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The Solubility of Th(IV) and U(IV) Hydrous Oxides in Concentrated NaCl and MgCl₂ Solutions

By Dhanpat Rai, Andrew R. Felmy, S. Michael Sterner, Dean A. Moore, Marvin J. Mason
Battelle, Pacific Northwest National Laboratory, Richland, Washington 99352, USA

and Craig F. Novak

Sandia National Laboratories, Albuquerque, New Mexico 87185-1320, USA

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Solubility product / Ion-interaction / Solubility / ThO₂(am) / UO₂(am) / Pitzer parameters

Summary

The solubilities of Th(IV) and U(IV) hydrous oxides can be used to set upper limits on Th(IV) and U(IV) concentrations that can leach out of salt repositories which contain concentrated Na and Mg chloride brines. Therefore, the solubilities of Th(IV) and U(IV) hydrous oxides were studied in concentrated solutions of NaCl (ranging up to 6.0 m) and MgCl₂ (ranging up to 3.0 m) over a wide range of H⁺ concentrations and equilibration periods. Extreme precautions (such as the use of pure U(IV) stock solutions, EuCl₂ reducing agent, and deoxygenated waters through equilibrations with Fe powder) were taken to ensure that the dissolved U was present as U(IV). Similar trends of rapidly decreasing solubilities, 3 to 4 orders of magnitude with a unit change in p_{c,H^+} , over very narrow ranges in p_{c,H^+} values, for both hydrous oxides and the oxidation state analyses of aqueous U indicate that U was being maintained as U(IV). The differences in solubility between the two hydrous oxides did not change significantly over wide ranges of chloride concentrations. These solubility data, along with other data available in the literature, are interpreted using Pitzer's ion-interaction model, which requires the use of 1) U⁴⁺, Th⁴⁺, and UOH³⁺ species and binary interactions of these species with Cl⁻, 2) cation-cation and cation-cation-anion interactions involving Th⁴⁺ with bulk electrolyte ions, and 3) log of the solubility products of UO₂(am) and ThO₂(am) of -53.45 and -45.5, respectively. The model predictions agree well with the experimental solubilities of U(IV) and Th hydrous oxides in dilute to concentrated NaCl and MgCl₂ solutions.

Introduction

Thorium and uranium are significant components of nuclear wastes. In the tetravalent state, these elements readily form fairly insoluble crystalline or hydrous oxides which can maintain low aqueous concentrations in natural waters and potential nuclear waste repository environments. For example, uranium(IV) hydrous oxides in dilute solutions show measurable solubilities only under acidic conditions (pH < 4) [1, 2], and Th(IV) hydrous oxides are nearly insoluble in a variety of electrolyte solutions [3, 4]. However, some of the

potential repositories, such as the Waste Isolation Pilot Plant (WIPP) located near Carlsbad, New Mexico, contain concentrated NaCl and MgCl₂ brines in which complexation/ion-interactions or significant changes in activity coefficients could cause the solubility relations of U(IV) and Th(IV) hydrous oxides to differ significantly from those in dilute solutions.

The comprehensive literature review of Wanner and Forest [5] shows that U(IV) forms very weak complexes with Cl⁻. However, Cl⁻ concentrations in a salt repository environment can become as high as 6.0 m. These high Cl⁻ concentrations may significantly influence solubility of U(IV) compounds and hence the aqueous concentrations of U(IV) that can leach out of the repository environment. Appropriate ion-interaction parameters and/or values of complexation constants applicable to the concentrated Cl⁻ solutions are not available in the literature to serve as the basis of reliable predictions of their impact on the solubility of U(IV) compounds. Most of the available Cl⁻ complexation data [5] were obtained in HCl and HClO₄ solutions and at Cl⁻ concentrations lower than those expected in a salt repository environment. Aguilar *et al.* [6] reported limited solubility data of amorphous UO₂ in ≤4 M NaCl solutions. However, data limitations and deficiencies in that study include 1) solubilities were reportedly determined only at pH 7.5, 2) the reported pH values of concentrated salt solutions measured with a pH electrode are meaningless [7] and thus, the results are difficult to interpret, 3) the high (4.65 × 10⁻⁶) reported solubilities at 0.05 M NaCl are noted to be similar to those reported by Bruno *et al.* [8], but are several orders of magnitude higher than others reported since [1, 2, 9]. Because of the difficulty of maintaining reducing conditions [1], such high solubilities are usually due to the presence of U(VI) rather than U(IV). Finally, the data are extremely limited (a total of only 7 data points) and at only one pH.

To date, studies of the solubility of hydrous Th(IV) oxide in chloride solutions (Felmy *et al.* [3] and associated references) have been conducted at chloride concentrations only up to 3 M. Recent thermodynamic models describing the aqueous ion-interactions of

$\text{Th}^{4+}-\text{Cl}^-$ have also been limited to chloride concentrations of approximately 3 M [10]. Since aqueous brines in potential salt repositories can contain ≥ 3 M NaCl as well as significant amounts of MgCl_2 , and because interpolation rather than extrapolation provides for more reliable predictions, experimental data on Th(IV) hydrous oxide solubility in concentrated NaCl/ MgCl_2 solutions are required.

The objective of this study was to measure the solubility of U(IV) and Th(IV) hydrous oxides in NaCl and MgCl_2 solutions to offer empirical insight into their solubilities under WIPP repository conditions and to provide a basis for the development of aqueous thermodynamic models describing the interactions of aqueous U and Th species with bulk electrolyte ions (i.e., Cl^- , Na^+ , and Mg^{2+}). Such thermodynamic models are useful for predicting the solubility of U and Th compounds over a wide range of NaCl and MgCl_2 concentration as well as in mixed electrolyte solutions in the environmentally important pH region. Study of the aqueous chemistry of U(IV) and Th(IV) also provides insight into the chemistry of other tetravalent actinides, such as Np(IV) and Pu(IV).

Methods and materials

Uranium and Th have a number of procedural commonalities. However, because Th exists only in the tetravalent state and tetravalent U can readily oxidize to the hexavalent state, there are also notable differences; it is essential to avoid oxidation of U(IV). All experiments were conducted in an atmospheric control chamber with an Ar atmosphere. Notable procedural differences involved 1) untreated distilled-deionized water for use in Th studies, versus use of water equilibrated with Fe powder for use in U studies; 2) NaCl and MgCl_2 solutions prepared with Fe-powder treated water contained approximately 70 mg of EuCl_2 per liter of solution for use in U studies; 3) 50-ml glass centrifuge tubes with Nalgene® sealing caps for U studies, versus polypropylene centrifuge tubes for Th studies; 4) preparation of the suspensions for Th and U solids in 30 ml and 40 ml of salt solutions, respectively, which, in the case of U contained approximately 50 mg of EuCl_2 ; and 5) solutions separated from U suspensions by Amicon Centricon (Amicon Corp.) filters with 30,000 molecular-weight cutoff and approximately 0.004- μm pore sizes and from Th suspensions by Amicon type F-25 Centriflo membrane cones with a 25,000 molecular-weight cutoffs and approximately 0.0018- μm pore sizes.

Because U(IV) is readily oxidized to U(VI) in the presence of O_2 , several precautions [1] were taken to minimize oxidation during preparation of stock solutions and during the equilibrations. These precautions included 1) preparing the concentrated U(IV) stock solution (~ 666 g U/L) in ~ 0.46 M HCl (where U(IV) is relatively stable), storing it under Ar in a sealed

container, and treating it with U metal immediately before use to ensure the absence of oxidized U; 2) conducting the experiments in low-redox-potential solutions with a calculated O_2 content reduced to $< 10^{-75}$ atm by prior equilibrations with Fe powder; 3) conducting the experiments in the presence of Eu^{2+} to maintain very low O_2 fugacities; 4) filling the sample tubes nearly to capacity to minimize gas space; and 5) sealing the sample tubes during equilibrations and sealing the ion-specific electrodes into the sample containers during measurements to avoid O_2 diffusion.

Reagents

All solutions for Th studies were prepared with distilled-deionized water that was deaerated by boiling and kept in Ar atmosphere until used. In case of U studies, all solutions were prepared with boiled distilled-deionized water that was further deaerated by thorough sparging with N_2 (99.99%) and equilibrating with 325-mesh Fe powder obtained from Alpha Products. These solutions were prepared and stored under Ar atmosphere in an atmospheric control chamber and were kept sealed in glass containers to avoid introduction of even a trace amount of O_2 into the solutions.

Uranium(IV) stock solution was prepared by dissolving Hanford reactor-grade uranium metal according to the procedure discussed by Rai *et al.* [1]. To eliminate any oxidized U species that might have been present in undetectable amounts, the stock solution was treated with U metal (immediately after pickling with concentrated HNO_3 to remove oxidized U species) before each use.

A 100-g/L Th stock solution was prepared by dissolving reagent-grade $\text{Th}(\text{NO}_3)_4 \cdot 4 \text{H}_2\text{O}$ in 0.1 M HNO_3 . Solid EuCl_2 was prepared from Eu_2O_3 of $> 99.9\%$ purity (relative to other rare earths) obtained from American Potash and Chemical Corp. The details of EuCl_2 preparation are reported in Rai *et al.* [1]. The EuCl_2 was stored under Ar in a desiccator containing Dri-rite®. A 5.0 M stock solution of carbonate-free NaOH was prepared in an atmospheric control chamber under Ar atmosphere using reagent grade NaOH obtained from Anachemia Acculute.

Stock solutions of 1.0, 1.82, 2.0, and 3.0 m MgCl_2 and 1.0, 4.0, and 6.0 m NaCl were prepared from reagent-grade chemicals. The stock solutions were acidified to about pH 4 to remove any excess carbonate that may have been present in the reagent-grade chemicals. To remove traces of $\text{O}_2(\text{g})$ from the stock solutions before use in U experiments, approximately 70 mg of EuCl_2 per liter of solution was added to the stock solutions.

Experimental procedures

The experimental procedures used in this study for U and Th experiments were similar to those used by Rai

et al. [1] and Felmy *et al.* [3], respectively. All experiments were conducted in an atmospheric control chamber with a prepurified Ar atmosphere (99.99% Ar, with <10 ppm O₂). The solubility of UO₂(am) and ThO₂(am) in all experiments was approached from the undersaturation direction.

The general procedure consisted of precipitating UO₂(am) and ThO₂(am) and suspending these solids in appropriate chloride solutions, equilibrating the suspensions for different periods, separating the solids from suspensions, and analyzing the aqueous phase.

UO₂(am) was precipitated by 1) pipetting 0.15 to 0.35 ml aliquots of U(IV) stock solution that had been treated with pickled U metal in concentrated HNO₃ immediately before use into 50-ml Oak-Ridge-type glass centrifuge tubes containing 10 ml deoxygenated water and 2) titrating this solution with NaOH to a pH of about 7. ThO₂(am) was precipitated by pipetting 0.625-ml aliquots of the stock solution into 50-ml Oak-Ridge-type polypropylene centrifuge tubes and titrating with NaOH. These precipitates were washed twice with 20 to 30 ml aliquots of deoxygenated water. The centrifuge tubes for U studies were kept tightly capped with Nalgene sealing caps as much of the time as possible during these operations.

Several sets of experiments were conducted with the washed precipitates to determine the solubility of 1) UO₂(am) in 0.03 to 0.1, 0.2, 1.0, and 6.0 m NaCl, and in 1.0, 2.0, and 3.0 m MgCl₂, and 2) ThO₂(am) in 4.0 and 6.0 m NaCl and in 1.0, 1.82, and 3.0 m MgCl₂. An aliquot (30-ml for Th studies and 40-ml for U studies) of the appropriate solution was added to the washed precipitates in centrifuge tubes. Approximately 50 mg of EuCl₂ was added to all of the tubes containing U suspensions. The tubes were capped tightly and placed on a shaker.

Periodically, the pH values of the suspensions were measured with an Orion-Ross combination glass electrode calibrated against pH buffers; the electrode was sealed in the tube to avoid continuous contact with the chamber atmosphere. These measured pH values are not meaningful for concentrated salt solutions of NaCl and MgCl₂, but they can be used in conjunction with correction factors obtained from modified Gran titration procedure [7] to reliably calculate hydrogen ion concentration. In the Gran titration method, the observed/measured pH [pH(obs)] is related to the concentration of hydrogen ions by the equation

$$\text{pH}(\text{obs}) = \text{pc}_{\text{H}^+} - A \quad (1)$$

where c_{H^+} is the hydrogen ion concentration in molarity units and A is a constant. The values of A for different salt solutions were determined (Table 1) according to the procedure described by Rai *et al.* [7].

The Eh values of the U suspensions were measured with a combination platinum electrode calibrated against quinhydrone buffers. The suspensions were centrifuged at 2000 g for 10 minutes. The supernatant from U experiments was filtered through Amicon Cen-

Table 1. Parameters for correcting pH(obs) to pc_{H^+}

Aqueous solution	A
1.0 m NaCl	0.14
4.0 m NaCl	0.489
6.0 m NaCl	0.976
1.0 m MgCl ₂	0.324
1.82 m MgCl ₂	0.708
2.0 m MgCl ₂	0.80
3.0 m MgCl ₂	1.32

^a $\text{pc}_{\text{H}^+} = \text{pH}(\text{obs}) + A$.

tricon (Amicon Corp.) filters with a 30,000 molecular-weight cutoff and approximately 0.004- μm pore sizes. A 0.5 ml solution was passed through the filters and the filtrate discarded before the solution for analysis was filtered. Filtration of Th suspensions was through Amicon type F-25 Centriflo membrane cones with an effective 2500 molecular-weight cutoff and approximately 0.0018- μm pore sizes. These filters are effective in separating solids from solutions [3, 4, 11, 12].

The membranes were pretreated in the following manner: 1) all membranes were soaked in $\sim 0.01 M$ HCl overnight; 2) the membranes were washed with deionized water and then in turn with small aliquots of deionized water, pH-adjusted deionized water (at the approximate pH of the sample), and finally an aliquot of the sample. An aliquot of the filtrate was acidified with Ultrex HNO₃ to determine the concentrations of U, Th, Eu, and Fe by inductively coupled plasma (ICP) and ICP-mass spectroscopy.

Hydrous oxides of U(IV) and Th(IV) are stable in a wide variety of electrolyte solutions, and equilibrium between these solids and chloride and carbonate solutions with a wide range in H⁺ concentrations is reached within a few days [1, 3, 13]. Therefore, the hydrous oxide suspensions were sampled at periods that exceeded the minimum required to reach equilibrium. In addition, the suspensions, in many cases, were sampled at more than one equilibration period to ascertain whether steady state conditions had indeed been reached.

X-ray diffraction patterns of several solids equilibrated for different periods were obtained using Co K _{α} radiation. Representative patterns from the NaCl and MgCl₂ suspensions are shown in Fig. 1. These data showed only a low intensity and very broad peak centered around 3.157 Å (about 33 degrees 2 θ). These patterns are similar to the amorphous solids studied by Rai *et al.* [1] and Bruno *et al.* [8]. Therefore, the solubility results reported in this paper are for the UO₂(am).

Oxidation state analyses of selected samples containing relatively high U concentrations were determined by UV-VIS-IR spectrophotometer and in those containing low concentrations by solvent extraction technique [14].

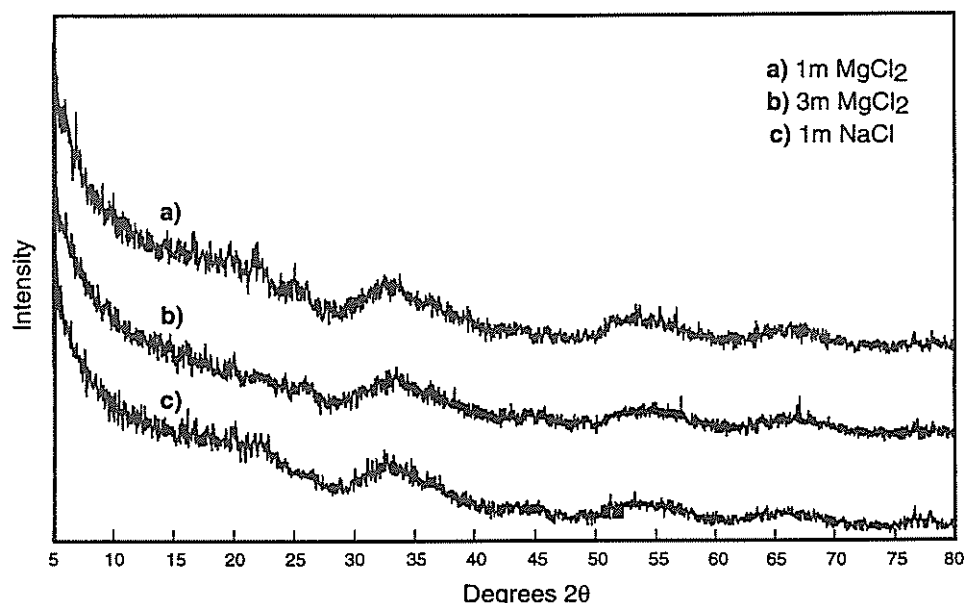


Fig. 1. Tracings of X-ray diffraction patterns of solids separated from suspensions equilibrated in different electrolytes. The lack of $\text{UO}_2(\text{c})$ peaks and the broad hump centered around $2\theta = 33$, where the most intense peak for $\text{UO}_2(\text{c})$ would be expected, are indications that the precipitates are of amorphous UO_2 .

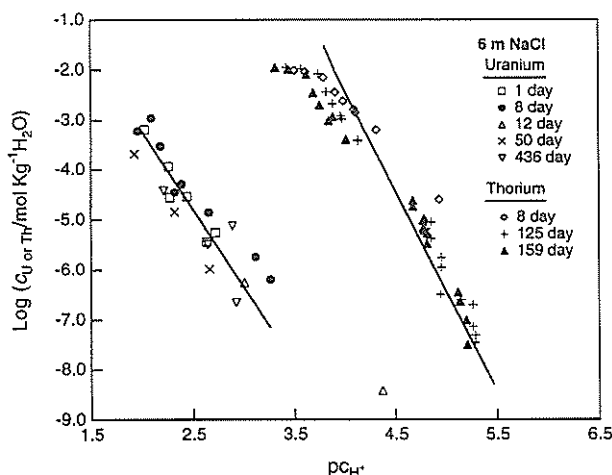


Fig. 2. Solubility of $\text{UO}_2(\text{am})$ and $\text{ThO}_2(\text{am})$ in 6.0 m NaCl at different equilibration periods. Solid lines represent predicted concentrations using the ion-interaction parameters reported in Table 3.

Results and discussion

This section discusses the influence of high chloride solutions on the solubility of Th(IV) and U(IV) hydrous oxides, the comparison of the aqueous behavior of Th(IV) and U(IV) in these systems, and the development of reliable aqueous thermodynamic models to predict the solubility behavior of the hydrous oxide compounds of these elements.

Solubility data for U(IV) and Th(IV) hydrous oxides in the same electrolyte solutions (i.e., 6 m NaCl, and 1, 2, and 3 m MgCl_2 ; Figs. 2–4) clearly show the analogous chemical behaviour of Th(IV) and U(IV) in these concentrated chloride solutions. The solubilities

of both hydrous oxides show similar trends of rapid decrease, 3 to 4 orders of magnitude with a unit change in $p\text{C}_{\text{H}^+}$ over narrow ranges in $p\text{C}_{\text{H}^+}$ values. This analogous solubility behavior has been found previously for Th(IV) and U(IV) hydrous oxides in concentrated carbonate solutions [13] and is a strong indication that, at least in these solutions, U has been maintained as U(IV). Furthermore, the differences in solubility between the two hydrous oxides do not change significantly in the different electrolyte solutions even though the chloride concentration varies from two to six molal.

Although there is certainly some variability in the data, especially for the solubility of $\text{UO}_2(\text{am})$ in 1.0 m MgCl_2 solutions, it does appear that steady state concentrations for U and Th in these hydrous oxide suspensions have been obtained at these high chloride concentrations (Figs. 2–6). In contrast to the results for the concentrated chloride solutions, the observed solubilities of U(IV) hydrous oxide in low chloride solutions are more scattered (Fig. 5). Although the exact reasons for the scatter in the data are not clear (at least for certain samples, especially the 0.03–0.1 m chloride data at 40–46 days of equilibration), a finite amount of U(VI) appears to have been present in the solutions as indicated by the uniform and constantly high concentration of U in the $p\text{C}_{\text{H}^+}$ range of about 3 to 5. This small amount of U(VI) seems to be present despite the precautions taken to maintain a reducing environment. However, at higher chloride concentrations the dominant oxidation state in most of the solutions was U(IV) (based on solvent extraction results reported in Table 2, spectrophotometric analyses of selected solutions containing high U concentrations where no U(VI) was detected, and $\text{UO}_2(\text{am})$ solubility

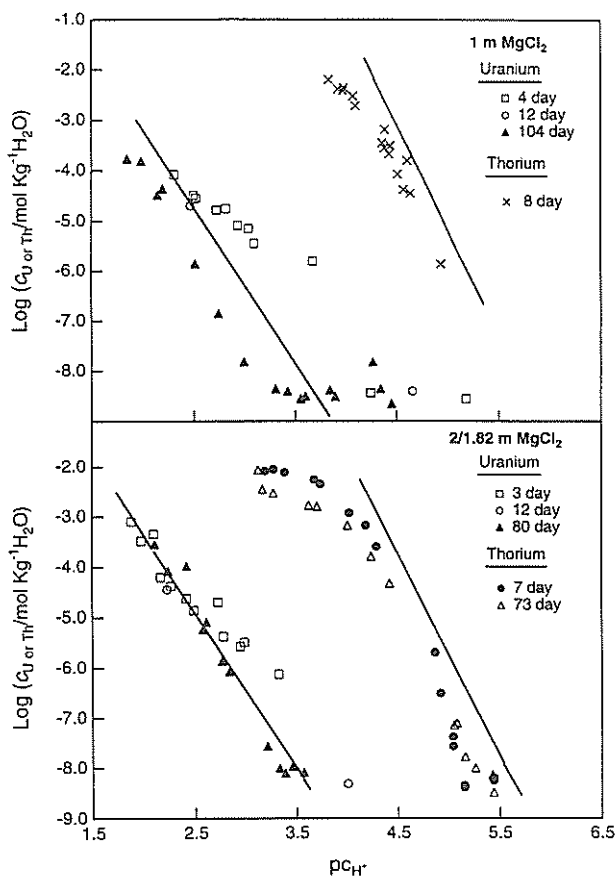


Fig. 3. Solubility of UO₂(am) in 1.0 and 2.0 m MgCl₂ and of ThO₂(am) in 1.0 and 1.82 m MgCl₂ at different equilibration periods. Solid lines represent predicted concentrations using the ion-interaction parameters reported in Table 3.

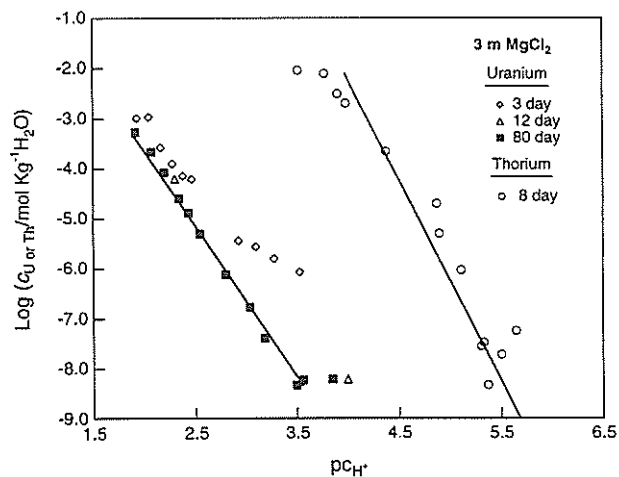


Fig. 4. Solubility of UO₂(am) and ThO₂(am) in 3.0 m MgCl₂ at different equilibration periods. Solid lines represent predicted concentrations using the ion-interaction parameters reported in Table 3.

behavior analogous to ThO₂(am), which does not oxidize).

Thermodynamic analysis

Description of the model

Our solubility data for U(IV) and Th hydrous oxides extend to high ionic strengths (>6 m). Therefore, an

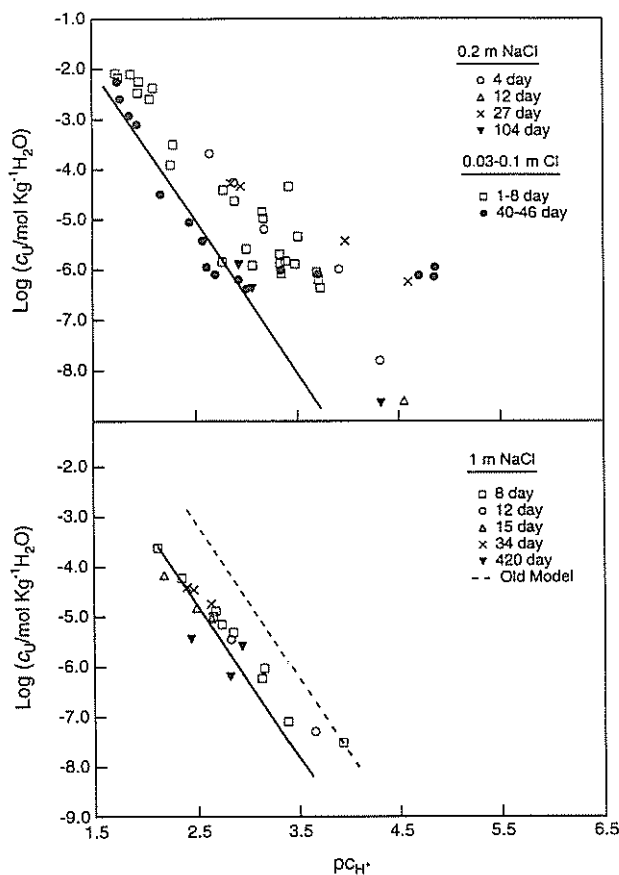


Fig. 5. Solubility of UO₂(am) in <0.2 and 1.0 m NaCl at different equilibration periods. UO₂(am) solubility data at 1–8 days equilibration period in 0.03–0.1 m Cl are from Rai *et al.* [1]. Solid lines represent predicted concentrations using the ion-interaction parameters reported in Table 3. The dashed line represents predicted concentrations using the model [1] parameterized from low ionic strength data.

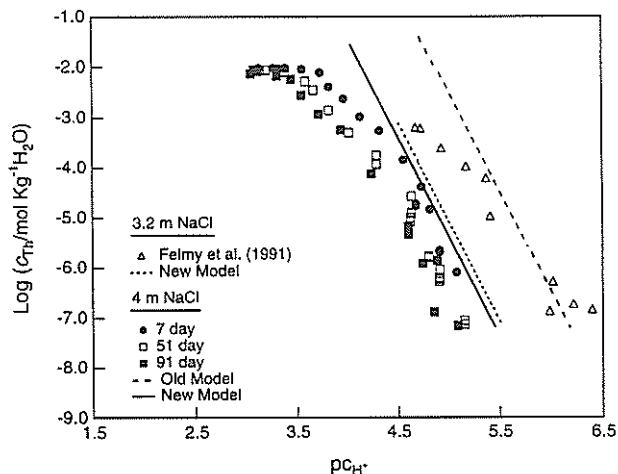


Fig. 6. Solubility of ThO₂(am) in 3.2 and 4.0 m NaCl at different equilibration periods. Solid line represents predicted concentrations for 4.0 m NaCl using the ion-interaction parameters reported in Table 3. The dashed line represents predicted concentrations for 4.0 m NaCl using Roy *et al.* [10] model.

Table 2. Oxidation state distribution of U in solutions equilibrated with $\text{UO}_2(\text{am})$

Equilibration solution	Equilibration period (days)	p_{CO_2}	Oxidation state (%)	
			U(IV)	U(VI)
6.0 m NaCl	50	1.97	95	5
6.0 m NaCl	50	2.20	90	10
6.0 m NaCl	50	2.37	94	6
6.0 m NaCl	50	2.72	97	3
1.0 m NaCl	34	2.65	80	20
1.0 m NaCl	34	2.48	46	54
1.0 m NaCl	34	2.41	29	71
U(IV) stock			80	20

accurate thermodynamic analysis of these systems requires that the thermodynamic model also be valid to high ionic strengths. Pitzer's ion-interaction model for the excess solution-free energy has been shown to accurately calculate solubilities of the solid phases of actinides and other elements in multicomponent electrolyte solutions ranging from zero to high concentrations [15–17]. Pitzer's model [18] emphasizes a detailed description of the specific ion interactions in the solution and was selected for interpreting the data. The ion-interaction parameters used in this study are summarized in Table 3.

Thermodynamic interpretation of solubility data

Our principal objective in this section is to develop the simplest thermodynamic models of the aqueous phase that will satisfactorily account for all of the experimental solubility data on U(IV) and Th(IV) hydrous

oxides in NaCl, MgCl_2 , and dilute solutions, and other reliable available data (osmotic coefficient data for ThCl_4 solutions, EMF data on mixed HCl-ThCl_4 , and spectroscopic data on U(IV) hydrolysis).

The existing Th-Cl model [9] was parameterized using osmotic coefficient and EMF data and $\text{ThO}_2(\text{am})$ solubility in 0.0–3.2 m NaCl. On the other hand, the existing U-Cl model [1] was parameterized using spectroscopic data on U(IV) hydrolysis and $\text{UO}_2(\text{am})$ solubility in <0.1 m NaCl. Preliminary predictions using these models (Figs. 5 and 6 for NaCl) suggest that calculated concentrations are several orders of magnitude higher than the observed solubilities. The difference between the calculated and observed concentrations for the high chloride solutions (6.0 m NaCl and 3.0 m MgCl_2 , data not shown) are even larger than shown in Figs. 5 and 6.

These models predict increasing solubility with increasing NaCl concentration, a trend observed in previous Th work [3] over the NaCl concentration range 0.6 to 3.0 M NaCl. However, the solubility data at higher chloride concentration imply that this trend for Th vanishes by about 3 m NaCl. In contrast to Th system, the solubilities of $\text{UO}_2(\text{am})$ do not appear to change as a function of NaCl or MgCl_2 at a given p_{CO_2} (Fig. 7). Therefore, existing models cannot be used to reliably predict the Th(IV) and U(IV) solubilities at these higher chloride concentrations.

No specific ion-interaction parameters are available for U^{4+} and UOH^{3+} , which are expected to be the important aqueous species in these solutions. In the absence of such parameters, Rai *et al.* [1] interpreted their $\text{UO}_2(\text{am})$ solubility in 0.03–0.1 m NaCl using 1) $\text{Th}^{4+}-\text{Cl}^-$ binary interaction parameters ($\beta^{(0)} = 1.014$, $\beta^{(1)} = 13.3$, and $C^\phi = -0.103$) from Pitzer and Mayorga [19] for $\text{U}^{4+}-\text{Cl}^-$, and 2) $\text{UOH}^{3+}-\text{Cl}^-$ pa-

Table 3. Pitzer ion-interaction parameters used in this study

	Binary parameters			C^ϕ	Reference
	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$		
Na^+, Cl^-	0.0765	0.2644	0.0	0.00127	[17]
$\text{Mg}^{2+}, \text{Cl}^-$	0.3524	1.6815	0.0	0.00519	
$\text{Na}^+, \text{ClO}_4^-$	0.0554	0.2755	0.0	-0.00118	[19]
Na^+, OH^-	0.0864	0.253	0.0	0.0044	[17]
H^+, Cl^-	0.1775	0.2945	0.0	0.0008	[17]
$\text{H}^+, \text{ClO}_4^-$	0.1747	0.2931	0.0	0.00819	[19]
$\text{Th}^{4+}, \text{Cl}^-$	1.092	13.7	-160.	-0.112	[10]
$\text{U}^{4+}, \text{Cl}^-$	1.644	15.5	0.0	0.1	This study
$\text{UOH}^{3+}, \text{Cl}^-$	1.00	7.856	0.0	0.0	This study
Common-ion ternary parameters			Reference		
$\phi_{\text{Na}^+, \text{H}^+}$	=	0.036			[17]
$\phi_{\text{Cl}^-, \text{OH}^-}$	=	-0.050			[17]
$\phi_{\text{Th}^{4+}, \text{Na}^+}$	=	0.42			This study
$\phi_{\text{Th}^{4+}, \text{Mg}^{2+}}$	=	0.60			This study
$\psi_{\text{Na}^+, \text{H}^+, \text{Cl}^-}$	=	-0.004			[17]
$\psi_{\text{Na}^+, \text{Cl}^-, \text{OH}^-}$	=	-0.006			[17]
$\psi_{\text{Th}^{4+}, \text{Na}^+, \text{Cl}^-}$	=	0.21			This study
$\psi_{\text{Th}^{4+}, \text{Mg}^{2+}, \text{Cl}^-}$	=	0.21			This study

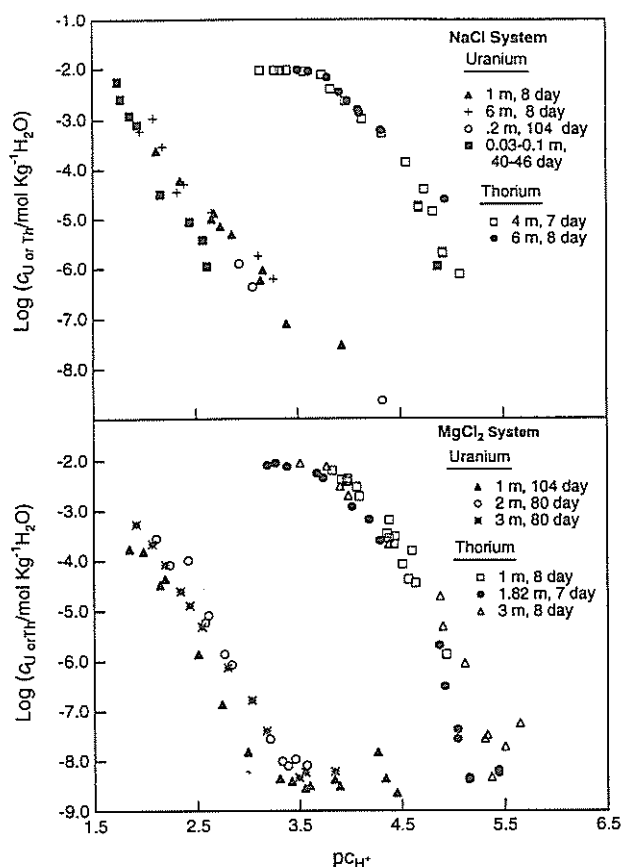


Fig. 7. Solubility of $\text{UO}_2(\text{am})$ and $\text{ThO}_2(\text{am})$ in several different concentrations of NaCl and MgCl_2 at equilibration periods selected to represent the data in a given system for thermodynamic modeling (primarily long-term equilibration data of U and short-term equilibration data for Th systems were selected using the ion-interaction parameters reported in Table 3).

rameters ($\beta^{(0)} = 0.17$, $\beta^{(1)} = 6.2$, and $C^\phi = 0.03$) that were obtained from fitting the U^{4+} hydrolysis data of Kraus and Nelson [20] in conjunction with $\text{U}^{4+}-\text{Cl}^-$ parameters as listed above. This model or any simple electrostatic model will provide reliable predictions of low ionic strength data. However, it will not provide reliable predictions of $\text{UO}_2(\text{am})$ solubility in concentrated solutions because 1) Th^{4+} is not a good analog for U^{4+} , since $\text{ThO}_2(\text{am})$ solubility increases with the increase in NaCl concentration from 0.0 to 3.0 molal NaCl [3], whereas the observed $\text{UO}_2(\text{am})$ solubilities in dilute and concentrated solutions are similar (Fig. 2), and 2) thermodynamic predictions are reliable when interpolated, but questionable when extrapolated, as they would be in this case. As expected, this model based on low ionic strength data overpredicts the $\text{UO}_2(\text{am})$ solubility in 1.0 m NaCl by about one order of magnitude, and in 6.0 m NaCl by several orders of magnitude (calculations for only 1 m NaCl are shown, Fig. 5).

To develop a model that can explain the observed solubilities in all of the solutions and that is consistent with the U(IV) hydrolysis data of Kraus and Nelson [20], several fitting parameters (binary between positively charged U species and Cl^- , and ternary between

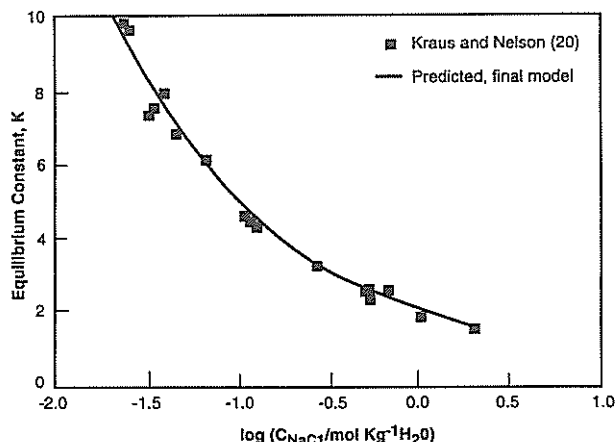


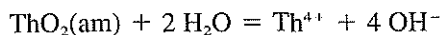
Fig. 8. Effect of NaCl concentration on the equilibrium constant of the reaction $[\text{U}^{4+} + \text{H}_2\text{O} = \text{U}(\text{OH})^{3+} + \text{H}^+]$. The data points are from Kraus and Nelson [20] and the curve represents predicted values based on data in Table 3 and those discussed in text.

positively charged U species and $\text{Mg}^{2+}-\text{Cl}^-$ or Na^+-Cl^-) in different combinations were tried. The simplest model that provided the best fit to all of the data included $\beta^{(0)} = 1.644$, $\beta^{(1)} = 15.5$, and $C^\phi = 0.0995$ for $\text{U}^{4+}-\text{Cl}^-$; $\beta^{(0)} = 1.0$ and $\beta^{(1)} = 7.856$ for $\text{UOH}^{3+}-\text{Cl}^-$; and $\Delta_r G^\circ/RT$ values for $\text{UOH}^{3+} = -308.7$, $\text{U}^{4+} = -214.19$, and $\text{UO}_2(\text{am}) = -399.67$. Other ancillary data, ion-interaction parameters, used in these calculations are reported in Table 3. These parameters for $\text{U}^{4+}-\text{Cl}^-$ and $\text{UOH}^{3+}-\text{Cl}^-$ appear to be reasonable in both sign and absolute value (e.g., see Pitzer [21] for comparison to values for 4:1 and 3:1 electrolyte parameters; $\text{Th}^{4+}-\text{Cl}^-$ parameters discussed below for comparison to $\text{U}^{4+}-\text{Cl}^-$). The value of the log of solubility product for the reaction ($\text{UO}_2(\text{am}) + 2 \text{H}_2\text{O} = \text{U}^{4+} + 4 \text{OH}^-$) that best described these data was calculated to be -53.45 . This value is about 1.5 orders of magnitude lower than that calculated from the low ionic strength and short-term data [1] and we believe that this value is more reflective of the solubility product for relatively aged $\text{UO}_2(\text{am})$. The predicted and observed concentrations in equilibrium with $\text{UO}_2(\text{am})$ are compared in Figs. 2–5. These comparisons show that this model can satisfactorily predict the solubility of $\text{UO}_2(\text{am})$ in both the dilute and concentrated solutions. Although not shown, the model predicts UOH^{3+} to be the dominant solution species in all cases. The observed effects of NaCl (ranging from 0.02 to 2 m) on the equilibrium constant of U(IV) hydrolysis reaction ($\text{U}^{4+} + \text{H}_2\text{O} = \text{UOH}^{3+} + \text{H}^+$) reported by Kraus and Nelson [20] and those predicted by the model are in excellent agreement (Fig. 8). Therefore, the model is applicable to low to high chloride systems and is consistent with not only the observed $\text{UO}_2(\text{am})$ solubility, but also with the spectrophotometric data involving hydrolysis of U(IV).

In the case of $\text{ThO}_2(\text{am})$ solubility in NaCl and MgCl_2 , strong specific ion interactions are likely to occur between the Th^{4+} ion and the bulk anion Cl^- . Roy *et al.* [10] obtained the necessary $\text{Th}^{4+}-\text{Cl}^-$ ion-

interaction parameters (i.e., $\beta^{(0)}$, $\beta^{(1)}$, and $C^{(b)}$) from an analysis of osmotic coefficient data for ThCl_4 solutions.

The solubility product of Th(IV) hydrous oxide was initially calculated by Felmy *et al.* [3] from the data of Ryan and Rai [4] for a low-total-Th-concentration ($\sim 1 \times 10^{-5} M$) dilute solution ($I \sim 0.005$). In this calculation, polynuclear species should not be important and formation of mononuclear hydrolysis species was neglected. The calculation yields $\log K = -45.5$ for the reaction



This value for $\log K$ is in excellent agreement with that of Ryan and Rai [4], if their correction for hydrolysis species is ignored.

The simple model discussed in this paper, which assumes the presence of only Th^{4+} ions (an amorphous Th oxide) and specific ion-interaction parameters for Th^{4+} with Cl^- , predicts higher solubilities than the measured values, at least for NaCl concentrations $> 3 M$ (Fig. 6). Important aqueous ion interactions are obviously being neglected, especially those between ions of like sign (i.e., $\Theta_{\text{Na}^+, \text{Th}^{4+}}$, $\Theta_{\text{Mg}^{2+}, \text{Th}^{4+}}$, $\Psi_{\text{Na}^+, \text{Th}^{4+}, \text{Cl}^-}$, and $\Psi_{\text{Mg}^{2+}, \text{Th}^{4+}, \text{Cl}^-}$). These parameters are important only in highly concentrated solutions, which is precisely where the current thermodynamic model fails. Several attempts were made to determine these parameters from the experimental solubility data in both NaCl and MgCl_2 solutions. The simplest combination that gave reasonable agreement with all of the solubility data yields, $\Theta_{\text{Na}^+, \text{Th}^{4+}} = 0.42$, $\Theta_{\text{Mg}^{2+}, \text{Th}^{4+}} = 0.60$, $\Psi_{\text{Na}^+, \text{Th}^{4+}, \text{Cl}^-} = 0.21$, and $\Psi_{\text{Mg}^{2+}, \text{Th}^{4+}, \text{Cl}^-} = 0.21$. These parameters are reasonable both in sign and absolute value when compared to the corresponding values for $\text{H}^+ - \text{Th}^{4+}$ (i.e., $\Theta_{\text{H}^+, \text{Th}^{4+}} = 0.60$ and $\Psi_{\text{H}^+, \text{Th}^{4+}, \text{Cl}^-} = 0.37$) reported by Roy *et al.* [10]. A comparison of this revised model with the experimental data in NaCl solutions (Figs. 2 and 6) and MgCl_2 solutions (Figs. 3 and 4) shows excellent agreement with all of the data in MgCl_2 solutions and with most of the data in NaCl solutions except for the 3.2 m NaCl data, which are at higher $p_{\text{C}_{\text{H}^+}}$ values (Fig. 6). Because of the higher $p_{\text{C}_{\text{H}^+}}$ values for the 3.2 m NaCl data, it is possible that hydrolysis species (such as ThOH^{3+}) could be important, although it is impossible to precisely determine such effects from this data alone (see the next paragraph for additional discussion of ThOH^{3+}). Nevertheless, with the possible exception of the 3.2 m NaCl data set, the present model gives very reasonable predictions for all Th(IV) hydrous oxide solubility data in NaCl and MgCl_2 solutions as well as the existing osmotic data on ThCl_4 solutions and the EMF data in the $\text{ThCl}_4\text{-HCl-H}_2\text{O}$ system.

It is of interest to discuss the importance of Th(IV) complexation with Cl^- and the possible hydrolysis behavior of Th(IV) in terms of the thermodynamic model we have described. In the case of Th(IV) complexation with chloride, such effects have been implicitly included by our use of Pitzer ion-interaction parameters

between Th^{4+} and Cl^- , especially the use of a large negative value for β^2 . Including the thermodynamic effects of Cl^- within the expressions for activity coefficients represents a much simpler formalism than introducing multiple $\text{Th}^{4+} - \text{Cl}$ -complexes within our model. In the case of Th(IV) hydrolysis, multiple hydrolysis species could be present in these solutions, and each of these species (e.g., ThOH^{3+} and $\text{Th}(\text{OH})_2^{2+}$) could also exhibit independent activity relations with the background electrolyte (described through ion-interaction parameters such as $\text{ThOH}^{3+} - \text{Cl}^-$). As a result, the potential importance of hydrolysis species can not be uniquely defined from these data alone. However, previous studies of monomeric hydrolysis (especially involving ThOH^{3+} and $\text{Th}(\text{OH})_2^{2+}$) are not inconsistent with our model. As an example, if we accept the equilibrium constant for the formation of the $\text{Th}(\text{OH})^{3+}$ species given by Grenthe and Lagerman [22] and use our values for the ion-interaction parameters for $\text{UOH}^{3+} - \text{Cl}^-$ as analogs for the $\text{ThOH}^{3+} - \text{Cl}^-$, then the calculated concentrations of ThOH^{3+} in our model never contributes significantly to the total calculated Th concentration in any of our NaCl or MgCl_2 solutions. In a similar fashion, if we accept the hypothesis that the formation constants for Th(IV) hydrolysis species are stepwise additive with a difference in $\log K$ values of approximately four for the first through fourth hydrolysis steps [22], then the second hydrolysis species contributes even less to the total calculated Th concentration than the first hydrolysis species unless unrealistically high negative values are used for the Pitzer ion-interaction parameters. Therefore, although the importance of hydrolysis species in these solutions can not be entirely discounted, especially in the 3.2 m NaCl solutions, it does appear that the changes in solubility can be modeled simply by assuming strong ion-interactions with the highly charged Th^{4+} ion rather than invoking numerous weaker interactions with the less highly charged hydrolysis species. More definitive spectroscopic, X-ray absorption, or other speciation measurements would need to be made on these solutions to better define the relative importance of hydrolysis and chloride complexation in these solutions.

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