

INFO #: 18813394

LOS ALAMOS NATIONAL LABORATORY
Jean-Francois Lucchini

Entered: 10/20/2008 2:33:00PM

NB 10/27/2008
12:00 AM PT
A

SHIP VIA: **Ariel**

Ariel

FILLED ON: 10/21/2008

Infotrieve, Inc.

1888 Century Park East, Ste 600

Los Angeles, CA 90067

Phone 800-422-4633 or 203-423-2175

Fax



Holdings

Send article only if in the Library collection

NB 10/27/2008
12:00 AM PT
A

SHIP TO: 14288 / 2205718

LOS ALAMOS NATIONAL LABORATORY

Jean-Francois Lucchini

A141

Please contact us if you have questions or comments regarding this article.

Email: service@infotrieve.com

Phone: (800) 422-4633

CUSTOMER INFO

PHONE: +1.575.234.5556

FAX: +1.575.887.3051

TEAM: T8-14288

COURIER:

ARTICLE INFORMATION

ARIEL:

0033-8230

NOTES:

Radiochimica Acta

82():pp. 17 25 1998

Main 1962-1993

Publisher 2000-2002 Online

A thermodynamic model for the solubility of $UO_2(am)$ in the aqueous K_2CO_3

Send article only if in the Library collection

CCD	0
SHIP VIA	Ariel
ORDER #	
BILLING REF	
ORDERED ON	10/20/2008
FILLED ON	10/21/2008
NEED BY	10/27/2008
ATTENTION	Jean-Francois Lucchini
INFO #	18813394

This document is protected by U.S. and International copyright laws. No additional reproduction is authorized. Complete credit should be given to the original source.

A Thermodynamic Model for the Solubility of $\text{UO}_2(\text{am})$ in the Aqueous K^+ - Na^+ - HCO_3^- - CO_3^{2-} - OH^- - H_2O System

By Dhanpat Rai, Andrew R. Felmy, Nancy J. Hess, Dean A. Moore

Pacific Northwest National Laboratory, Richland, Washington 99352, USA

and Mikazu Yui

Power Reactor and Nuclear Fuel Development Corporation, Tokai Works, Tokai, Japan

(Received December 15, 1997; accepted in revised form March 31, 1998)

*UO₂(am) / Solubility / Thermodynamics / U(IV)
hydrous oxide / U(CO₃)₅⁶⁻ / Carbonate complexes*

Summary

Solubility data for $\text{UO}_2(\text{am})$ were determined in the aqueous K^+ - Na^+ - HCO_3^- - CO_3^{2-} - OH^- - H_2O system extending to high concentrations of carbonate, bicarbonate, and mixed carbonate-hydroxide. Several precautions were taken, including the use of reductants (Fe powder and $\text{Na}_2\text{S}_2\text{O}_4$), to maintain uranium in the tetravalent state. A combination of techniques (UV-Vis-IR, X-ray absorption spectroscopy [XAS], and solvent extraction) were used to identify species and oxidation states in the solid and aqueous phases. The most important species in CO_3^{2-} and relatively concentrated HCO_3^- solutions was $\text{U}(\text{CO}_3)_5^{6-}$, which was identified by UV-Vis-IR and XAS techniques. The predicted minimum set of dominant species that reasonably described all of the experimental data were 1) $\text{U}(\text{CO}_3)_5^{6-}$ in low to high concentrations of carbonate and hydroxide and in high concentrations of bicarbonate, and 2) $\text{U}(\text{OH})_2(\text{CO}_3)_2^{2-}$ in low concentrations of bicarbonate. Because $\text{U}(\text{CO}_3)_5^{6-}$ is highly charged, the values of formation constants involving this species depend on the choice of ion-interaction parameters. The values of $\beta^{(0)}$ and $\beta^{(1)}$, Pitzer modeling parameters, for $\text{U}(\text{CO}_3)_5^{6-}$ with Na^+ or K^+ that best described the experimental data were 1.5 and 31.3, respectively, and are similar to the recently determined values ($\beta^{(0)} = 1.31$ and $\beta^{(1)} = 30.0$) for analogous Th(IV) species. The logarithm of the thermodynamic equilibrium constant for the $\text{UO}_2(\text{am})$ dissolution reaction ($\text{UO}_2(\text{am}) + 5\text{CO}_3^{2-} + 4\text{H}^+ \rightleftharpoons \text{U}(\text{CO}_3)_5^{6-} + 2\text{H}_2\text{O}$) was found to be 33.8, and for ($\text{UO}_2(\text{am}) + 2\text{HCO}_3^- \rightleftharpoons \text{U}(\text{OH})_2(\text{CO}_3)_2^{2-}$). This value was found to be -4.8. These values, when combined with the solubility product of $\text{UO}_2(\text{am})$ ($\log K_{\text{sp}} = -53.44$), provided the following values of the logarithm of the equilibrium constant: for ($\text{U}^{4+} + 5\text{CO}_3^{2-} \rightleftharpoons \text{U}(\text{CO}_3)_5^{6-}$) the value was 31.29 and for ($\text{U}^{4+} + 2\text{CO}_3^{2-} + 2\text{OH}^- \rightleftharpoons \text{U}(\text{OH})_2(\text{CO}_3)_2^{2-}$) the value was 41.33.

Introduction

Carbonic acid, bicarbonate ion, or carbonate ion, are ubiquitous components of groundwater systems. Various carbonate species form aqueous complexes with several actinide ions including Am^{3+} , UO_2^{2+} , NpO_2^+ , Th^{4+} , Np^{4+} , Pu^{4+} , and U^{4+} . The carbonate complexes with the tetravalent actinides can be especially strong [1–3]. Such strong complexes may increase the solubility of oxides and hydrous oxides of tetravalent actinides, which could be the solubility-controlling solids in nuclear waste repositories.

Grenthe *et al.* [1] provided a comprehensive review of the literature for U(IV)-carbonate complexation. Except for the $\text{U}(\text{CO}_3)_5^{6-}$ and $\text{U}(\text{CO}_3)_4^{4-}$ complexes identified through spectroscopic techniques [4, 5], they found no definitive experimental information for proposed U(IV) complexes, such as $\text{U}(\text{OH})_2\text{CO}_3^0$, $\text{U}(\text{OH})_2(\text{CO}_3)_2^{2-}$, $\text{U}(\text{OH})_3(\text{CO}_3)_2^{4-}$, or $\text{U}(\text{OH})_2(\text{CO}_3)_4^{6-}$ [6, 7]. Reasons for the lack of reliable information on U(IV) carbonate species and our resulting inability to predict the solubility behavior of $\text{UO}_2(\text{am})$ in carbonate systems are 1) lack of analytical techniques to identify species in low concentrations, typical of most environmentally important systems, 2) difficulties in preventing oxidation of U(IV) to U(VI) during experiments and analyses, and 3) inadequate experimental data on $\text{UO}_2(\text{am})$ solubility in carbonate solutions over a wide range of carbonate and OH concentrations. Although none of the mixed hydroxide and carbonate species of U(IV) have been identified, a great deal of evidence indicates that such species are important in describing the aqueous behavior of tetravalent actinides [3, 8, 9].

Bruno and colleagues [5] used Vis-UV spectrophotometry to study the equilibrium between the penta and tetracarbonate complexes of U(IV). They reported the logarithms of the equilibrium constants as 3.5 and -1.12 in 3 M NaClO_4 and at zero ionic strength, respectively, for the reaction $\text{U}(\text{CO}_3)_4^{4-} + \text{CO}_3^{2-} \rightleftharpoons \text{U}(\text{CO}_3)_5^{6-}$. The logarithm of the equilibrium constant for ($\text{U}^{4+} + 5\text{CO}_3^{2-} \rightleftharpoons \text{U}(\text{CO}_3)_5^{6-}$) in 3 M NaClO_4 was estimated to be 40 by Ciavatta *et al.* [4] from their potentiometric data involving equilibrium between the U(IV)-U(VI) couple. This value was later revised to 38.6 by Bruno *et al.* [5] and to 36.86 by Grenthe *et al.* [1], who used different revised auxiliary data in their calculations. Uncertainties in the reported equilibrium constants are large, even for these species that can be identified spectrophotometrically. Also, it is difficult to extrapolate equilibrium constants for these highly charged species ($\text{U}(\text{CO}_3)_4^{4-}$ and $\text{U}(\text{CO}_3)_5^{6-}$) from data in concentrated electrolytes to zero ionic strength. Bruno *et al.* [5] also state that the specific ion interaction (S.I.T.) theory, used to interpret these data, "is less satisfactory for equilibria involving complexes with very high negative charges where ionic pairing with the cat-

ion of the ionic medium may occur." Therefore, there is a clear need for better understanding of the equilibria in the U(IV) carbonate system.

We recently [2] reported extensive data on the solubility of $\text{UO}_2(\text{am})$ in carbonate and mixed carbonate-hydroxide systems. Extreme precautions were taken during the experiments to maintain uranium in the tetravalent state. In spite of these precautions, it was difficult to maintain uranium in the tetravalent state in some of the systems, especially involving low carbonate and bicarbonate. Oxidation-state analyses and systematic trends in most of the U(IV) solubility data similar to those for Th(IV), which is not redox sensitive, indicated that dissolved uranium was present as U(IV) in most of the sets. To the best of our knowledge, no other reliable solubility data exist that cover such a broad range of carbonate, bicarbonate, and hydroxide concentrations for U(IV) hydrous oxide.

To augment these $\text{UO}_2(\text{am})$ solubility data [2], additional studies were conducted as part of this research using $\text{Na}_2\text{S}_2\text{O}_4$ as the reductant in the variable carbonate and bicarbonate systems. In addition, the solubility of $\text{UO}_2(\text{am})$ was determined over a larger range in hydroxide concentrations, but at a fixed carbonate concentration. X-ray absorption spectroscopy was used to identify aqueous species and solid phases in these systems. The data presented by Rai *et al.* [2], along with these new data, are collectively used in developing a reliable thermodynamic model that describes the solubility of $\text{UO}_2(\text{am})$ in these concentrated solutions. We used the ion-interaction model of Pitzer [10, 11] to interpret these data. The Pitzer approach emphasizes a detailed description of the effects of all of the specific ion interactions in the system. We also used this approach to interpret the analogous Th(IV)- CO_3 system [9], thus the modeling results on these two important actinides can be directly compared.

Methods and materials

Detailed experimental procedures are described by Rai *et al.* [2]. A brief summary of the important aspects is presented here.

Special precautions for U(IV)

Because U(IV) is readily oxidized to U(VI) in the presence of O_2 , several precautions were taken by Rai *et al.* [2] and in this study to minimize oxidation during preparation of the stock solution and during equilibration. These precautions included 1) preparing the concentrated U(IV) stock solution (~ 666 g U/L) in ~ 0.46 M HCl, in which U(IV) is relatively stable, storing the solution under N_2 in a sealed container, and treating it with uranium metal immediately before use to ensure the absence of more oxidized uranium species; 2) conducting the experiments in solutions prepared with low-redox potential waters obtained by equilibration with Fe powder (calculated O_2 content reduced to $<10^{-7.5}$ atm); 3) conducting the experi-

ments in the presence of Fe powder or $\text{Na}_2\text{S}_2\text{O}_4$ to maintain very low O_2 fugacities; 4) filling the sample tubes to near capacity to minimize the gas space; 5) sealing the sample tubes during equilibration, sealing the ion-specific electrodes into the sample containers during measurements to avoid O_2 diffusion; and 6) conducting the experiments in an atmospheric control chamber with an argon atmosphere.

Experimental procedure

All experiments were conducted in a controlled atmosphere chamber with a prepurified argon atmosphere (99.99%, with <10 ppm O_2). The solubility of $\text{UO}_2 \cdot x\text{H}_2\text{O}(\text{am})$ in all experiments was approached from the undersaturation direction.

The general procedure consisted of precipitating the $\text{UO}_2 \cdot x\text{H}_2\text{O}(\text{am})$, washing the precipitate, suspending the precipitate in the appropriate carbonate solutions, equilibrating the suspensions for different periods, separating the solids from solutions, and analyzing the aqueous phase. In the case of experiments using $\text{Na}_2\text{S}_2\text{O}_4$, the precipitates were washed with water that contained this reducing agent. Solids from equilibrated suspensions were separated from solutions by filtration through Amicon Centricon (Amicon Corp., Lexington, MA) filters with 30,000 molecular-weight cutoff and approximately 0.004 nm pore sizes. The aqueous phase was analyzed for 1) total uranium by inductively coupled plasma mass spectroscopy (ICP-MS); 2) uranium oxidation states in a few selected samples were analyzed by solvent extraction methods [12], Vis-UV spectroscopy, and XAS; 3) carbonate complexes were analyzed by UV-Vis spectroscopy and XAS; and 4) the solid phases were identified by XAS and X-ray diffraction.

X-ray absorption spectra on the samples were collected at the Stanford Synchrotron Radiation Laboratory at the U L_{III}-edge to 13 \AA^{-1} in fluorescence mode using a 13 element Ge detector. The extended X-ray absorption fine structure (EXAFS) and X-ray absorption near edge structure (XANES) were extracted from the absorption spectrum following standard practice [13]. The EXAFS was modeled using crystallographic data from the literature for guanidinium pentacarbonatothorate tetrahydrate [14] as input for the *ab initio*, multiple scattering code FEFF7.02 [15, 16].

The solubility of $\text{UO}_2 \cdot x\text{H}_2\text{O}(\text{am})$ and modeling of these data discussed in this report pertain to the following systems:

- NaHCO_3 0.02 to 1.03 m
- KHCO_3 0.02 to 1.04 m
- Na_2CO_3 0.0003 to 2.05 m with 0.01 molar NaOH
- K_2CO_3 0.3 to 6.24 m with 0.01 molar NaOH or KOH
- NaOH 0.01 to 0.10 m with 3.0 m K_2CO_3
- KOH 0.01 to 0.8 m with 3.3 m K_2CO_3 .

The complete solubility data corresponding to these systems are reported in appendix Tables A.1 through A.3.)

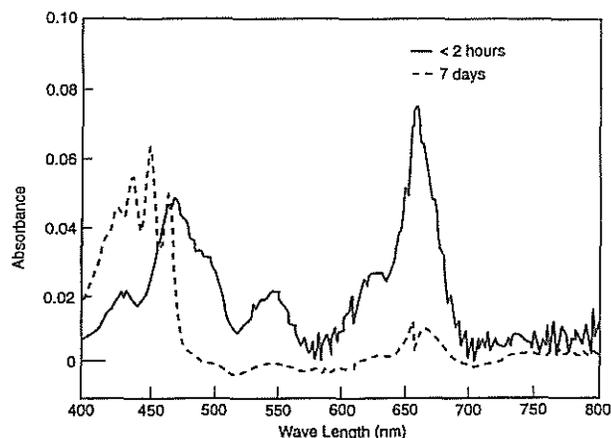


Fig. 1. Tracings of Vis-UV spectrophotometric pattern of a solution from $\text{UO}_2(\text{am})$ in 0.9 m NaHCO_3 (<2 hours) indicating the presence of only U(IV) and the absence of U(VI). (U(IV) had oxidized upon standing for 7 days and showed characteristic peaks for U(VI) carbonate solutions.)

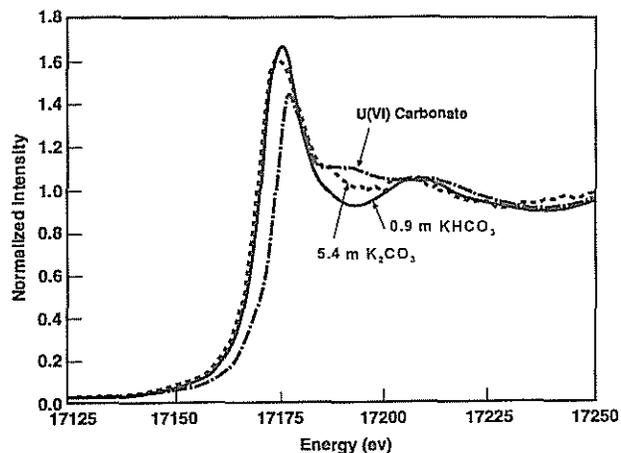


Fig. 2. Normalized XAS spectra. A weak shoulder at 17180 eV in 5.4 m K_2CO_3 indicates the presence of a small fraction of U(VI) in this sample. Both samples show the presence of $\text{U}(\text{CO}_3)_2^{2-}$.

Thermodynamic model

The aqueous thermodynamic model used in this study to interpret the solubility data is the ion-interaction model of Pitzer and coworkers [10, 11]. The Pitzer thermodynamic model was used because it is applicable from zero to high concentration, and our solubility data in carbonate and bicarbonate solutions extend to high ionic strength. General difficulties in describing the activity relations for highly charged aqueous species in concentrated electrolytes are discussed by Felmy *et al.* [9].

The thermodynamic analyses described in this paper were conducted using the INSIGHT model [17]. INSIGHT calculates chemical equilibria involving multiple solid and aqueous species, including the formation of aqueous complexes. In the present application, INSIGHT was used to evaluate parameters for the Pitzer ion-interaction electrolyte model.

Table 1. Oxidation state analysis of samples by solvent extraction

$(C_{\text{K}_2\text{CO}_3}/\text{mol kg}^{-1})^a$	U(IV) (%)	$(C_{\text{KHCO}_3}/\text{mol kg}^{-1})^b$	U(IV) (%)	$(C_{\text{KOH}}/\text{mol kg}^{-1})^c$	U(IV) (%)
0.001	<1	0.02	23	0.01	58
0.003	<1	0.04	87	0.02	94
0.01	<1	0.06	88	0.03	95
0.03	<1	0.07	90	0.05	98
0.10	<1	0.08	95	0.06	97
0.30	35	0.09	93	0.07	94
0.51	80	0.10	95	0.08	97
0.82	87	0.20	97	0.09	96
1.03	93	0.30	>99	0.10	96
1.35	97	0.41	98	0.11	93
1.79	96	0.51	>99	0.34	37
2.12	94	0.62	>99	0.56	<1
2.47	95	0.72	>99	0.68	<1
2.96	98	0.83	>99	0.79	<1
3.33	97	0.93	>99		
3.72	98	1.05	>99		
4.26	92				
4.70	96				
5.13	94				
5.44	97				

^a Also contained 0.01 molar hydroxide, after 13-day equilibration.

^b 2-day equilibration.

^c In the presence of 3.3 m K_2CO_3 , after 14-day equilibration.

Results and discussion

Aqueous species

Solubilities of $\text{UO}_2(\text{am})$ were modeled in 1) fixed NaOH and varying concentrations of Na_2CO_3 or K_2CO_3 , 2) fixed total carbonate and varying concentrations of NaOH or KOH, and 3) varying concentrations of NaHCO_3 or KHCO_3 . General trends in the solubility data of some of these systems and comparisons to the Th(IV) data are presented by Rai *et al.* [2] along with evidence that uranium, in most cases, was maintained as U(IV). Spectrophotometric and XAS analyses, possible only for samples very high in uranium and very high in HCO_3^- and CO_3^{2-} , show primarily the presence of U(IV) and only small amounts of U(VI) (Figs. 1 and 2), supporting the conclusion that uranium was present as U(IV). Solvent extraction techniques were used to analyze the oxidation state of all of the samples involving $\text{Na}_2\text{S}_2\text{O}_4$. The results indicated that several dilute carbonate and bicarbonate and high KOH solutions contained either high concentrations of U(VI), or the concentrations were very close to the detection limits such that it was difficult to reliably ascertain the oxidation states (Table 1). It should be noted that there are several inherent difficulties in determining oxidation states by solvent extraction. For example, the oxidation state distribution could change after the representative aliquots are separated from the sample containers due to inadvertent introduction of oxygen or change in reactivity of redox agents in response to changes in pH of the samples. Hence, solvent extraction results should be used in

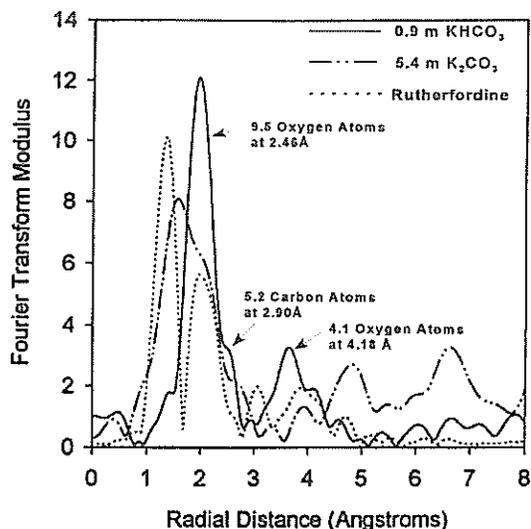


Fig. 3. Comparison of the Fourier transforms of uranium aqueous solutions to Rutherfordine, U(IV) carbonate. The fitting results to EXAFS for the U(IV) bicarbonate solution are annotated and clearly indicate the presence of $U(CO_3)_3^{6-}$ species.

conjunction with other data to infer the dominant oxidation states. Therefore, the combination of solvent extraction, UV-Vis-IR spectroscopy, and XAS, similarity of trends in uranium data to trends in thorium data [2], and the consistency in thermodynamic analyses of data in large regions where the oxidation states and the aqueous species are very well known, all indicate that U(IV) is the dominant oxidation state in most of these samples. In addition, we performed XAS analysis on selected solutions to determine the identity of U(IV)- CO_3 complexes in concentrated carbonate solutions. As an example, the spectrum of a sample (taken within 2 hours of sampling) from a $UO_2(am)$ suspension in 0.9 m $NaHCO_3$ (Fig. 1) interpreted using the data reported by Bruno *et al.* [5] showed that more than 90% of the uranium was present as $U(CO_3)_3^{6-}$. Analysis of the XANES and EXAFS clearly indicates that the oxidation state of the uranium bicarbonate solution is U(IV), and the presence of five carbonate groups in bidentate complexation is consistent with the $U(CO_3)_3^{6-}$ solution species (Fig. 3). Similar analysis of the uranium carbonate solution indicated partial oxidation of uranium to U(VI) had occurred prior to the XAS measurements. The Fourier transforms of the EXAFS of these two solutions are compared with the U(VI) carbonate, rutherfordine, in Fig. 3.

Solid phase characteristics

Tracings of the X-ray diffraction patterns from four different samples representing a range in experimental conditions are shown in Fig. 4. These data show the presence in two samples of a very broad low-intensity peak (at 30 to 35 degrees 2θ), in a region where the most intense peak of $UO_2(c)$ is expected. The other two samples are essentially void of any characteristic peak for any crystalline uranium solid.

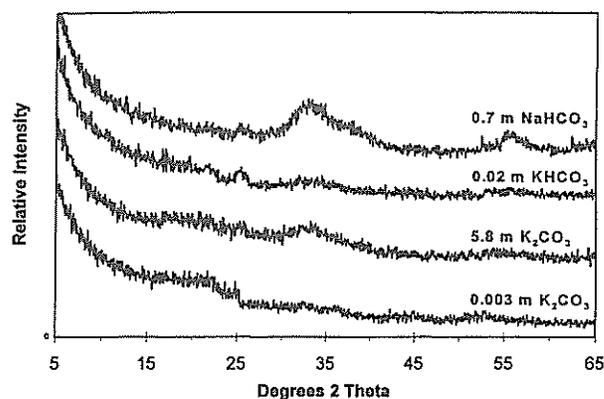


Fig. 4. Tracings of X-ray diffraction patterns of solids separated from suspensions equilibrated in different electrolyte. Lack of $UO_2(c)$ peaks and broad humps in some samples centered around $2\theta = 33$, where the most intense peak for $UO_2(c)$ is expected, along with XAS analyses that show the precipitates to be primarily U(IV) are indications that the precipitates are of amorphous UO_2 .

The results of EXAFS analyses of the precipitates from suspensions in carbonate (0.2 and 3.3 m K_2CO_3) and bicarbonate (0.04 and 1.0 m $KHCO_3$) solutions indicate that the precipitates consist of U(IV) dioxide. No evidence was found for the existence of other phases (e.g., phases containing carbonate or sulfate). These data, in conjunction with the X-ray diffraction analyses (Fig. 4), indicate that $UO_2(am)$ is the primary solid phase. The independent studies with $UO_2(am)$ in solutions ranging in concentrations up to 0.1 M [18] sulfate, concentrations which are more than two orders of magnitude higher in sulfate than those expected in this study, also indicate $UO_2(am)$ to be the solubility-controlling solid. Thermodynamic analyses presented later, for carbonate and high bicarbonate solutions, show the dominant aqueous species of U(IV) carbonate is $U(CO_3)_3^{6-}$, and the observed solubility behavior is completely consistent with the presence of this species and $UO_2(am)$ as the solubility-controlling phase. In this regard, our uranium model is also completely consistent with the thorium model where $ThO_2(am)$ is shown to be in equilibrium with $Th(CO_3)_3^{6-}$ [8, 9].

Thermodynamic interpretation of $UO_2(am)$ solubility

In analyzing the data of Rai *et al.* [2], we consider only those data where the observed uranium concentrations are significantly higher than the instrumental detection limits. All of the new data on the solubility of $UO_2(am)$ in the presence of $Na_2S_2O_4$ are discussed, and results of the oxidation state analyses of the samples are now available. In the calculations we include $U(CO_3)_3^{6-}$, which has been identified spectrophotometrically and by XAS in some of the higher carbonate and bicarbonate solutions, in combination with $U(OH)_2(CO_3)_2^{2-}$ that best describe the hydroxide and carbonate/bicarbonate dependence of the $UO_2(am)$ solubility reactions.

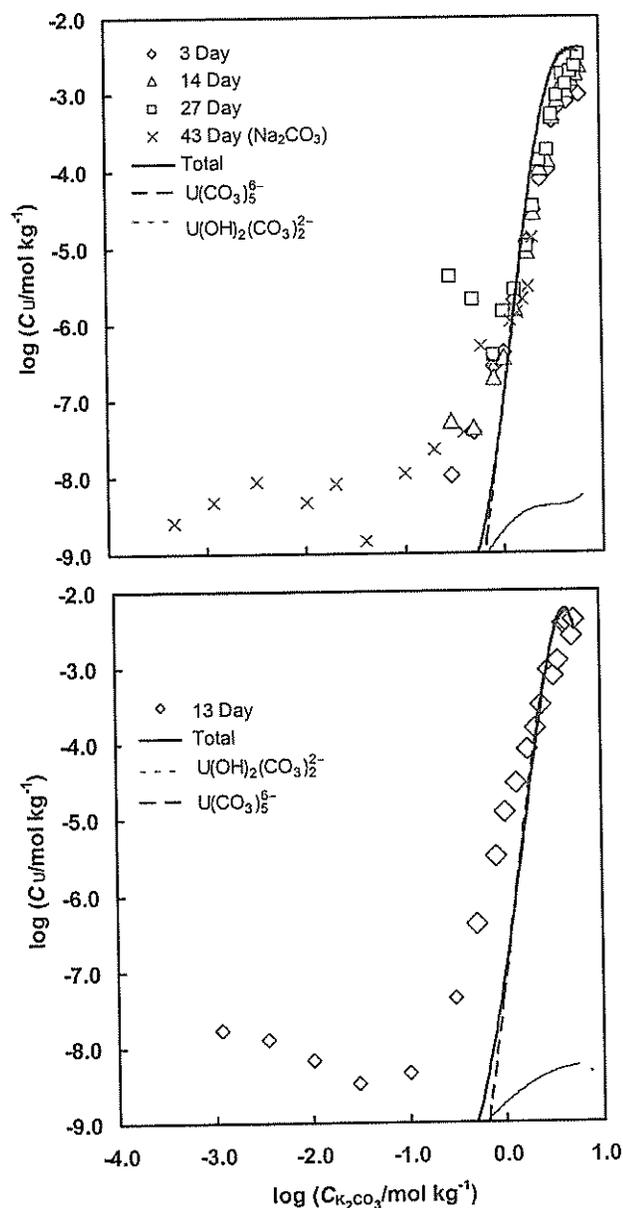


Fig. 5. Comparison of predicted and observed solubility of $\text{UO}_2(\text{am})$ in K_2CO_3 solutions, unless otherwise noted, containing 0.01 molar hydroxide. Iron powder was used as the reductant in the top figure and $\text{Na}_2\text{S}_2\text{O}_4$ was used in the bottom figure. Smaller symbols represent samples where the dominant oxidation state was found to be U(VI) . Lines represent predicted concentrations using the model parameters reported in Tables 2 and 3.

As a first attempt to explain the observed solubility behavior of $\text{UO}_2(\text{am})$ in carbonate systems, we fixed the log of the solubility product of $\text{UO}_2(\text{am})$ at -53.44 , the value recently determined by Rai *et al.* [18], and determined the values of the equilibrium constant for the reaction $\text{UO}_2(\text{am}) + 5\text{CO}_3^{2-} + 4\text{H}^+ \rightleftharpoons \text{U}(\text{CO}_3)_5^{6-} + 2\text{H}_2\text{O}$ and of $\beta^{(0)}$ and $\beta^{(1)}$ Pitzer ion-interaction parameters for $\text{U}(\text{CO}_3)_5^{6-}$ with Na^+ or K^+ . Because the solubilities of $\text{UO}_2(\text{am})$ in Na_2CO_3 and K_2CO_3 (Fig. 5) and in NaHCO_3 and KHCO_3 (comparison of data reported by Rai *et al.* [2] and those obtained in this study) are similar, we also assumed that the ion-interaction parameters are identical for $\text{U}(\text{CO}_3)_5^{6-}$ -

Na^+ and $\text{U}(\text{CO}_3)_5^{6-}$ - K^+ . The values of $\beta^{(0)} = 1.5$ and of $\beta^{(1)} = 31.3$ for $\text{U}(\text{CO}_3)_5^{6-}$ with Na^+ or K^+ and the log of the equilibrium constant of 33.8 for $\text{UO}_2(\text{am}) + 5\text{CO}_3^{2-} + 4\text{H}^+ \rightleftharpoons \text{U}(\text{CO}_3)_5^{6-} + 2\text{H}_2\text{O}$ were obtained that best described the solubility of $\text{UO}_2(\text{am})$ in K_2CO_3 solutions in 0.01 M hydroxide containing Fe powder or $\text{Na}_2\text{S}_2\text{O}_4$ reductants. The close agreement of the predicted concentrations, using the above modeling parameters, with the experimental data in K_2CO_3 solutions shows that the dramatic observed increases in the solubility with the increase in carbonate are very well represented by this simple one-species model (Fig. 5). The agreement is also very close for solubility in high Na_2CO_3 , where the tetravalent state is easily maintained (Fig. 5). At carbonate < 0.1 m, the observed U concentrations vary from 10^{-8} to 10^{-9} m and are either close to the detection limit, or the U is difficult to maintain in the tetravalent state. Therefore, no attempt was made to interpret low carbonate data. Reasonable agreement between the experimental data and the predicted concentrations also were observed for the solubility of $\text{UO}_2(\text{am})$ at a fixed carbonate concentration (3.0 or 3.3 m K_2CO_3) in variable concentrations of NaOH or KOH (Fig. 6).

The ideal way to study the $\text{UO}_2(\text{am})$ solubility in the bicarbonate region would be to conduct solubility as a function of fixed partial pressure of $\text{CO}_2(\text{g})$. However, to equilibrate the samples with a given partial pressure of $\text{CO}_2(\text{g})$ requires that the samples be kept open to the glove box atmosphere, which results in oxidation of U(IV) to U(VI) . Therefore, studies were conducted as a function of bicarbonate solutions, where it was possible to seal the tubes from the glove box atmosphere. To interpret these data, reliable values of pH or hydrogen ion concentration are required. Making a reasonable assumption that the measured pH values are reliable for samples containing < 0.1 m bicarbonate and that the values of the hydrogen ion concentrations of solutions > 0.1 m bicarbonate can be calculated from the input molalities and the thermodynamic parameters including the associated Pitzer ion-interaction values, predictions of the $\text{UO}_2(\text{am})$ solubility were made using the model proposed for the carbonate system. The agreement between the experimental values and the predicted concentrations in the high bicarbonate region is very close (Fig. 7). These modeling results are consistent with the observed aqueous species ($\text{U}(\text{CO}_3)_5^{6-}$) determined by UV-Vis-IR spectroscopy and XAS in the high bicarbonate concentration region (Figs. 1 and 3). In the region for low bicarbonate concentration, observed uranium concentrations are significantly higher than predicted (Fig. 7). Therefore, additional species are required to adequately explain these results. It should be noted that the observed uranium concentrations in the high bicarbonate region did not change with time, while in the low bicarbonate region, the measured concentrations in some cases differed with time, presumably due to difficulties in maintaining uranium in the tetravalent state. In the low bicarbonate region, data are similar

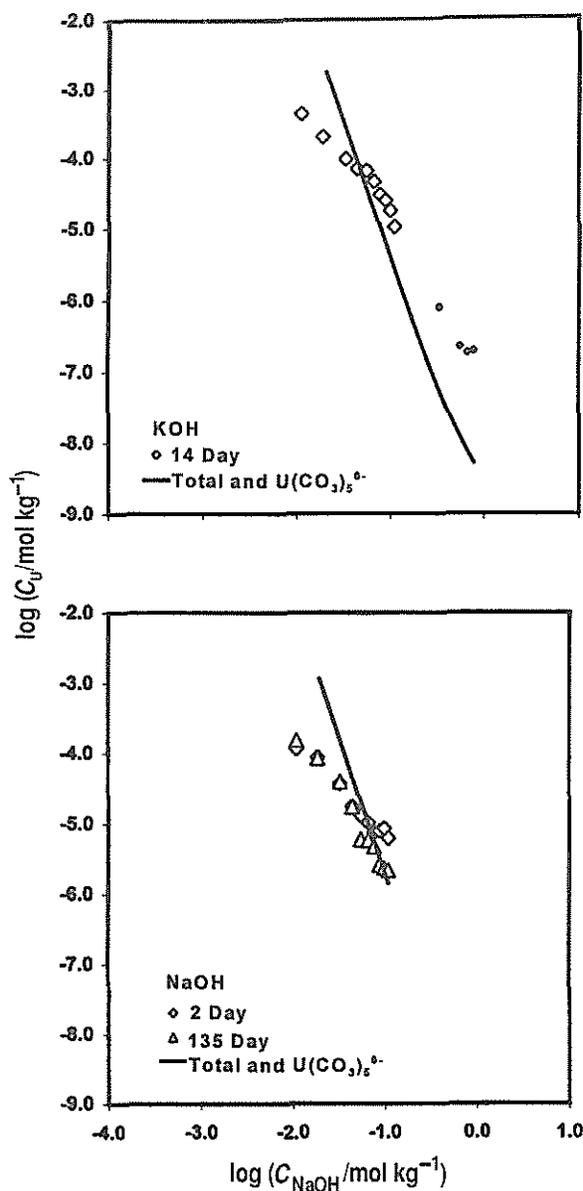


Fig. 6. Comparison of predicted and observed solubility of $\text{UO}_2(\text{am})$ in 3.3 m K_2CO_3 solutions containing different concentrations of KOH (top) or in 3.0 m K_2CO_3 solutions containing different concentrations of NaOH (bottom). Smaller symbols represent samples where the dominant oxidation state was found to be U(VI). Lines represent predicted concentrations using the model parameters reported in Tables 2 and 3.

for the 13-day NaHCO_3 system containing Fe powder as the reductant and the 2-day KHCO_3 system containing $\text{Na}_2\text{S}_2\text{O}_4$ as the reductant. Given this fact and the fact that U(IV) is the dominant species in KHCO_3 solutions (Fig. 7 and Table 1), only 13-day data from the NaHCO_3 system, along with 2-day data from the KHCO_3 system, were used for further interpretations. The modeling of these data using several different species, including $\text{U}(\text{OH})_3\text{CO}_3^-$ (a species reported for thorium by Osthols *et al.* [8] and by Felmy *et al.* [9]) indicated the species that best described the observed data was $\text{U}(\text{OH})_2(\text{CO}_3)_2^{2-}$ (Fig. 7), although the existence of these species cannot be independently verified

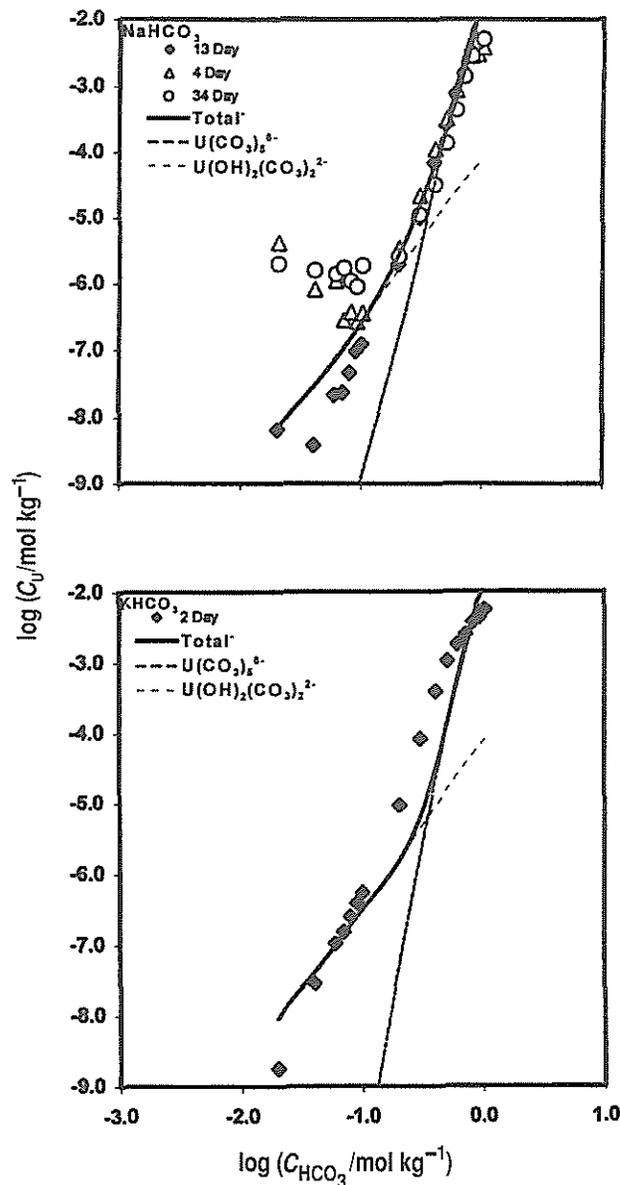


Fig. 7. Comparison of predicted and observed solubility of $\text{UO}_2(\text{am})$ in NaHCO_3 (top) and KHCO_3 (bottom) solutions. Solvent extraction analyses of all of the samples for the KHCO_3 set were completed and the results show that the dominant oxidation state is U(IV). Lines represent predicted concentrations using the model parameters reported in Tables 2 and 3.

with currently available techniques. The log of the equilibrium constant for the $\text{UO}_2(\text{am})$ dissolution reaction involving this species ($\text{UO}_2(\text{am}) + 2\text{HCO}_3^- \rightleftharpoons \text{U}(\text{OH})_2(\text{CO}_3)_2^{2-}$) was found to be -4.8 .

The final model that explains all of the data sets where uranium is present in the tetravalent state included $\beta^{(0)} = 1.5$ for either $\text{U}(\text{CO}_3)_5^{6-}\text{-Na}^+$ or $\text{U}(\text{CO}_3)_5^{6-}\text{-K}^+$; $\beta^{(1)} = 31.3$ for either $\text{U}(\text{CO}_3)_5^{6-}\text{-Na}^+$ or $\text{U}(\text{CO}_3)_5^{6-}\text{-K}^+$; and the following dominant dissolution reactions:

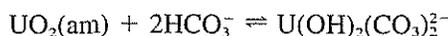
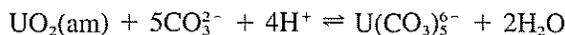


Table 2. Pitzer ion-interaction parameters used in this study

Species	Binary Parameters				Reference
	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	C^{ϕ}	
Na ⁺ -CO ₃ ²⁻	0.0399	1.389	0.00	0.0044	[18]
Na ⁺ -HCO ₃ ⁻	0.0277	0.0411	0.00	0.00	[18]
Na ⁺ -OH ⁻	0.0864	0.253	0.00	0.0044	[18]
K ⁺ -CO ₃ ²⁻	0.1488	1.43	0.00	-0.0015	[18]
K ⁺ -HCO ₃ ⁻	0.0296	-0.013	0.00	-0.008	[18]
K ⁺ -OH ⁻	0.1298	0.32	0.00	0.0041	[18]
Na ⁺ -U(CO ₃) ₆ ⁴⁻	1.5	31.3	0.00	0.00	This study
K ⁺ -U(CO ₃) ₆ ⁴⁻	1.5	31.3	0.00	0.00	This study
Common-ion ternary parameters reference (all values reported by Harvie <i>et al.</i> [18])					
H ⁺ -Na ⁺				0.036	
H ⁺ -K ⁺				0.005	
Na ⁺ -K ⁺				-0.012	
Na ⁺ -K ⁺ -CO ₃ ²⁻				0.003	
Na ⁺ -K ⁺ -HCO ₃ ⁻				-0.003	
CO ₃ ²⁻ -HCO ₃ ⁻				-0.04	
CO ₃ ²⁻ -HCO ₃ ⁻ -Na ⁺				0.002	
CO ₃ ²⁻ -HCO ₃ ⁻ -K ⁺				0.012	
CO ₃ ²⁻ -OH ⁻				0.10	
CO ₃ ²⁻ -OH ⁻ -Na ⁺				-0.017	
CO ₃ ²⁻ -OH ⁻ -K ⁺				-0.01	
CO ₂ (aq)-K ⁺				0.051	
CO ₂ (aq)-Na ⁺				0.10	

Table 3. Dimensionless standard molar Gibbs energy of formation of different species

Species	$\Delta G_f^\circ/RT$	Reference
U ⁴⁺	-214.207	[19]
U(CO ₃) ₆ ⁴⁻	-1345.45	This study
U(OH) ₂ (CO ₃) ₂ ²⁻	-862.1	This study
UO ₂ (am)	-399.674	[17]
CO ₃ ²⁻	-212.944	[18]
HCO ₃ ⁻	-236.751	[18]
OH ⁻	-63.435	[18]
H ₂ O(l)	-95.663	[18]
CO ₂ (aq)	-155.68	[18]

with 33.8 and -4.8, respectively, representing values of the logarithm of the thermodynamic equilibrium constants for these reactions. These values, when combined with the solubility product of UO₂(am) (log = -53.44), provided logarithm values of 31.29 for the equilibrium constant of (U⁴⁺ + 5CO₃²⁻ = U(CO₃)₆⁴⁻) and 41.33 for (U⁴⁺ + 2CO₃²⁻ + 2OH⁻ = U(OH)₂(CO₃)₂²⁻).

The dominant aqueous complexes in different experimental solutions predicted by this model are shown in Figs. 5 through 7. The predicted dominant species are U(CO₃)₆⁴⁻ in the CO₃²⁻, concentrated HCO₃⁻, moderate CO₃²⁻, and high OH⁻ concentrations, which is consistent with spectrophotometric and XAS data; and U(OH)₂(CO₃)₂²⁻ in dilute to moderate HCO₃⁻ concentrations. All of the ($\Delta G_f^\circ/RT$) values of necessary species and ion-interaction parameters used in these calculations are reported in Tables 2 and 3.

This model satisfactorily represents an extensive set of experimental data covering a broad range of carbonate, bicarbonate, and hydroxide concentrations. The model assumes the formation of only a minimum number of aqueous species. One of the species, U(CO₃)₆⁴⁻, is analogous to that required to interpret the Th(IV)-CO₃ system [8, 9]. In this regard, it is of interest to compare our calculated association constants for complexation reactions for species in the Th(IV) system with the values for the U(IV) system. The log *K* value for the formation of Th(CO₃)₆⁴⁻ ranges from 27.1 to 30.3,^a while for U(CO₃)₆⁴⁻, the value is calculated to be 31.3 from the data reported in this study and is reported as 36.86 by Grenthe *et al.* [1]. The exact reasons are not known for large differences between values obtained in this study and those reported by Grenthe *et al.* [1] but certainly must be affected by the different aqueous thermodynamic models used (Pitzer vs. SIT) and other modeling parameters as indicated by Felmy *et al.* [9]. However, the higher value for the uranium system, as compared with the thorium system, is consistent with the expected stronger complexes due to the decreasing ionic radius of uranium and the observed shorter bond lengths between the uranium ion and carbon or oxygen atoms (U-C = 2.90 Å, Th-C = 2.97 Å; U-O = 2.46 Å, Th-O = 2.49) as determined by XAS.

Acknowledgments

This research was conducted at the Pacific Northwest National Laboratory, operated by Battelle for the U.S. Department of Energy (DOE) under Contract DE-AC06-76RLO 1980. The research was funded by the Power Reactor and Nuclear Fuel Development Corporation (PNC) of Japan, under an agreement with DOE for a project on "Development of Fundamental Thermodynamic and Adsorption Data." We thank Drs. Sumio Masuda, Noriaki Sasaki, Hiroyuki Umeki, and Mr. Kaname Miyahara of PNC for their support and technical discussions throughout the study period.

References

- Grenthe, I. J., Fuger, R. J., Konigs, M., Lemire, R. J., Muller, A. B., Nguyen-Trung, C., Wanner, H.: *Chemical Thermodynamics of Uranium*, Vol. 1. Elsevier Science Publishing Company, Inc., North-Holland, New York (1992).
- Rai, Dhanpat, Felmy, A. R., Moore, D. A., Mason, M. J.: The Solubility of Th(IV) and U(IV) Hydrated Oxides in Concentrated NaHCO₃ and Na₂CO₃ Solutions. *Materials Research Society Symposium*, 353, 1143-1150 (1995).
- Clark, D. L., Hobart, D. E., Neu, M. P.: Actinide Carbonate Complexes and Their Importance in Actinide Environmental Chemistry. *Chem. Rev.* 95, 25-48 (1995).

^a The values for the Th(IV) complexes calculated from data reported by Felmy *et al.* [9] vary depending on the choice of solubility product used in the calculations. The solubility products for the hydrated oxides vary with the speciation scheme used in the original calculations. The values for the solubility products used in the calculations reported here were taken from Felmy *et al.* [21] and Ostholts *et al.* [8] and represent the range of recently published values.

4. Ciavatta, L., Ferri, D., Grenthe, I., Salvatore, S., Spahiu, K.: Studies on Metal Carbonate Equilibria. 4. Reduction of the Tris(carbonato)dioxouranate(VI) Ion, $\text{UO}_2(\text{CO}_3)_3^{4-}$, in Hydrogen Carbonate Solutions. *Inorg. Chem.* **22**, 2088–2092 (1983).
5. Bruno, J., Grenthe, I. J., Robouch, P.: Studies of Metal Carbonate Equilibria. 20. Formation of Tetra(carbonato)uranium(IV) Ion, $\text{U}(\text{CO}_3)_4^{4-}$, in Hydrogen Carbonate Solutions. *Inorg. Chim. Acta* **158**, 221–226 (1989).
6. Cukman D., Caja, J., Pravidic, V.: The Electrochemical Oxidation of Uranium(IV) in Sodium Bicarbonate Solutions. *J. Electroanal. Chem.* **19**, 267–274 (1968).
7. Stabrovskii, A. I.: Polarography of Uranium Compounds in Carbonate and Bicarbonate Solutions. *Russ. J. Inorg. Chem.* **5**, 389–394 (quoted in Grenthe *et al.* 1992) (1960).
8. Osthols, E., Bruno, J., Grenthe, I.: On the Influence of Carbonate on Mineral Dissolution: III. The Solubility of Microcrystalline ThO_2 in CO_2 - H_2O Media. *Geochim. Cosmochim. Acta* **58**(2), 613–623 (1994).
9. Felmy, A. R., Rai, D., Sterner, S. M., Mason, M. J., Hess, N. J., Conradson, S. D.: Thermodynamic Models for Highly Charged Aqueous Species: Solubility of Th(IV) Hydrated Oxide in Concentrated NHCO_3 and Na_2CO_3 Solutions. *J. Solution Chem.* **26**(3), 233–248 (1997).
10. Pitzer, K. S.: Thermodynamics of Electrolytes. I. Theoretical Basis and General Equations. *J. Phys. Chem.* **77**(2), 268–272 (1973).
11. Pitzer, K. S.: Ion Interaction Approach: Theory and Data Correlation. Chapter 3 in: *Activity Coefficients in Electrolyte Solutions*, 2nd ed., ed. K. S. Pitzer, CRC Press, Boca Raton, Florida (1991).
12. Schramke, J. A., Rai, D., Choppin, G. R., Fulton, R. W.: Determination of Aqueous Plutonium Oxidation States by Solvent Extraction. *J. Radioanal. Nucl. Chem. Articles* **130**, 333–346 (1989).
13. Lee, P. A., Citrin, P. H., Eisenberger, P., Kincaid, B. M.: Extended X-Ray Absorption Fine Structure – Its Strengths and Limitations as a Structural Tool. *Rev. Mod. Phys.* **53**, 769 (1981).
14. Voliotis, P. S.: Etude Structurale des Carbonates Complexes de Cerium et de Thorium II. Structure Cristalline et Moleculaire du Pentacarbonatothorate de Guanidine Tetrahydrate, $[\text{C}(\text{NH}_2)_3]_6[\text{Th}(\text{CO}_3)_5] \cdot 4\text{H}_2\text{O}$. *Acta Crystallogr.* **B31**, 2612 (1975).
15. Rehr, J. J., Zabinsky, S. I., Albers, R. C.: High-Order Multiple Scattering Calculations of X-ray-Absorption Fine Structure. *Phys. Rev. Lett.* **69**, 3397–3400 (1992).
16. Zabinsky, S. I., Rehr, J. J., Ankudinov, A., Albers, R. C., Eller, M. J.: Multiple Scattering Calculations of X-Ray Absorption Spectra. *Phys. Rev.* **B52**, 2995 (1995).
17. Sterner, S. M., Felmy, A. R., Rustad, J. R., Pitzer, K. S.: Thermodynamic Analysis of Aqueous Solutions Using INSIGHT. PNWD-SA-4436. Pacific Northwest National Laboratory, Richland, Washington (1997).
18. Rai, D., Felmy, A. R., Sterner, S. M., Moore, D. A., Mason, M. J., Novak, C. F.: The Solubility of Th(IV) and U(IV) Hydrated Oxides in Concentrated NaCl and MgCl_2 Solutions. *Radiochim. Acta* **79**, 239–247 (1997).
19. Harvie, C. E., Moller, N., Weare, J. H.: The Prediction of Mineral Solubilities in Natural Waters: The Na-K-Mg-Ca-H-Cl-SO₄-OH-HCO₃-CO₃-H₂O System in High Ionic Strengths at 25°C. *Geochim. Cosmochim. Acta* **48**, 723–751 (1984).
20. Fuger, J., Oetting, F. L.: *The Chemical Thermodynamics of Actinide Elements and Compounds. Part 2. The Actinides Aqueous Ions*. International Atomic Energy Agency, Vienna, Austria (1976).
21. Felmy A. R., Rai, D., Mason, M. J.: The Solubility of Hydrated Thorium(IV) Oxide in Chloride Media: Development of an Aqueous Ion-interaction Model. *Radiochim. Acta* **55**, 177–185 (1991).

APPENDIX

Complete sets of $\text{UO}_2(\text{am})$ solubility in different solutions presented in Figs. 5–7 are reported in the following three tables (Tables A.1, A.2, and A.3).

Table A.1. $\text{UO}_2(\text{am})$ solubility at different equilibration periods in K_2CO_3 or Na_2CO_3 solutions containing Fe powder unless otherwise identified (data corresponding to Fig. 5)

log ($C_{\text{K}_2\text{CO}_3}/\text{mol kg}^{-1}$)	log ($C_{\text{U}}/\text{mol kg}^{-1}$)				log ($C_{\text{Na}_2\text{CO}_3}/\text{mol kg}^{-1}$)	log ($C_{\text{U}}/\text{mol kg}^{-1}$) 43 Day
	3 Day	14 Day	27 Day	13 Day ^a		
-2.94				-7.77	-3.33	-8.60
-2.46				-7.90	-2.93	-8.33
-1.99				-8.16	-2.50	-8.06
-1.52				-8.48	-1.99	-8.33
-1.00				-8.35	-1.70	8.09
-0.52	-7.99	-7.28	-5.38	-7.35	-1.40	-8.84
-0.30	-7.42	-7.37	-5.68	-6.39	-1.00	-7.95
-0.09	-6.57	-6.71	-6.42	-5.50	-0.70	-7.65
0.01	-6.39	-6.44	-5.85	-4.91	-0.40	-7.42
0.13	-5.69	-5.80	-5.57	-4.54	-0.22	-6.30
0.25	-4.95	-5.06	-5.00	-4.09	-0.09	-6.52
0.33	-4.52	-4.55	-4.49	-3.81	0.08	-5.96
0.39	-4.13	-3.98	-3.89	-3.50	0.15	-5.86
0.47	-4.01	-3.87	-3.75	-3.04	0.21	-5.68
0.52	-3.37	-3.31	-3.29	-3.12	0.26	-5.52
0.57	-3.19	-3.08	-3.04	-2.92	0.31	-4.88
0.63	-3.00	-2.84	-2.76	-2.43		
0.67	-3.11	-2.96	-2.89	-2.41		
0.71	-2.97	-2.81	-2.73	-2.60		
0.74				-2.39		
0.76	-2.98	-2.74	-2.65			
0.80	-3.02	-2.63	-2.51			

^a Different set of samples containing 0.01 molar $\text{Na}_2\text{S}_2\text{O}_4$ instead of Fe powder as the reductant.

Table A.2. $\text{UO}_2(\text{am})$ solubility in 3.0 or 3.3 molal K_2CO_3 solutions containing different concentrations of KOH or NaOH (data corresponding to Fig. 6)

log ($C_{\text{OH}}/\text{mol kg}^{-1}$)	log ($C_{\text{U}}/\text{mol kg}^{-1}$)		
	2 Day ^a	135 Day ^a	14 Day ^b
-1.96	-3.94	-3.82	-3.37
-1.73	-4.06	-4.07	-3.70
-1.48	-4.42	-4.40	-4.02
-1.36	-4.75	-4.75	-4.15
-1.26	-4.88	-5.22	-4.18
-1.18	-4.99	-5.24	-4.33
-1.12	-5.12	-5.32	-4.52
-1.06	-5.10	-5.59	-4.60
-1.01	-5.07	-5.62	-4.74
-0.96	-5.20	-5.66	-4.97
-0.48			-6.09
-0.26			-6.64
-0.18			-6.73
-0.11			-6.70

^a Set containing 3.0 molal K_2CO_3 , NaOH, and Fe powder.^b Set containing 3.3 molal K_2CO_3 , KOH, and 0.01 molar $\text{Na}_2\text{S}_2\text{O}_4$.**Table A.3.** $\text{UO}_2(\text{am})$ solubility in bicarbonate solutions (data corresponding to Fig. 7)

log ($C_{\text{KHCO}_3}/\text{mol kg}^{-1}$)	4 Day ^a		13 Day ^a		34 Day ^a		log ($C_{\text{KHCO}_3}/\text{mol kg}^{-1}$)	2 Day ^b	
	pH _m	log U	pH _m	log U	pH _m	log U		pH _m	log U
-1.69	9.36	-5.38	9.45	-8.19	9.81	-5.70	-1.70	7.24	-8.75
-1.39	9.27	-6.09	9.36	-8.42	9.59	-5.81	-1.40	7.41	-7.54
-1.21	9.06	-5.96	9.16	-7.66	9.41	-5.86	-1.22	7.45	-6.98
-1.14	8.99	-6.55	9.09	-7.63	9.30	-5.77	-1.15	7.48	-6.82
-1.09	9.04	-6.43	9.16	-7.34	9.32	-5.96	-1.10	7.59	-6.60
-1.03	8.93	-6.58	9.05	-7.02	9.18	-6.05	-1.05	7.61	-6.41
-0.99	8.91	-6.44	9.02	-6.90	9.13	-5.73	-1.00	7.62	-6.27
-0.69	8.69	-5.47	8.87	-5.71	8.97	-5.60	-0.69	7.90	-5.04
-0.51	8.63	-4.66	8.84	-5.01	8.94	-4.95	-0.52	7.90	-4.09
-0.39	8.55	-3.95	8.72	-4.17	8.77	-4.49	-0.39	7.96	-3.41
-0.29	8.49	-3.49	8.71	-3.59	8.76	-3.86	-0.29	7.98	-2.97
-0.21	8.46	-3.06	8.62	-3.11	8.66	-3.35	-0.21	8.00	-2.74
-0.14	8.42	-2.77	8.57	-2.80	8.62	-2.85	-0.14	8.00	-2.60
-0.09	8.38	-2.55	8.51	-2.48	8.55	-2.54	-0.08	8.00	-2.43
-0.03	8.37	-2.52	8.46	-2.40	8.51	-2.33	-0.03	8.01	-2.37
0.01	8.37	-2.42	8.43	-2.34	8.47	-2.30	0.02	8.00	-2.26

^a Set containing Fe powder as the reductant, $\log U = (C_{\text{U}}/\text{mol kg}^{-1})$, and $\text{pH}_m =$ measured pH. The measured pH values at high bicarbonate concentrations are not meaningful (see text for details).^b Set containing 0.01 molar $\text{Na}_2\text{S}_2\text{O}_4$ as the reductant, $\log U = \log (C_{\text{U}}/\text{mol kg}^{-1})$, and $\text{pH}_m =$ measured pH. The measured pH values at high bicarbonate concentrations are not meaningful (see text for details).