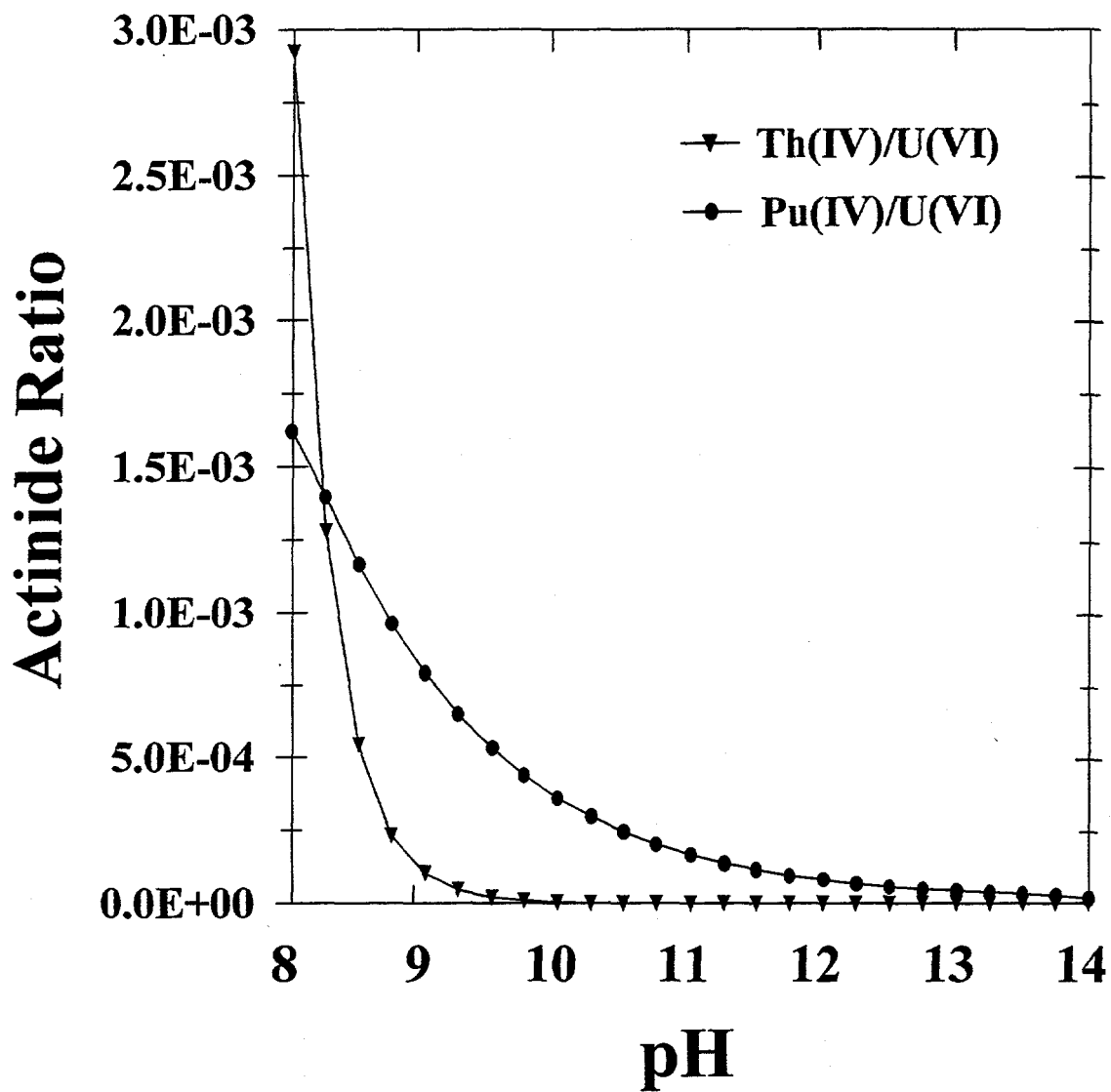


Fig. 9. Relative solubility of Th(IV) ( $\log K_{sp} = -42$ ) and Pu(IV) ( $\log K_{sp} = -56$ ) with respect to the solubility of U(VI) ( $\log K_{sp} = -23.74$ ) in a 1.0 M Tc solution as a function of pH.

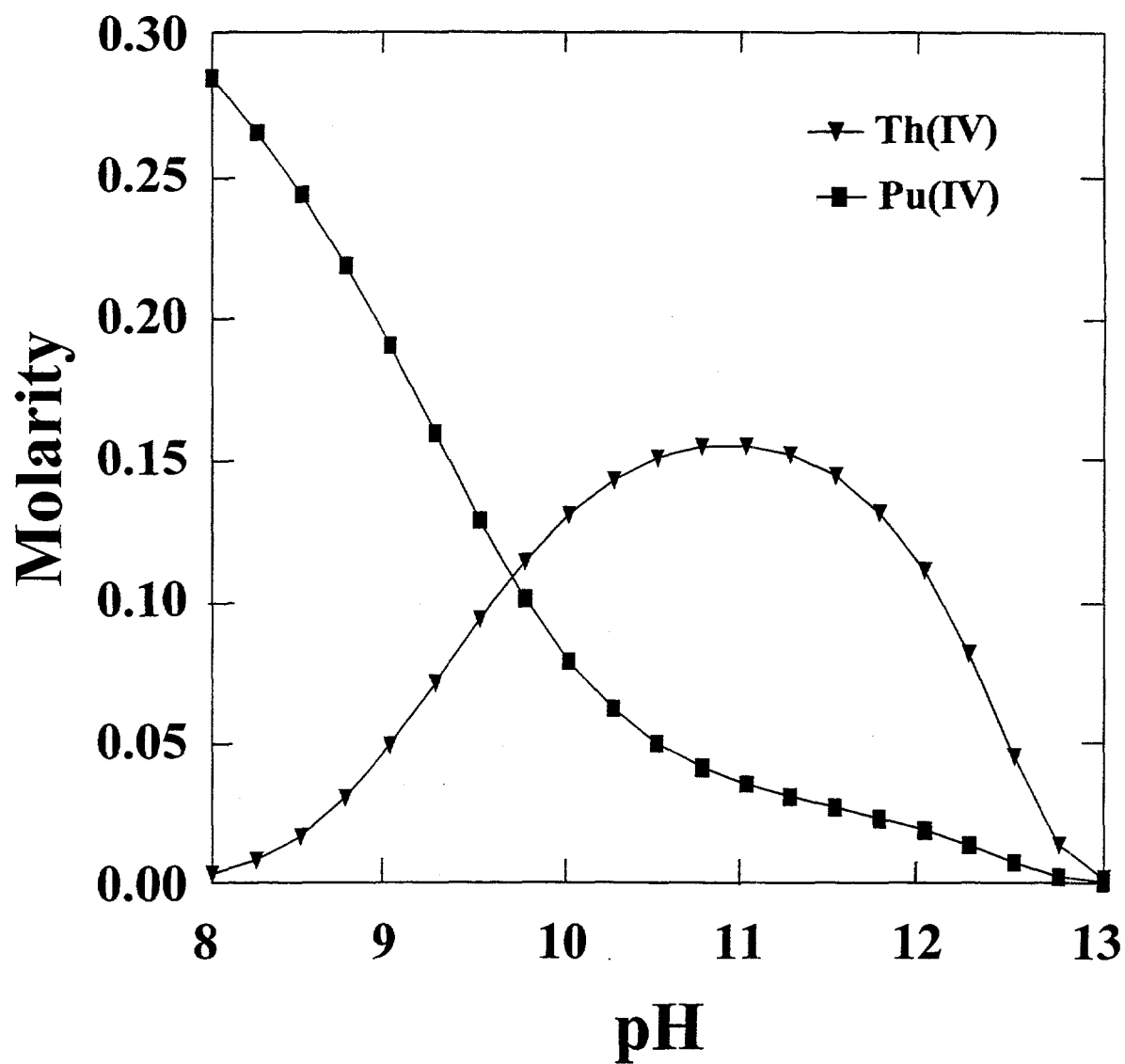


Fig. 10. Combined solubility of Pu(IV) ( $\log K_{sp} = -52$ ) and Th(IV) ( $\log K_{sp} = -39$ ) in a 1.0 *M* TC solution as a function of pH.

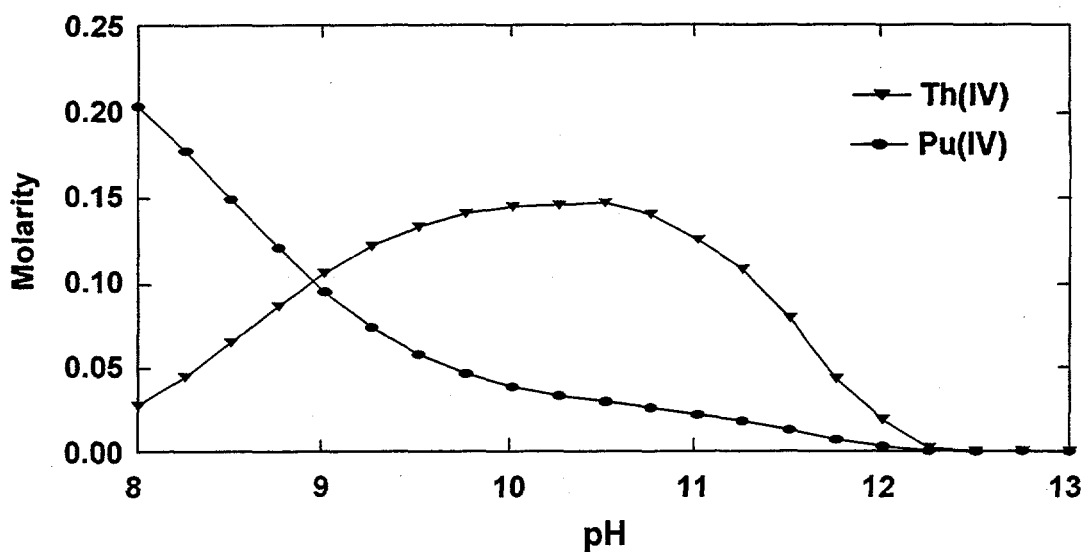


Fig. 11. Combined solubility of Pu(IV) ( $\log K_{sp} = -56$ ) and Th(IV) ( $\log K_{sp} = -42$ ) in a 1.0 M TC solution as a function of pH.

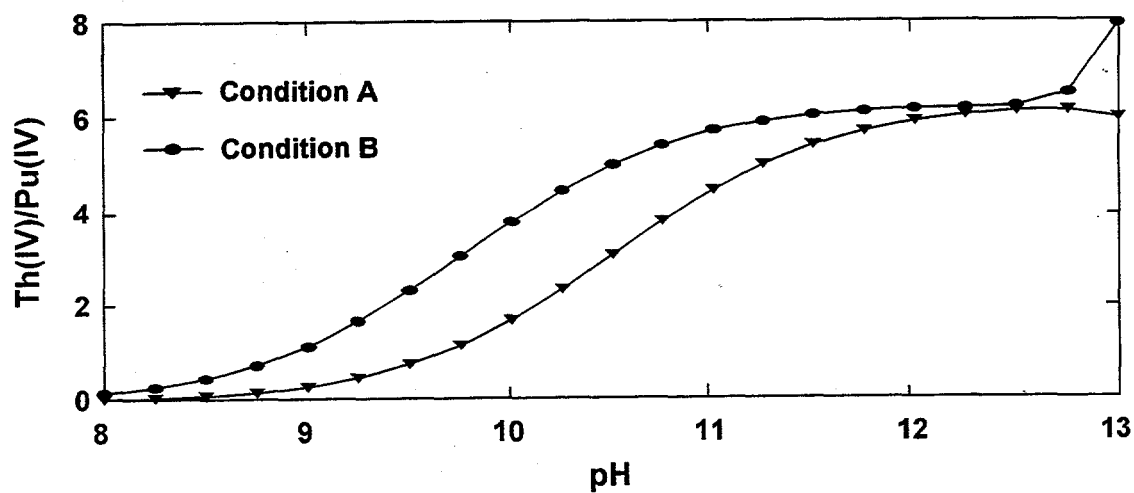


Fig. 12. Calculated Th(IV)-to-Pu(IV) ratio in a 1.0 M TC solution as a function of pH for condition A,  $\log K_{sp} [\text{Th(IV)}] = -39$  and  $\log K_{sp} [\text{Pu(IV)}] = -52$ , and condition B,  $\log K_{sp} [\text{Th(IV)}] = -42$  and  $\log K_{sp} [\text{Pu(IV)}] = -56$ .



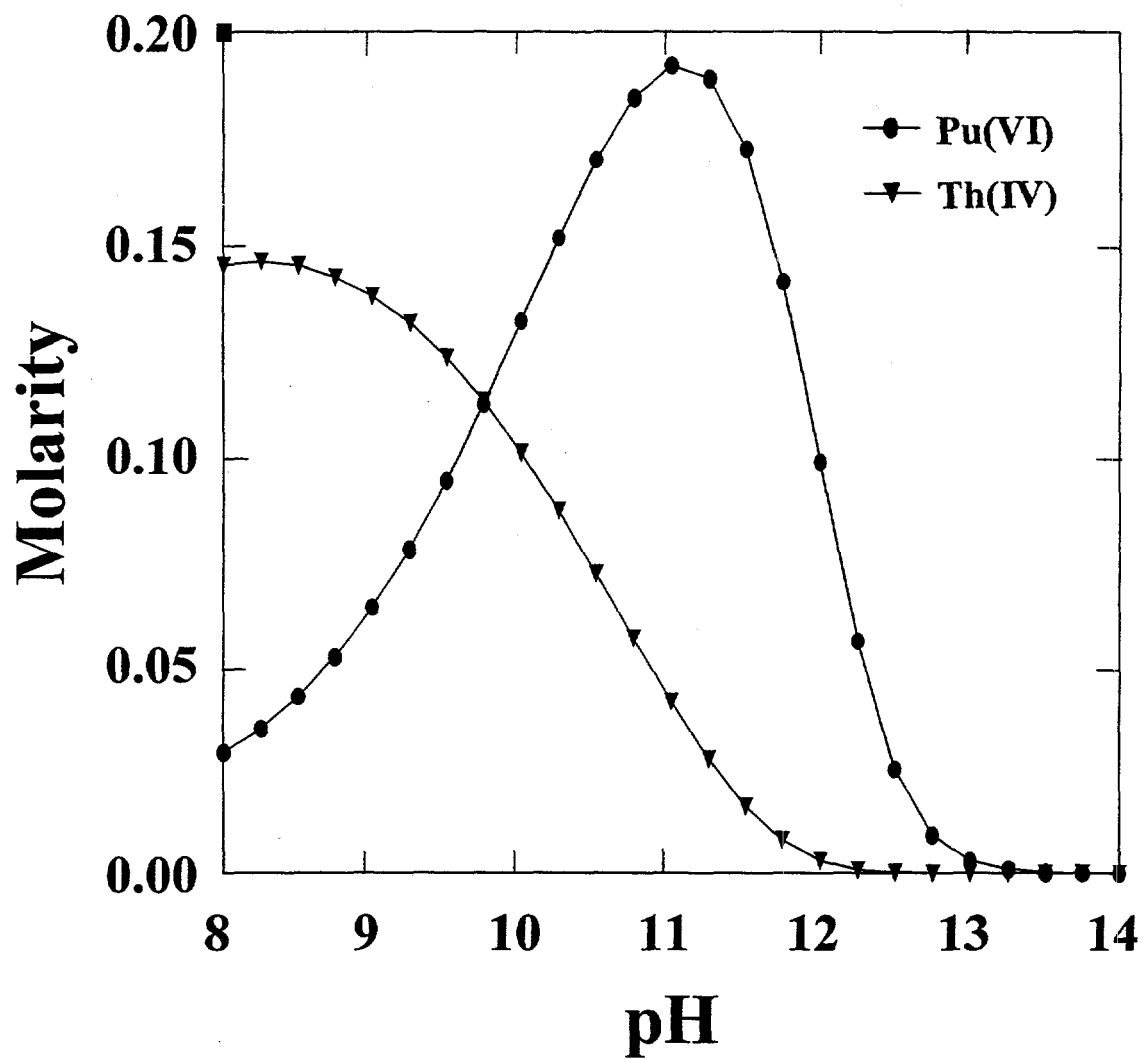


Fig. 13. Calculated combined solubility of Pu(VI) ( $\log K_{sp} = -22.7$ ) and Th(IV) ( $\log K_{sp} = -42$ ) in a 1.0 M Tc solution as a function of pH.

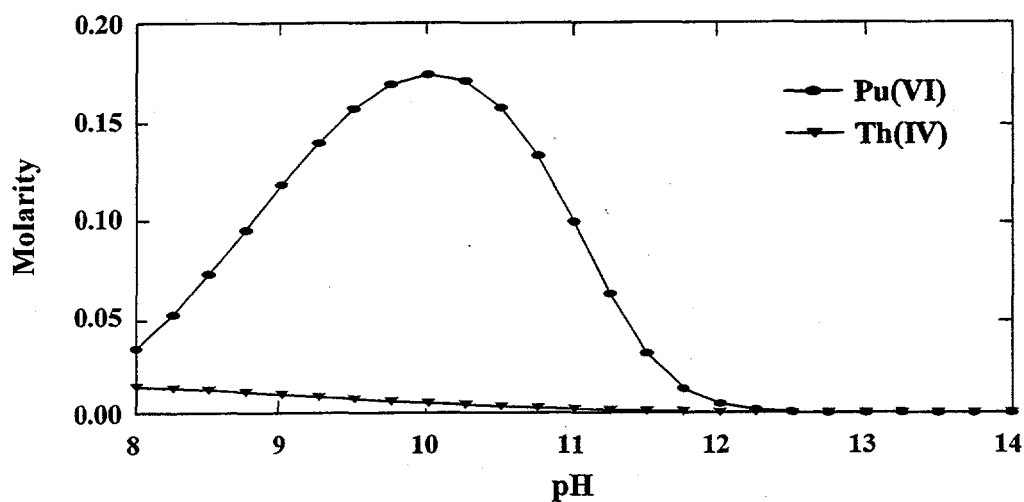


Fig. 14. Calculated combined solubility of Pu(VI) ( $\log K_{sp} = -24.5$ ) and Th(IV) ( $\log K_{sp} = -49.4$ ) in a 1.0 M TC solution as a function of pH.

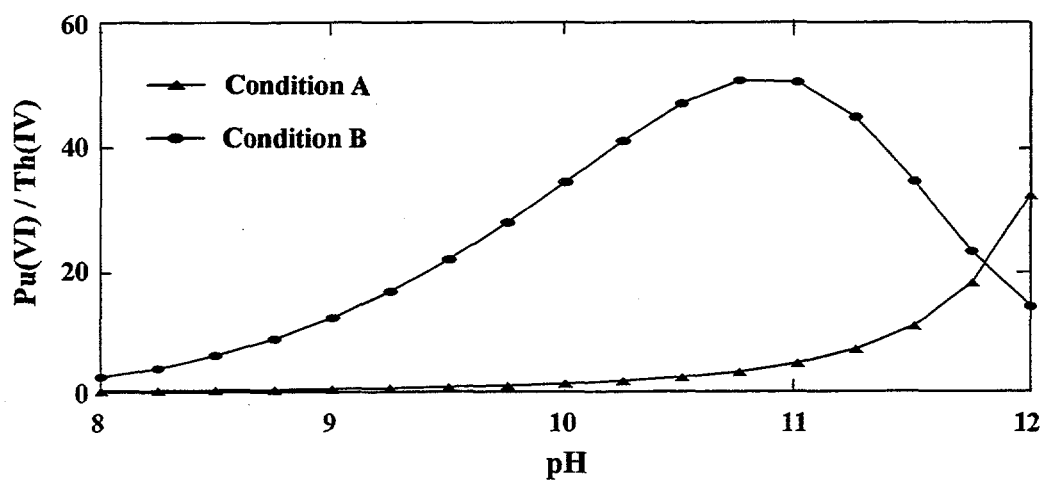


Fig. 15. Calculated Pu(VI)-to-Th(IV) ratio in a 1.0 M TC solution as a function of pH for condition A,  $\log K_{sp} [\text{Pu(VI)}] = -22.7$  and  $\log K_{sp} [\text{Th(IV)}] = -42$ , and condition B,  $\log K_{sp} [\text{Pu(VI)}] = -24.5$  and  $\log K_{sp} [\text{Th(IV)}] = -49.4$ .

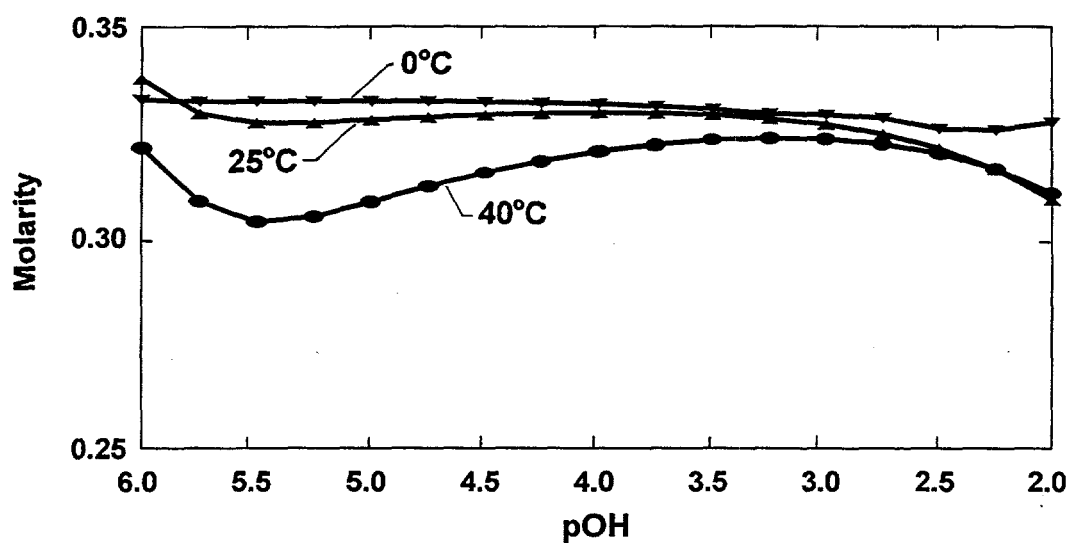


Fig. 16. Calculated U(VI) solubility in a 1 M Tc solution at 0, 25, and 40°C as a function of pOH.

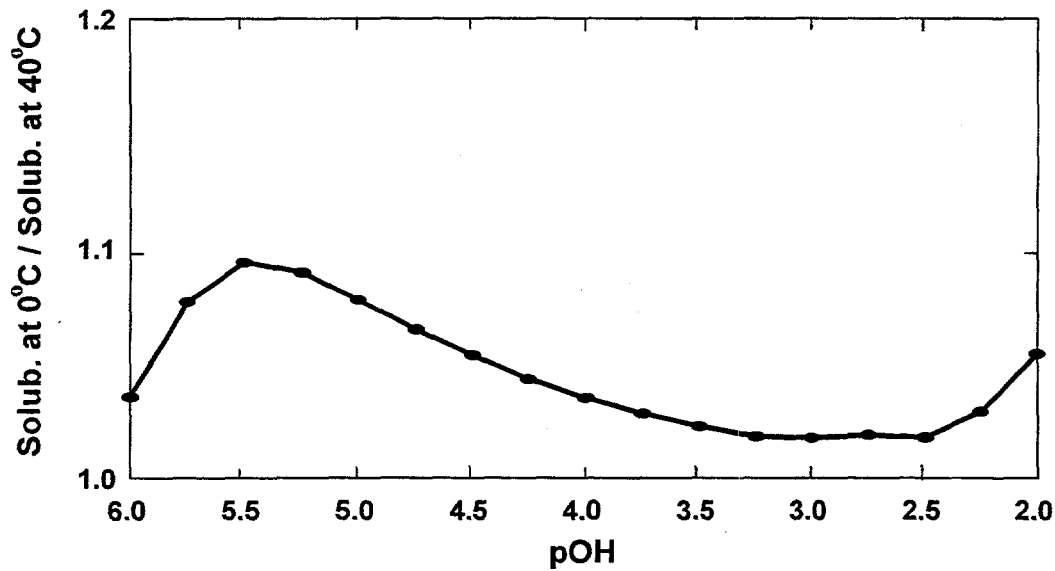


Fig. 17. Calculated solubility of U(VI) species in a 1 M Tc solution at 0°C relative to the solubility at 40°C as a function of pOH.

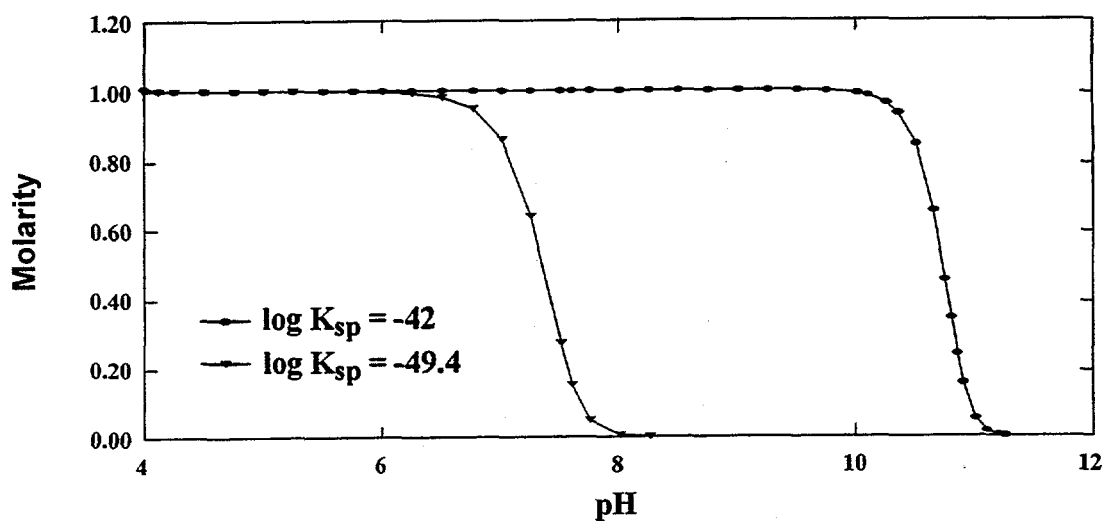


Fig. 18. Calculated solubility of Th(IV) using two different values for the  $K_{sp}$  in a 1.0 M total EDTA solution as a function of pH.

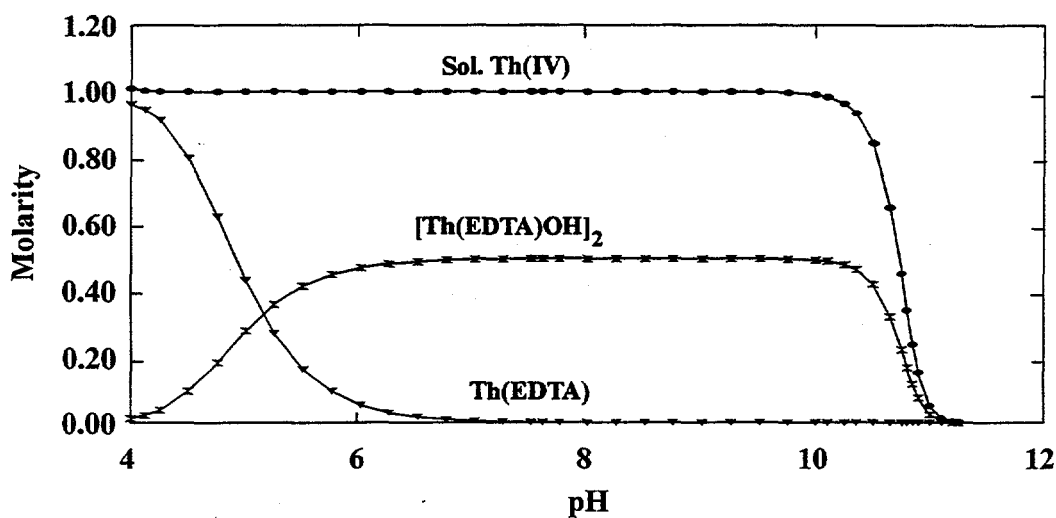


Fig. 19. Calculated main species distribution for Th(IV) in equilibrium with a 1.0 M total EDTA solution as a function of pH.

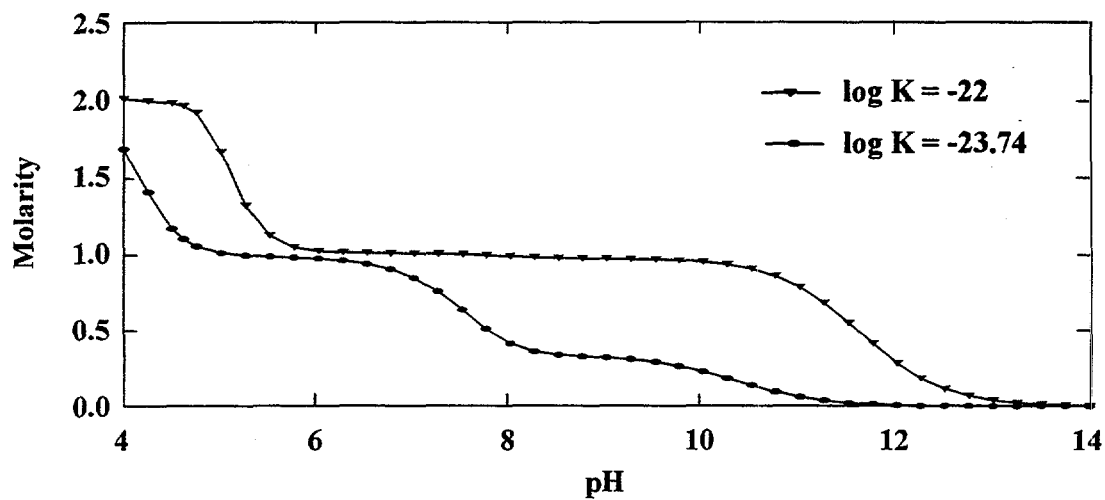


Fig. 20. Calculated solubility of U(VI) using two different  $K_{sp}$  values in a 1.0 M total EDTA solution as a function of pH.

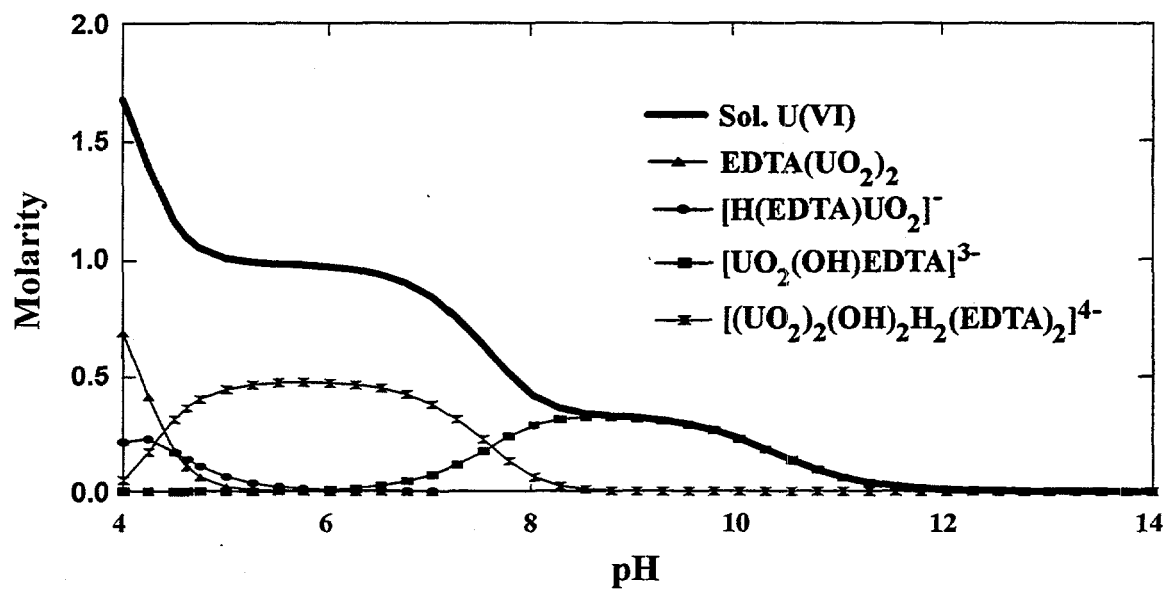


Fig. 21. Calculated main species distribution for U(VI) ( $\log K_{sp} = -23.74$ ) in equilibrium with a 1.0 M total EDTA solution as a function of pH.

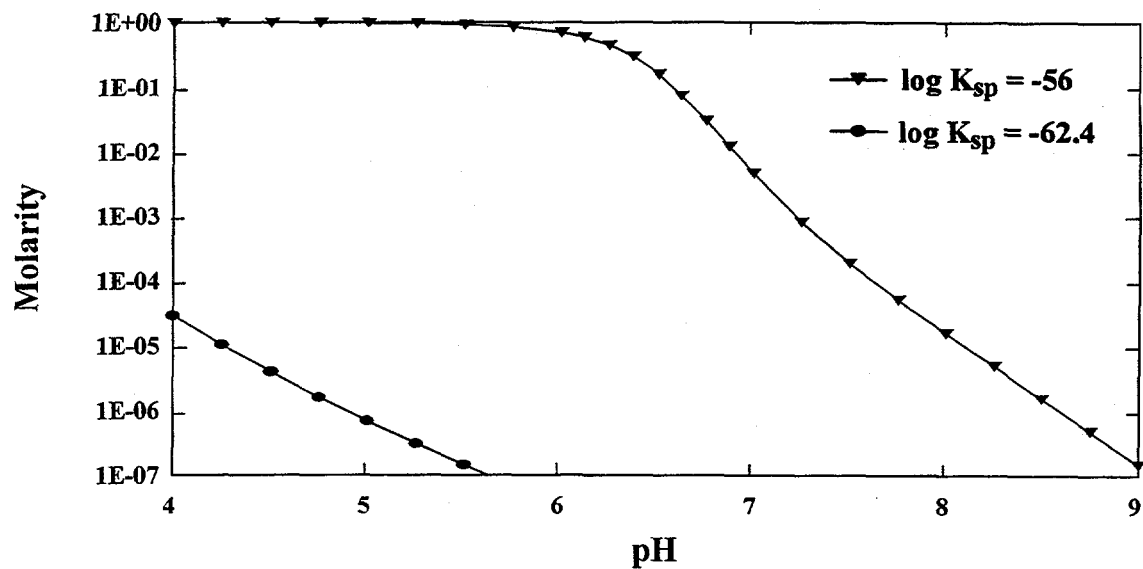


Fig. 22. Calculated solubility of Pu(IV) using two different  $K_{sp}$  values in a  $1.0\text{ M}$  total EDTA solution as a function of pH.

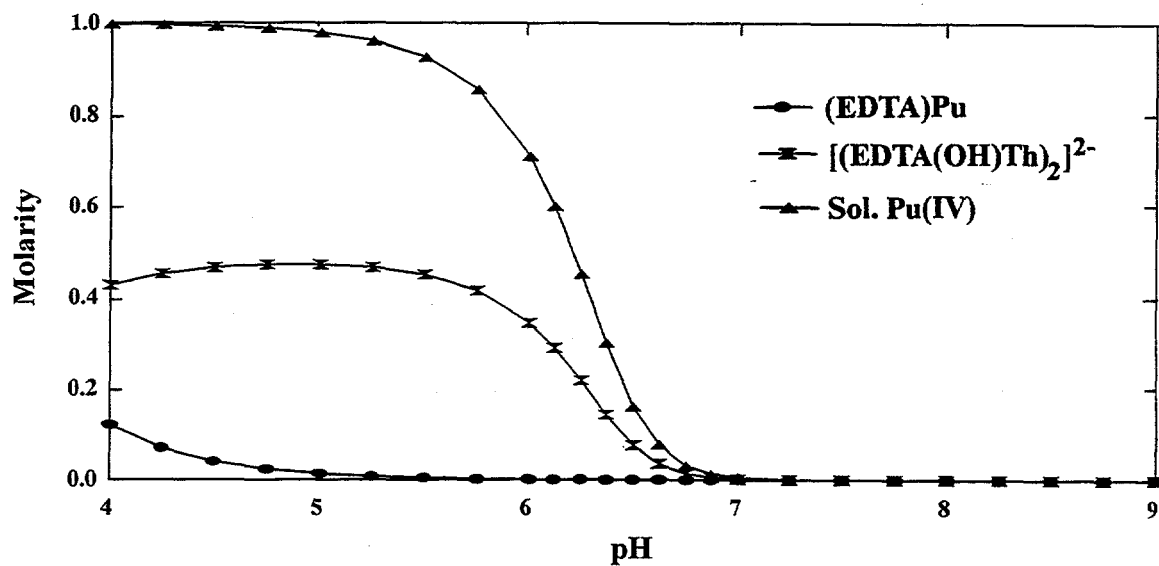


Fig. 23. Calculated main species distribution for Pu(IV) ( $\log K_{sp} = -56$ ) in equilibrium with a  $1.0\text{ M}$  total EDTA solution as a function of pH.

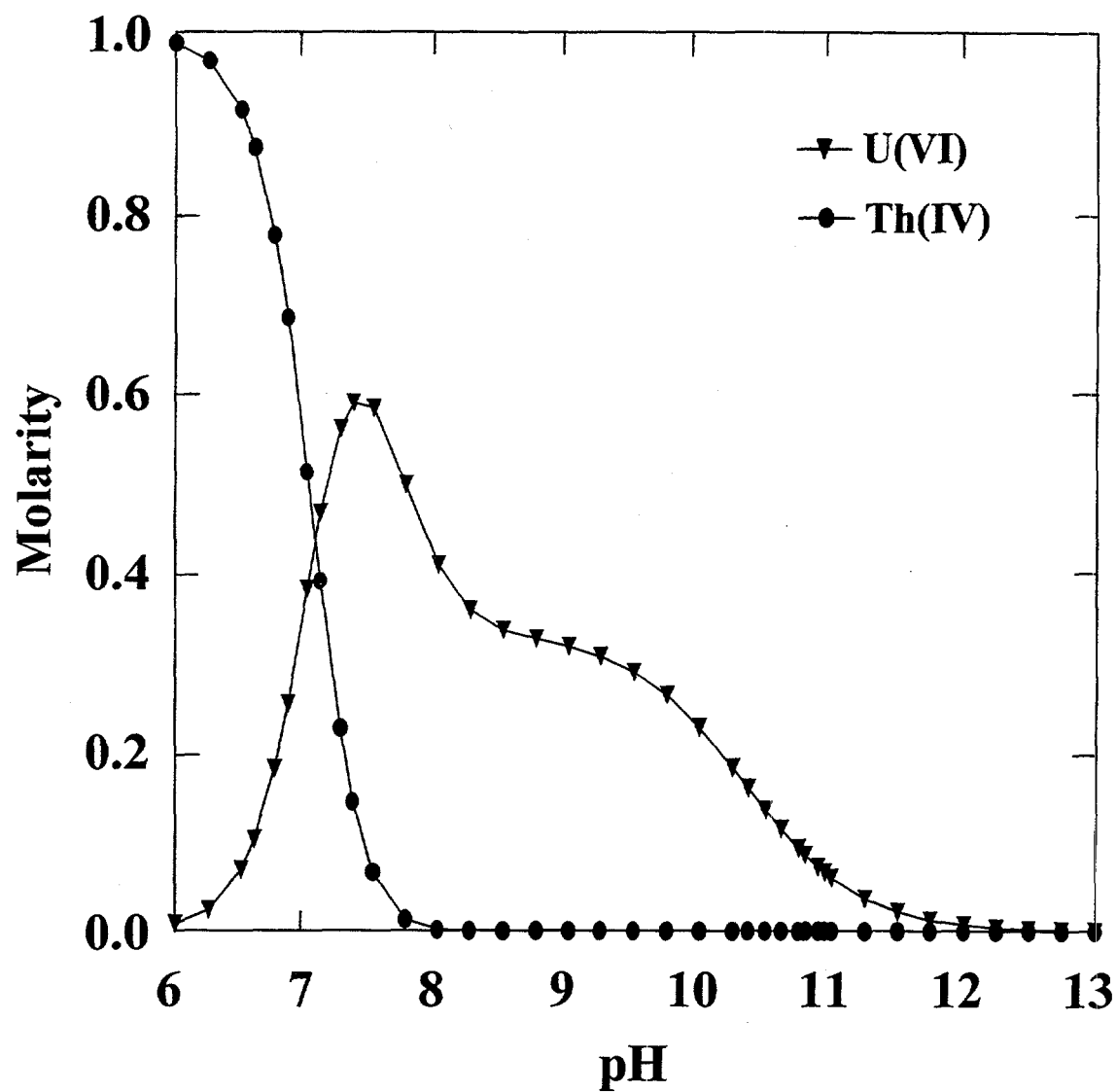


Fig. 24. Calculated combined solubility of Th(IV) ( $\log K_{sp} = -49.4$ ) and U(VI) ( $\log K_{sp} = -23.74$ ) in a 1.0 M total EDTA solution as a function of pH.

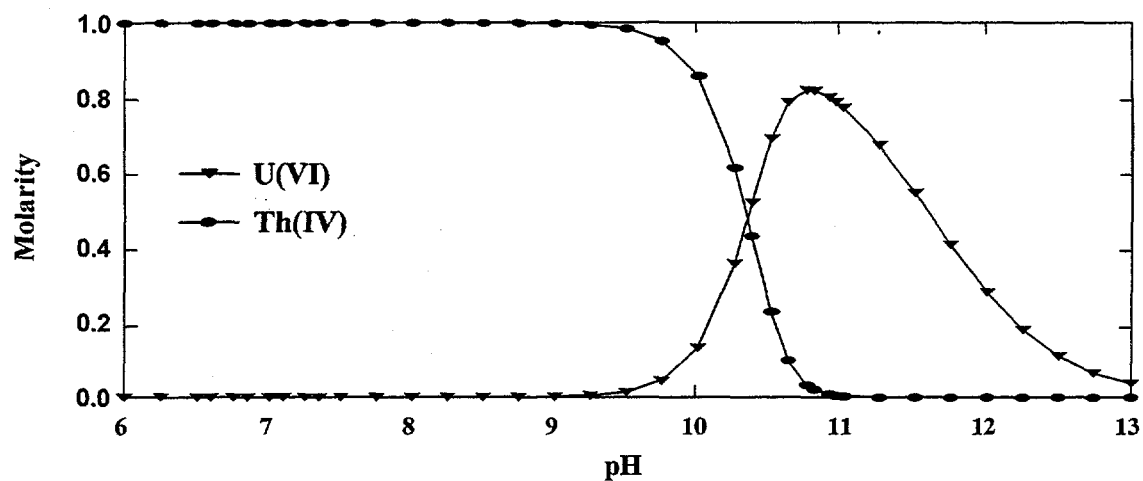


Fig. 25. Calculated combined solubility of Th(IV) ( $\log K_{sp} = -42$ ) and U(VI) ( $\log K_{sp} = -22$ ) in a 1.0 M total EDTA solution as a function of pH.

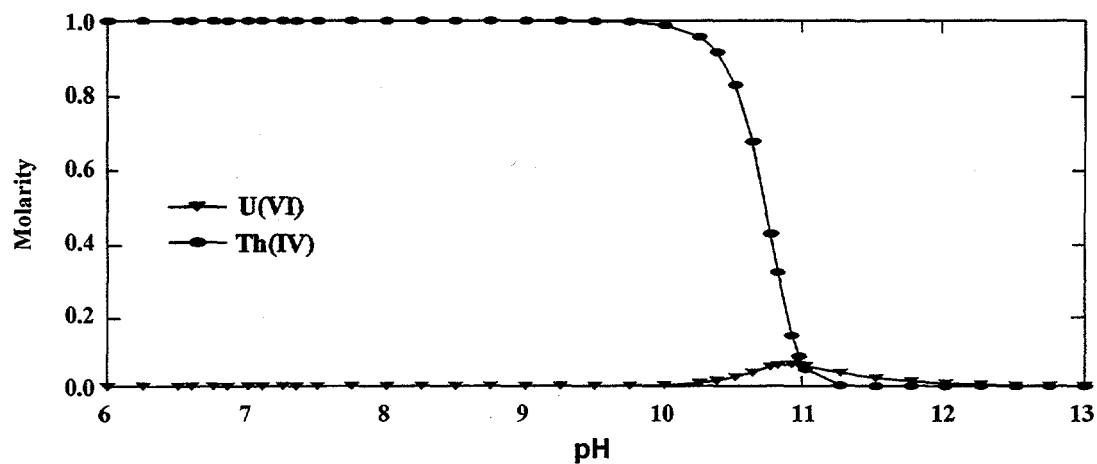


Fig. 26. Calculated combined solubility of Th(IV) ( $\log K_{sp} = -42$ ) and U(VI) ( $\log K_{sp} = -23.74$ ) in a 1.0 M total EDTA solution as a function of pH.





## APPENDIX

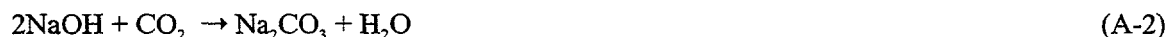
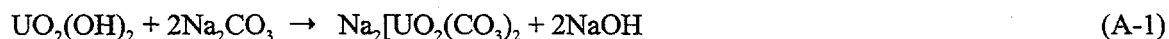


## A-1. EQUILIBRIUM SPECIES IN ALKALINE SOLUTIONS OF ACTINIDE CARBONATE COMPLEXES

Values of all equilibrium species at 1 M TC are shown in Tables A-1 to A-6. Estimated metal hydroxide solubilities at the partial pressure of  $\text{CO}_2$  ( $p\text{CO}_2$ ) in air (0.00033 atm) are presented in Tables A-7 to A-9. A value for the Henry's constant of 0.03 mol/L/atm was used in the calculation at the  $p\text{CO}_2$ . This is the value of Henry's constant at about 0.5 to 1 M sodium salt concentration.<sup>1</sup> It is particularly noteworthy that at the lower pH values, the  $\text{CO}_2$  pressure required to achieve 1 M TC is much greater than the  $p\text{CO}_2$  in the atmosphere. In fact, there is only one pH value at which  $\text{CO}_2$  is in equilibrium at 1 M TC in any of the systems of actinides and carbonates depicted in Tables A-1 to A-6.

It is also to be noted that in the presence of atmospheric  $\text{CO}_2$ , extremely high concentrations of actinides, TCs, and hydroxide ions are required to achieve equilibrium with atmospheric  $\text{CO}_2$  at the higher pH values. (See Tables A-7 to A-9). The calculated values of NaOH equivalents in the tables represent the initial NaOH concentration in tank wastes that would be required to achieve equilibrium at that final pH, TC, and soluble actinide values. A few of the equilibrium conditions calculated at high pH are obviously unrealistic for such high concentrations of TC and soluble actinides (Table A-7, at pH 9.75 and above). Such soluble concentrations could not be attained—carbonate salts of the actinides would precipitate when solubilities of the actinide carbonate complexes are exceeded.

In reality, the conversion of actinide hydroxides to soluble carbonate complexes is limited to a few moles per liter because of hydroxide depletion. This is readily seen from Reactions (A-1) and (A-2):

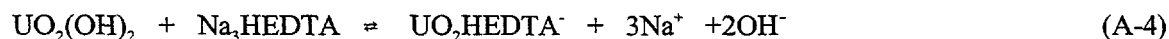
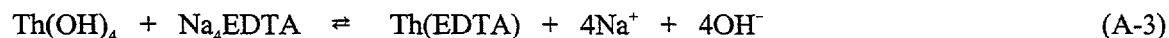


The buffering effect from Reaction 2 is not sufficient to maintain the supply of carbonate ions indefinitely unless additional NaOH is added to the tank. Two moles of carbonate are consumed in Reaction 1, but only 1 mol of carbonate is regenerated by the second reaction.

## A-2. EQUILIBRIUM SPECIES IN ALKALINE SOLUTIONS OF ACTINIDES AND EDTA

Equilibrium species in solution from the dissolution of  $\text{Th}(\text{OH})_4$  and  $\text{Pu}(\text{OH})_4$  in alkaline solutions of 1 M total EDTA are shown in Tables A-10 and A-11. Calculations in this report were made at a total EDTA concentration of 1 M to illustrate the trends in actinide solubility with pH only.

Solubilities of actinide-EDTA complexes to 1 M concentrations of total EDTA can only be achieved at high pH values. This is because hydroxide ions are released in reactions of metal hydroxides with  $\text{EDTA}^{4-}$  and with  $\text{HEDTA}^{3-}$ . This is illustrated by Reactions (A-3) and (A-4):



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<sup>1</sup>T. K. Sherwood, R. L. Pigford, and C. R. Wilke, pp. 365–67 in *Mass Transfer*, McGraw-Hill, New York, 1975.

The number of moles of hydroxide ion released when 1 mol of actinide hydroxide undergoes metathesis reactions with NaEDTA is always 2 or greater. Therefore, one could not achieve pH values that are significantly less than about 14 by adding alkaline waste solutions containing EDTA to waste tanks until 1 M total EDTA is achieved. This is because too much hydroxide is liberated when metal hydroxides (U, Fe, Al, Th, Pu, etc.) are solubilized. However, even at lower levels of total EDTA, the pathway for transport by solution and redeposition of metal hydroxides still exists.

Table A-1. Calculated equilibrium species in a  $\text{UO}_2\text{OH}_2(\text{s})\text{-NaOH}(\text{aq})\text{-Na}_2\text{CO}_3(\text{aq})\text{-NaHCO}_3(\text{aq})\text{-carbonic acid}^a$  system in a 1 M TC solution  
[Calculated using  $\log K_{\text{sp}} = -23.74$  for  $\text{UO}_2\text{OH}_2(\text{s})^b$

pH	Concentrations of Equilibrium Species, mol/L											p CO <sub>2</sub> , atm	Total Anion (equiv. /L)	NaOH required to form anions
	[UO <sub>2</sub> CO <sub>3</sub> ]	[UO <sub>2</sub> (CO <sub>3</sub> ) <sub>2</sub> ·2]	[UO <sub>2</sub> (CO <sub>3</sub> ) <sub>3</sub> ·4]	[UO <sub>2</sub> (CO <sub>3</sub> ) <sub>6</sub> ·6]	[UO <sub>2</sub> (OH) <sub>3</sub> ·1]	Total U	[CO <sub>3</sub> ]	[HCO <sub>3</sub> ]	[OH]	[CO <sub>2</sub> ]				
8.00	2.20E-07	7.13E-04	2.90E-01	1.55E-02	1.13E-07	3.37E-01	1.585E-04	3.380E-02	1.008E-08	7.54E-04	2.51E-02	1.2897	1.2897	
8.50	4.91E-08	3.54E-04	3.21E-01	1.89E-03	3.57E-07	3.27E-01	3.532E-04	2.382E-02	3.188E-06	1.68E-04	5.60E-03	1.3214	1.3214	
9.00	1.08E-08	1.66E-04	3.27E-01	1.96E-04	1.13E-06	3.28E-01	7.857E-04	1.633E-02	1.008E-05	3.64E-05	1.21E-03	1.3279	1.3279	
9.44	2.76E-09	8.49E-05	3.29E-01	2.62E-05	3.11E-06	3.28E-01	1.507E-03	1.167E-02	2.777E-05	9.46E-06	3.15E-04	1.3304	1.3304	
9.50	2.30E-09	7.75E-05	3.29E-01	1.99E-05	3.57E-06	3.29E-01	1.653E-03	1.114E-02	3.188E-05	7.87E-06	2.62E-04	1.3307	1.3307	
10.00	4.95E-10	3.60E-05	3.30E-01	1.99E-06	1.13E-05	3.30E-01	3.563E-03	7.597E-03	1.008E-04	1.70E-06	5.65E-05	1.3333	1.3333	
10.50	1.07E-10	1.67E-05	3.29E-01	1.99E-07	3.57E-05	3.29E-01	7.672E-03	5.173E-03	3.188E-04	3.65E-07	1.22E-05	1.3371	1.3371	
11.00	2.29E-11	7.71E-06	3.27E-01	1.98E-08	1.13E-04	3.27E-01	1.649E-02	3.161E-03	1.008E-03	7.85E-08	2.62E-06	1.3443	1.3443	
11.50	4.91E-12	3.54E-06	3.21E-01	1.89E-09	3.57E-04	3.21E-01	3.531E-02	2.381E-03	3.188E-03	1.68E-08	5.60E-07	1.3596	1.3596	
12.00	1.04E-12	1.60E-06	3.08E-01	1.74E-10	1.13E-03	3.09E-01	7.503E-02	1.600E-03	1.008E-02	3.57E-09	1.19E-07	1.3940	1.3940	
12.50	2.18E-13	6.97E-07	2.81E-01	1.45E-11	1.13E-02	2.84E-01	1.568E-01	1.057E-03	3.188E-02	7.46E-10	2.49E-08	1.4729	1.4729	
13.00	4.38E-14	2.82E-07	2.28E-01	9.55E-13	1.13E-02	2.39E-01	3.151E-01	6.719E-04	1.008E-01	1.50E-08	5.00E-08	1.6553	1.6553	
13.50	6.03E-15	9.47E-08	1.41E-01	3.63E-14	3.57E-02	1.76E-01	5.778E-01	3.896E-04	3.188E-01	2.75E-11	9.17E-10	2.0729	2.0729	
13.75	3.98E-15	4.78E-08	1.37E-01	6.35E-15	6.35E-02	1.53E-01	7.304E-01	2.769E-04	5.67E-01	1.10E-11	3.68E-10	2.4506	2.4506	
14.00	1.20E-15	2.10E-08	4.64E-02	3.96E-16	1.13E-01	1.59E-01	8.605E-01	1.835E-04	1.01E+00	4.10E-12	1.37E-10	3.0280	3.0280	

<sup>a</sup>Carbonic acid =  $\text{CO}_2(\text{g}) + \text{H}_2\text{CO}_3(\text{aq}) + \text{CO}_2(\text{aq})$ .

<sup>b</sup>Only at pH 9.44 is the system in equilibrium with ambient air. Values for  $\text{UO}_2^{2+}$  were omitted; all were  $<1.8 \text{ E-}12$ .

Table A-2. Calculated equilibrium species in  $\text{Th}(\text{OH})_4(\text{s})\text{-NaOH}(\text{aq})\text{-Na}_2\text{CO}_3(\text{aq})\text{-NaHCO}_3(\text{aq})\text{-carbonic acid}^a$  system in a 1 M TC solution  
[Calculated using  $\log K_{\text{sp}} = -49.4$  for  $\text{Th}(\text{OH})_4(\text{s})^b$

pH	Concentrations of Equilibrium Species, mol/L								p CO <sub>2</sub> , atm	Total Anion (equiv. /L)	NaOH required to form anions
	Th(CO <sub>3</sub> ) <sub>5</sub> · 6]	[Th(OH) <sub>3</sub> (CO <sub>3</sub> ) <sub>4</sub> · 1]	Total Th	[CO <sub>3</sub> ]	[HCO <sub>3</sub> ]	[OH]	[CO <sub>2</sub> ]	TC			
8.00	1.42E-05	1.51E-02	1.51E-02	4.498E-03	9.590E-01	1.008E-06	2.14E-02	1.00000	7.14E-01	0.9831	
8.50	4.59E-05	1.51E-02	1.52E-02	1.429E-02	9.635E-01	3.188E-06	6.80E-03	1.00000	2.27E-01	1.0075	1.0075
9.00	1.27E-04	1.47E-02	1.49E-02	4.402E-02	9.385E-01	1.008E-05	2.09E-03	1.00000	6.98E-02	1.0421	1.0421
9.50	2.56E-04	1.35E-02	1.37E-02	1.272E-01	8.575E-01	3.188E-05	6.05E-04	1.00000	2.02E-02	1.1269	1.1269
10.00	2.41E-04	1.06E-02	1.08E-02	3.155E-01	6.726E-01	1.008E-04	1.50E-04	1.00000	5.00E-03	1.3157	1.3157
10.50	5.67E-05	6.29E-03	6.34E-03	5.933E-01	4.001E-01	3.188E-04	2.82E-05	1.00000	9.41E-04	1.5937	1.5937
10.77	1.34E-05	4.16E-03	4.17E-03	7.311E-01	2.647E-01	5.936E-04	1.00E-05	1.00000	3.34E-04	1.7316	1.7316
11.00	2.89E-06	2.75E-03	2.76E-03	8.220E-01	1.753E-01	1.008E-03	3.91E-06	1.00000	1.30E-04	1.8230	1.8230
11.50	5.54E-08	9.91E-04	9.92E-04	9.359E-01	6.310E-02	3.188E-03	4.45E-07	1.00000	1.48E-05	1.9391	1.9391
12.00	6.93E-10	3.28E-04	3.28E-04	9.788E-01	2.087E-02	1.008E-02	4.66E-08	1.00000	1.55E-06	1.9889	1.9889
13.00	7.63E-14	3.34E-05	3.34E-05	9.978E-01	2.128E-03	1.008E-01	4.75E-10	1.00000	1.58E-08	2.0987	2.0987
14.00	7.70E-18	3.35E-06	3.35E-06	9.998E-01	2.132E-04	1.008E+00	4.76E-12	1.00000	1.59E-10	3.0079	3.0079

<sup>a</sup>Carbonic acid =  $\text{CO}_2(\text{g}) + \text{H}_2\text{CO}_3(\text{aq}) + \text{CO}_2(\text{aq})$ .

<sup>b</sup>Only at pH 10.77 is the system in equilibrium with ambient air. Values for  $\text{PuO}_2^{2+}$  were omitted; all were  $<3.9 \text{ E-}26$ .

Table A-3. Calculated equilibrium species in  $\text{Pu}(\text{OH})_4(\text{s})\text{--NaOH}(\text{aq})\text{--Na}_2\text{CO}_3(\text{aq})\text{--NaHCO}_3(\text{aq})\text{--carbonic acid}^a$  system in a 1 M TC solution  
[Calculated using  $\log K_{\text{sp}} = -56$  for  $\text{Pu}(\text{OH})_4(\text{s})$ ]<sup>b</sup>

pH	Concentrations of Equilibrium Species, mol/L														p CO <sub>2</sub> , atm	Total Anion (equiv. /L)	NaOH required to form anions
	[PuCO <sub>3</sub> <sup>3+</sup> ]	[Pu(CO <sub>3</sub> ) <sub>2</sub> ]	[Pu(CO <sub>3</sub> ) <sub>3</sub> <sup>3-2</sup> ]	[(Pu(CO <sub>3</sub> ) <sub>3</sub> ) <sup>3-2</sup> ]	[Pu(CO <sub>3</sub> ) <sub>3</sub> <sup>3-4</sup> ]	[Pu(OH)(CO <sub>3</sub> ) <sub>2</sub> <sup>3-4</sup> ]	Total Pu	[CO <sub>3</sub> ]	[HCO <sub>3</sub> ]	[OH]	[CO <sub>2</sub> ]	TC					
8.00	1.16E-18	1.11E-08	2.10E-02	1.59E-01	7.59E-03	3.61E-16	1.88E-01	1.199E-03	2.527E-01	1.008E-06	5.71E-03	1.00000	1.90E-01	0.9821	0.9821	0.9821	
8.50	3.63E-20	1.08E-09	6.43E-03	1.52E-01	2.27E-02	3.53E-15	1.81E-01	3.751E-03	2.529E-01	1.168E-06	1.79E-03	1.00000	5.95E-02	1.0182	1.0182	1.0182	
9.00	1.08E-21	9.59E-11	1.70E-03	1.20E-01	5.32E-02	3.13E-14	1.75E-01	1.117E-02	2.382E-01	1.008E-05	5.32E-04	1.00000	1.77E-02	1.0622	1.0622	1.0622	
9.50	3.03E-23	7.54E-12	3.74E-04	7.39E-02	9.21E-02	2.46E-13	1.66E-01	3.131E-02	2.111E-01	1.188E-05	1.49E-04	1.00000	4.97E-03	1.1229	1.1229	1.1229	
10.00	8.02E-25	5.27E-13	6.92E-05	3.62E-02	1.19E-01	1.72E-12	1.55E-01	8.281E-02	1.766E-01	1.009E-04	3.94E-05	1.00000	1.31E-03	1.2020	1.2020	1.2020	
10.50	2.01E-26	3.32E-14	1.01E-05	1.44E-02	1.19E-01	1.09E-11	1.33E-01	2.079E-01	1.402E-01	1.189E-04	9.90E-06	1.00000	3.30E-04	1.3271	1.3271	1.3271	
11.00	4.67E-28	2.97E-14	1.01E-05	1.38E-02	1.19E-01	1.09E-11	1.32E-01	2.154E-01	1.397E-01	1.333E-04	9.35E-06	1.00000	3.12E-04	1.3339	1.3339	1.3339	
11.50	8.38E-30	1.79E-15	1.37E-06	4.15E-03	7.97E-02	5.83E-11	8.38E-02	4.821E-01	1.028E-01	1.009E-03	2.29E-06	1.00000	7.85E-05	1.5628	1.5628	1.5628	
12.00	9.47E-32	7.35E-16	1.14E-06	7.03E-06	2.73E-04	2.40E-10	1.88E-04	6.656E-01	5.836E-02	1.189E-03	4.12E-07	1.00000	1.37E-05	1.8836	1.8836	1.8836	
12.50	9.62E-34	7.59E-17	1.19E-11	7.48E-08	2.98E-06	2.48E-10	2.80E-04	9.778E-01	2.085E-02	1.009E-02	4.65E-08	1.00000	1.55E-06	1.9881	1.9881	1.9881	
13.00	9.68E-36	7.68E-18	1.19E-11	7.48E-08	2.98E-06	2.48E-10	3.03E-06	9.933E-01	6.697E-03	3.188E-02	4.73E-09	1.00000	1.58E-07	2.0252	2.0252	2.0252	
13.50	9.68E-38	7.68E-20	1.21E-13	7.62E-10	3.03E-08	2.50E-10	3.13E-08	9.979E-01	2.128E-03	1.009E-01	4.75E-10	1.00000	1.59E-08	2.0987	2.0987	2.0987	
13.75	9.68E-39	7.68E-21	1.22E-15	7.67E-12	3.03E-10	2.51E-10	3.13E-10	9.993E-01	6.738E-04	3.188E-01	4.76E-11	1.00000	1.59E-09	2.3181	2.3181	2.3181	
14.00	9.68E-40	7.68E-22	1.22E-16	7.68E-13	3.05E-11	2.51E-10	3.13E-11	9.996E-01	3.790E-04	5.669E-01	1.50E-11	1.00000	5.01E-10	2.5665	2.5665	2.5665	
14.00	9.68E-40	7.68E-22	1.22E-17	7.68E-14	3.06E-12	2.51E-10	3.13E-12	9.998E-01	2.132E-04	1.008E+00	4.76E-12	1.00000	1.59E-10	3.0079	3.0079	3.0079	

<sup>a</sup>Carbonic acid =  $\text{CO}_2(\text{g}) + \text{H}_2\text{CO}_3(\text{aq}) + \text{CO}_2(\text{aq})$ .

<sup>b</sup>Only at pH 10.52 is the system in equilibrium with ambient air. Values for  $\text{Pu}^{4+}$  were omitted; all were  $<9.7 \text{ E-}33$ .

Table A-4. Calculated equilibrium species in  $\text{PuO}_2(\text{OH})_2(\text{s})\text{--NaOH}(\text{aq})\text{--Na}_2\text{CO}_3(\text{aq})\text{--NaHCO}_3(\text{aq})\text{--carbonic acid}^a$  system in a 1 M TC solution  
[Calculated using  $\log K_{\text{sp}} = -24.5$  for  $\text{PuO}_2(\text{OH})_2(\text{s})$ ]<sup>b</sup>

pH	Concentrations of Equilibrium Species, mol/L														p CO <sub>2</sub> , atm	Total Anion (equiv. /L)	NaOH required to form anions
	$[\text{PuO}_2(\text{CO}_3)]$	$[\text{PuO}_2(\text{CO}_3)]$	$[\text{PuO}_2(\text{CO}_3)]$	$[\text{PuO}_2(\text{CO}_3)]$	$[\text{PuO}_2(\text{CO}_3)]$	$[\text{PuO}_2(\text{CO}_3)]$	$[\text{PuO}_2(\text{CO}_3)]$	$[\text{PuO}_2(\text{CO}_3)]$	$[\text{PuO}_2(\text{CO}_3)]$	$[\text{PuO}_2(\text{CO}_3)]$	$[\text{PuO}_2(\text{CO}_3)]$	$[\text{PuO}_2(\text{CO}_3)]$	$[\text{PuO}_2(\text{CO}_3)]$	$[\text{PuO}_2(\text{CO}_3)]$			
8.00	5.08E-07	2.08E-04	3.40E-02	2.26E-05	3.42E-02	4.09E-03	8.73E-01	1.00E-06	1.95E-02	1.00000	6.50E-01	1.0186	1.0186	1.0186	6.50E-01	1.0186	1.0186
8.50	1.41E-07	1.60E-04	7.23E-02	1.03E-05	7.25E-02	1.136E-02	7.85E-01	3.18E-06	5.41E-03	1.00000	1.80E-01	1.0783	1.0783	1.0783	1.80E-01	1.0783	1.0783
9.00	3.57E-08	1.03E-04	1.18E-01	2.74E-06	1.18E-01	2.884E-02	6.149E-01	1.00E-05	1.37E-03	1.00000	4.57E-02	1.1457	1.1457	1.1457	4.57E-02	1.1457	1.1457
9.50	8.40E-09	5.77E-05	1.57E-01	4.84E-07	1.57E-01	6.828E-02	4.604E-01	3.18E-05	3.25E-04	1.00000	1.08E-02	1.2250	1.2250	1.2250	1.08E-02	1.2250	1.2250
10.00	1.89E-09	2.87E-05	1.74E-01	5.96E-08	1.74E-01	1.523E-01	3.248E-01	1.00E-04	7.25E-05	1.00000	2.42E-03	1.3266	1.3266	1.3266	2.42E-03	1.3266	1.3266
10.50	3.92E-10	1.24E-05	1.57E-01	4.81E-09	1.57E-01	1.523E-01	3.248E-01	1.00E-04	1.51E-05	1.00000	5.02E-04	1.4736	1.4736	1.4736	5.02E-04	1.4736	1.4736
10.83	2.58E-10	9.66E-06	1.45E-01	2.27E-09	1.45E-01	3.768E-01	1.833E-01	4.300E-04	9.85E-06	1.00000	3.28E-04	1.5222	1.5222	1.5222	3.28E-04	1.5222	1.5222
11.00	7.22E-11	4.21E-06	9.78E-02	1.87E-10	9.78E-02	5.628E-01	1.243E-01	1.00E-03	2.77E-06	1.00000	9.25E-05	1.6815	1.6815	1.6815	9.25E-05	1.6815	1.6815
11.50	1.05E-11	8.98E-07	3.04E-02	3.88E-12	3.04E-02	8.513E-01	5.740E-02	3.188E-03	4.05E-07	1.00000	1.35E-05	1.8849	1.8849	1.8849	1.35E-05	1.8849	1.8849
12.00	1.20E-12	1.16E-07	4.45E-03	3.88E-15	4.45E-03	9.661E-01	2.060E-02	1.00E-02	4.60E-08	1.00000	1.53E-06	1.9806	1.9806	1.9806	1.53E-06	1.9806	1.9806
12.50	1.23E-13	1.22E-08	4.81E-04	4.55E-16	4.81E-04	9.818E-01	6.888E-03	3.188E-02	4.72E-09	1.00000	1.57E-07	2.0242	2.0242	2.0242	1.57E-07	2.0242	2.0242
13.00	1.24E-14	1.23E-09	4.90E-05	4.71E-21	4.90E-05	9.977E-01	2.127E-03	3.188E-01	4.76E-11	1.00000	1.58E-08	2.0986	2.0986	2.0986	1.58E-08	2.0986	2.0986
13.50	1.24E-15	1.24E-10	4.92E-06	4.76E-24	4.92E-06	9.993E-01	6.738E-04	3.188E-01	4.76E-11	1.00000	1.59E-09	2.3181	2.3181	2.3181	1.59E-09	2.3181	2.3181
13.75	3.91E-16	3.91E-11	1.58E-06	1.51E-25	1.58E-06	9.998E-01	3.790E-04	5.669E-01	1.50E-11	1.00000	5.01E-10	2.5665	2.5665	2.5665	5.01E-10	2.5665	2.5665
14.00	1.24E-16	1.24E-11	4.93E-07	4.77E-27	4.93E-07	9.998E-01	2.132E-04	1.008E+00	4.76E-12	1.00000	1.59E-10	3.0079	3.0079	3.0079	1.59E-10	3.0079	3.0079

<sup>a</sup>Carbonic acid =  $\text{CO}_2(\text{g}) + \text{H}_2\text{CO}_3(\text{aq}) + \text{CO}_2(\text{aq})$ .

<sup>b</sup>Only at pH 10.63 is the system in equilibrium with ambient air. Values for  $\text{PuO}_2^{2+}$  were omitted; all were  $<3.1 \text{ E-}13$ .

Table A-5. Calculated equilibrium species in  $\text{PuO}_2(\text{OH})_2(\text{s})\text{--NaOH}(\text{aq})\text{--Na}_2\text{CO}_3(\text{aq})\text{--NaHCO}_3(\text{aq})\text{--carbonic acid}^a$  system in a 1 M TC solution  
[Calculated using  $\log K_{\text{sp}} = -22.7$  for  $\text{PuO}_2(\text{OH})_2(\text{s})^b$ ]

pH	Concentrations of Equilibrium Species, mol/L												p CO <sub>2</sub> , atm	Total Anion (equiv. /L)	NaOH required to form anions
	[PuO <sub>2</sub> (CO <sub>3</sub> )]	[PuO <sub>2</sub> (CO <sub>3</sub> ) <sup>2-</sup> ]	[PuO <sub>2</sub> (CO <sub>3</sub> ) <sup>3-</sup> ]	4	[PuO <sub>2</sub> (CO <sub>3</sub> ) <sup>6-</sup> ]	6	Total Pu	[CO <sub>3</sub> ]	[HCO <sub>3</sub> ]	[OH]	[CO <sub>2</sub> ]	TC			
8.00	1.32E-05	2.24E-03	1.51E-01	2.84E-02	2.39E-01	1.694E-03	3.613E-01	1.008E-06	8.08E-03	1.00000	2.69E-01	1.1450	1.1450	1.285	
8.50	3.25E-06	1.35E-03	2.24E-01	6.23E-03	2.44E-01	4.182E-03	2.806E-01	3.188E-06	1.98E-03	1.00000	6.60E-02	1.2265	1.2265	1.285	
9.00	7.37E-07	6.95E-04	2.61E-01	8.43E-04	2.64E-01	9.429E-03	2.010E-01	1.008E-05	4.49E-04	1.00000	1.50E-02	1.2699	1.2699	1.285	
9.50	1.62E-07	3.37E-04	2.78E-01	9.66E-05	2.80E-01	2.078E-02	1.401E-01	3.188E-05	9.89E-05	1.00000	3.30E-03	1.3000	1.3000	1.285	
10.00	3.53E-08	1.59E-04	2.86E-01	1.01E-05	2.86E-01	4.5713E-02	9.623E-02	1.008E-04	2.15E-05	1.00000	7.16E-04	1.3313	1.3313	1.285	
10.26	1.58E-08	1.06E-04	2.85E-01	3.03E-06	2.85E-01	6.716E-02	9.699E-02	1.834E-04	9.65E-06	1.00000	3.22E-04	1.3520	1.3520	1.285	
10.50	7.54E-09	7.27E-05	2.79E-01	9.67E-07	2.80E-01	9.848E-02	6.505E-02	3.188E-04	4.59E-06	1.00000	1.53E-04	1.3762	1.3762	1.285	
11.00	1.57E-09	3.15E-05	2.52E-01	7.87E-08	2.52E-01	2.008E-01	4.282E-02	1.008E-03	9.56E-07	1.00000	3.19E-05	1.4539	1.4539	1.285	
11.50	3.09E-10	1.22E-05	1.93E-01	4.59E-09	1.93E-01	3.955E-01	2.667E-02	3.188E-03	1.88E-07	1.00000	6.28E-06	1.5913	1.5913	1.285	
12.00	5.35E-11	3.67E-06	1.00E-01	1.24E-10	1.00E-01	6.851E-01	1.461E-02	1.008E-02	3.26E-08	1.00000	1.09E-06	1.7953	1.7953	1.285	
12.50	7.20E-12	6.63E-07	2.43E-02	7.31E-13	2.43E-02	9.209E-01	6.209E-03	3.188E-02	4.38E-09	1.00000	1.46E-07	1.9771	1.9771	1.285	
13.00	7.73E-13	7.64E-08	3.01E-03	1.12E-15	3.01E-03	9.889E-01	2.108E-03	1.008E-01	4.71E-10	1.00000	1.57E-08	2.0927	2.0927	1.285	
13.50	7.80E-14	7.79E-09	3.10E-04	1.19E-18	3.10E-04	9.984E-01	6.732E-04	3.188E-01	4.75E-11	1.00000	1.58E-09	2.3175	2.3175	1.285	
13.75	2.47E-14	2.47E-09	9.82E-05	3.78E-20	9.82E-05	9.993E-01	3.789E-04	5.669E-01	1.50E-11	1.00000	5.01E-10	2.5863	2.5863	1.285	
14.00	7.81E-15	7.81E-10	3.11E-05	1.20E-21	3.11E-05	9.997E-01	2.132E-04	1.008E+00	4.76E-12	1.00000	1.59E-10	3.0078	3.0078	1.285	

<sup>a</sup>Carbonic acid =  $\text{CO}_2(\text{g}) + \text{H}_2\text{CO}_3(\text{aq}) + \text{CO}_2(\text{aq})$ .

<sup>b</sup>Only at pH 10.3 is the system in equilibrium with ambient air. Values for  $\text{PuO}_2^{2+}$  were omitted; all were  $<2.0 \text{ E-11}$ .

Table A-6. Solubility of a precipitate of the mixed hydroxides of U(VI), Pu(IV), and Th(IV) in alkaline carbonate  
[Calculated using  $\log K_{\text{sp}} = -23.74$  for  $\text{UO}_2(\text{OH})_2$ , -56 for  $\text{Pu}(\text{OH})_4$ , and -42 for  $\text{Th}(\text{OH})_4$ ]

pH	Concentrations of Equilibrium Species, mol/L								p CO <sub>2</sub> , atm	Total Anion (equiv. /L)	NaOH required to form anions
	Total U	Total Pu	Total Th	[CO <sub>3</sub> ]	[HCO <sub>3</sub> ]	[OH]	[CO <sub>2</sub> ]	TC			
8.00	3.371E-01	9.733E-05	5.503E-04	1.585E-04	3.379E-02	1.01E-06	7.54E-04	1.00000	2.514E-02	1.289	1.289
8.50	3.271E-01	1.750E-05	3.848E-04	3.532E-04	2.381E-02	3.19E-06	1.68E-04	1.00000	5.603E-03	1.321	1.321
9.00	3.278E-01	3.269E-06	2.616E-04	7.566E-04	1.632E-02	1.01E-05	3.64E-05	1.00000	1.215E-03	1.328	1.328
9.42	3.289E-01	8.545E-07	1.888E-04	1.461E-03	1.185E-02	2.65E-05	1.01E-05	1.00000	3.351E-04	1.330	1.330
9.50	3.291E-01	6.661E-07	1.775E-04	1.653E-03	1.114E-02	3.19E-05	7.87E-06	1.00000	2.622E-04	1.331	1.331
10.00	3.296E-01	1.469E-07	1.205E-04	3.563E-03	7.596E-03	1.01E-04	1.70E-06	1.00000	5.652E-05	1.333	1.333
10.50	3.291E-01	3.531E-08	8.178E-05	7.671E-03	5.172E-03	3.19E-04	3.65E-07	1.00000	1.217E-05	1.337	1.337
11.00	3.268E-01	9.464E-09	5.547E-05	1.649E-02	3.515E-03	1.01E-03	7.85E-08	1.00000	2.616E-06	1.343	1.343
11.50	3.211E-01	2.879E-09	3.751E-05	3.531E-02	2.381E-03	3.19E-03	1.68E-08	1.00000	5.601E-07	1.356	1.356
12.00	3.089E-01	9.729E-10	2.518E-05	7.503E-02	1.600E-03	1.01E-02	3.57E-09	1.00000	1.190E-07	1.384	1.384
12.50	2.843E-01	3.423E-10	1.662E-05	1.568E-01	1.057E-03	3.19E-02	7.46E-10	1.00000	2.487E-08	1.441	1.441
13.00	2.394E-01	1.276E-10	1.056E-05	3.151E-01	6.719E-04	1.01E-01	1.50E-10	1.00000	4.999E-09	1.554	1.554
13.50	1.763E-01	1.044E-10	6.122E-06	5.778E-01	3.896E-04	3.19E-01	2.75E-11	1.00000	9.167E-10	1.754	1.754
14.00	1.594E-01	1.873E-10	2.883E-06	8.605E-01	1.835E-04	1.01E+00	4.10E-12	1.00000	1.365E-10	2.020	2.020



Table A-7. Effect of pH on the uranium and TC in solution at  $p\text{CO}_2 = 3.33\text{E}-4$  atm

pH	Concentrations of Equilibrium Species, mol/L										p $\text{CO}_2$ , atm	Total Anion (equiv. /L)	NaOH required to form anions (mol/L)	Total Carbon (mol/L)
	[UO <sub>2</sub> CO <sub>3</sub> ]	[UO <sub>2</sub> (CO <sub>3</sub> ) <sub>2</sub> <sup>2-</sup> ]	[UO <sub>2</sub> (CO <sub>3</sub> ) <sub>3</sub> <sup>3-</sup> ]	[UO <sub>2</sub> (CO <sub>3</sub> ) <sub>3</sub> <sup>3-</sup> ]	[UO <sub>2</sub> (OH) <sub>3</sub> <sup>3-</sup> ]	Total U	[CO <sub>3</sub> ]	[HCO <sub>3</sub> ]	[OH]	[CO <sub>2</sub> ]				
8.0	2.92E-09	1.25E-07	6.75E-07	8.36E-14	1.13E-07	9.16E-07	2.100E-06	4.478E-04	1.008E-06	9.99E-06	3.33E-04	4.560E-04	4.560E-04	4.62E-04
8.5	2.92E-09	1.25E-06	6.75E-05	8.36E-11	3.57E-07	6.91E-05	2.100E-05	1.416E-03	3.188E-06	9.99E-06	3.33E-04	1.734E-03	1.734E-03	1.85E-03
9.0	2.92E-09	1.25E-05	6.75E-03	8.36E-08	1.13E-06	6.76E-03	2.100E-04	4.478E-03	1.008E-05	9.99E-06	3.33E-04	3.193E-02	3.193E-02	2.50E-02
9.44	2.89E-09	9.31E-05	3.77E-01	3.44E-05	3.11E-06	3.78E-01	1.578E-03	1.221E-02	2.777E-05	9.90E-06	3.30E-04	1.529E+00	1.529E+00	1.15E+00
9.5	2.92E-09	1.25E-04	6.75E-01	8.36E-05	3.57E-06	6.75E-01	2.100E-03	1.416E-02	3.188E-05	9.99E-06	3.33E-04	2.719E+00	2.719E+00	2.04E+00
9.6	2.92E-09	1.25E-04	1.70E+00	3.34E-04	4.50E-06	1.70E+00	3.300E-03	1.783E-02	4.013E-05	1.00E-05	3.33E-04	6.619E+00	6.619E+00	5.12E+00
9.75	2.92E-09	3.95E-04	6.75E+01	8.36E-02	1.13E-05	6.77E+01	2.100E-02	4.478E-02	5.669E-05	9.99E-06	3.33E-04	2.704E+01	2.704E+01	2.03E+01
10	2.92E-09	1.25E-03	6.75E+02	8.36E-01	3.57E-05	7.00E+02	2.100E-01	1.416E-01	3.188E-04	9.99E-06	3.33E-04	2.706E+02	2.706E+02	2.03E+02
10.5	2.92E-09	1.25E-02	6.75E+03	8.36E+04	1.13E-04	9.26E+03	2.10E+00	4.478E-01	1.008E-03	9.99E-06	3.33E-04	3.201E+06	3.201E+06	2.53E+06
11	2.92E-09	1.25E-01	6.75E+05	8.36E+07	3.57E-04	3.18E+05	2.10E+01	1.42E+00	3.188E-03	9.99E-06	3.33E-04	7.716E+08	7.716E+08	7.04E+08
11.5	2.92E-09	1.25E+00	6.75E+07	8.36E+07	3.57E-04	3.18E+05	2.10E+01	1.42E+00	3.188E-03	9.99E-06	3.33E-04	7.716E+08	7.716E+08	7.04E+08

Table A-8. Effect of pH on the thorium and TC in solution at  $p\text{CO}_2 = 3.33\text{E}-4$  atm

pH	Concentrations of Equilibrium Species, mol/L										p CO <sub>2</sub> , atm	Total Anion (equiv. /L)	NaOH required to form anions
	Th(CO <sub>3</sub> ) <sub>5</sub> <sup>4-</sup>	[Th(OH) <sub>3</sub> (CO <sub>3</sub> ) <sup>3-</sup> ]	Total Th	[CO <sub>3</sub> ]	[HCO <sub>3</sub> ]	[OH]	[CO <sub>2</sub> ]	TC					
8.0	3.15E-22	7.04E-06	7.04E-06	2.100E-06	4.478E-04	1.008E-06	9.99E-06	0.00047	3.33E-04	0.0005	0.0005		
8.5	3.15E-19	2.22E-05	2.22E-05	2.10E-05	1.416E-03	3.188E-06	9.99E-06	0.00147	3.33E-04	0.0015	0.0015		
9.0	3.15E-16	7.04E-05	7.04E-05	2.10E-04	4.478E-03	1.008E-05	9.99E-06	0.00477	3.33E-04	0.0050	0.0050		
9.5	3.15E-13	2.22E-04	2.22E-04	2.10E-03	1.416E-02	3.188E-05	9.99E-06	0.01649	3.33E-04	0.0186	0.0186		
10.0	3.15E-10	7.04E-04	7.04E-04	2.10E-02	4.478E-02	1.008E-04	9.99E-06	0.06649	3.33E-04	0.0876	0.0876		
10.13	1.93E-09	9.52E-04	9.52E-04	3.84E-02	6.062E-02	1.360E-04	1.00E-05	0.09993	3.34E-04	0.1384	0.1384		
10.3	1.97E-08	1.40E-03	1.40E-03	8.35E-02	8.923E-02	2.011E-04	9.98E-06	0.17414	3.33E-04	0.2578	0.2578		
10.5	3.15E-07	2.22E-03	2.22E-03	2.10E-01	1.416E-01	3.188E-04	9.99E-06	0.35383	3.33E-04	0.5641	0.5641		
10.60	1.20E-06	2.78E-03	2.78E-03	3.30E-01	1.767E-01	4.013E-04	9.91E-06	0.50954	3.30E-04	0.8399	0.8399		
10.77	1.34E-05	4.16E-03	4.17E-03	7.31E-01	2.647E-01	5.936E-04	1.00E-05	1.00000	3.34E-04	1.7316	1.7316		
11.0	3.15E-04	7.04E-03	7.35E-03	2.10E+00	4.478E-01	1.008E-03	9.99E-06	2.55638	3.33E-04	4.6577	4.6577		
11.2	4.94E-03	1.11E-02	1.61E-02	5.27E+00	7.083E-01	1.598E-03	9.98E-06	6.00917	3.33E-04	11.2807	11.2807		



Table A-11. Calculated equilibrium species in solution for the  $\text{Pu}(\text{OH})_4(\text{s})\text{---H}_2\text{O--NaOH--EDTA}$  system at 1 M total EDTA concentration<sup>a</sup>  
[Calculated using  $\log K_{\text{sp}} = -56$  for  $\text{Pu}(\text{OH})_4(\text{s})$ ]

pH	Concentrations of Equilibrium Species in Solution, mol/L										Anion Charge Equivs	Na + equivs Required
	PuEDTA	[Pu(EDTA)OH <sup>-</sup> ]	[Pu <sub>2</sub> (EDTA) <sub>2</sub> (OH) <sub>2</sub> ]	[Pu <sub>4</sub> ]	Total Pu	Free EDTA Ligands	[EDTA <sup>4-</sup> ]	Total EDTA	[OH <sup>-</sup> ]			
4	1.204E-01	2.2927E-02	4.274E-01	9.68E-17	0.9980	1.99E-03	9.87E-12	1.0000	1.008E-10	0.882	0.882	
4.5	3.970E-02	2.3914E-02	4.650E-01	9.68E-19	0.9935	6.45E-03	3.26E-10	1.0000	3.188E-10	0.967	0.967	
5	1.264E-02	2.4068E-02	4.710E-01	9.68E-21	0.9786	2.14E-02	1.04E-08	1.0000	1.008E-09	1.010	1.010	
5.5	3.898E-03	2.3481E-02	4.483E-01	9.68E-23	0.9239	7.60E-02	3.20E-07	1.0000	3.188E-09	1.087	1.087	
6	1.074E-03	2.0453E-02	3.401E-01	9.68E-25	0.7018	2.98E-01	8.81E-06	1.0000	1.008E-08	1.427	1.427	
6.5	1.566E-04	9.4305E-03	7.231E-02	9.68E-27	0.1542	8.46E-01	1.28E-04	1.0000	3.188E-08	2.447	2.447	
7	7.264E-06	1.3836E-03	1.556E-03	9.68E-29	4.50E-03	9.95E-01	5.96E-04	1.0000	1.008E-07	2.878	2.878	
8	8.083E-09	1.5396E-05	1.927E-07	9.68E-33	1.58E-05	1.00E+00	6.63E-03	1.0000	1.008E-06	2.994	2.994	
9	7.711E-12	1.4687E-07	1.754E-11	9.68E-37	1.47E-07	1.00E+00	6.33E-02	1.0000	1.008E-05	3.062	3.062	
10	4.917E-15	9.3659E-10	7.132E-16	9.68E-41	9.37E-10	1.00E+00	4.03E-01	1.0000	1.008E-04	3.403	3.403	
11	1.062E-18	2.0228E-12	3.327E-21	9.68E-45	2.02E-12	1.00E+00	8.71E-01	1.0000	1.008E-03	3.872	3.872	
12	1.201E-22	2.2882E-15	4.257E-27	9.68E-49	2.29E-15	1.00E+00	9.85E-01	1.0000	1.008E-02	3.996	3.996	
13	1.217E-26	2.3185E-18	4.371E-33	9.68E-53	2.32E-18	1.00E+00	9.99E-01	1.0000	1.008E-01	4.099	4.099	
14	1.219E-30	2.3218E-21	4.383E-39	9.68E-57	2.32E-21	1.00E+00	1.00E+00	1.0000	1.008E+00	5.008	5.008	

<sup>a</sup>Free EDTA ligands =  $[\text{EDTA}^{4-}] + [\text{HEDTA}^{3-}] + [\text{H}_2(\text{EDTA})_2^{2-}] + [\text{H}_3(\text{EDTA})] + [\text{H}_4(\text{EDTA})]$ ; anion charge equivalents =  $[\text{Pu}(\text{EDTA})\text{OH}] + 2[\text{Pu}_2(\text{EDTA})_2(\text{OH})_2] + 4[\text{EDTA}^{4-}] + 3[\text{HEDTA}^{3-}] + 2[\text{H}_2(\text{EDTA})_2^{2-}] + [\text{H}_3(\text{EDTA})] + [\text{OH}^-]$

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