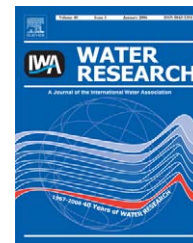


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Solubility of schoepite: Comparison and selection of complexation constants for U(VI)

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ABSTRACT

Solubility of $\text{UO}_3 \cdot n\text{H}_2\text{O}$ and sorption of U(VI) onto ferric (hydr)oxides were measured at pH 5.9, 6.8, and 7.8 at $10^{-3.5}$ atm CO_2 using reaction times up to 48 days. Precipitation was fastest in the presence of hydrous ferric oxide and slower with hematite or without an initial solid phase. Solubility after 48 days was statistically similar for low to intermediate initial supersaturation conditions and increased for the highest initial supersaturation. Schoepite was identified for low-to-intermediate initial conditions of supersaturation and was not found for the highest initial supersaturation. Predicted concentrations of monomeric and polymeric species differed considerably with the different suites of complexation constants, resulting in significant differences in predicted oxidation–reduction potential and mobility of U(VI) in groundwater. Solubilities for low to intermediate initial supersaturation were best represented using complexation constants from Langmuir, D. [1978. Uranium solution–mineral equilibria at low temperatures with applications to sedimentary ore deposits. *Geochim. Cosmochim. Acta* 42, 547–569] and $\log^*K_{sp} = 5.39$ for schoepite, while solubilities for very high initial supersaturation were consistent with amorphous $\text{UO}_3 \cdot n\text{H}_2\text{O}$.

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1. Introduction

U(VI) exists predominantly as uranyl (UO_2^{2+}) for acidic conditions, and forms hydroxyl and carbonate complexes with increasing pH. Phosphate and fluoride are also strong complexing agents. A variety of polymeric species have been proposed (Baes and Mesmer, 1976; Langmuir, 1978; Grenthe et al., 1992; Waite et al., 1994; Gianguzza et al., 2004). Correct prediction of U(VI) speciation is required for prediction of mobility and reactivity (Baes and Mesmer, 1976; Nordstrom et al., 1990) as a function of precipitation (Diaz Arocas, 1996; Diaz Arocas and Grambow, 1998), sorption of uranyl on geological materials (Hsi and Langmuir, 1985; Silva, 1992; Waite et al., 1994; Bruno et al., 1995; Morrison et al., 1995; Duff and Amrhein, 1996; Moyes et al., 2000; Giammar and Hering, 2001; Wazne et al., 2003), and reduction potential (Charlet et al., 1998; Liger et al., 1999).

There is substantial disagreement about thermodynamic constants for formation of soluble or solid species of U(VI) (Langmuir, 1978; Sylva and Davidson, 1979; Fuger et al., 1992; Grenthe et al., 1992; Clark et al., 1999; Gianguzza et al., 2004; Merkel and Planer-Friedrich, 2005) due to experimental difficulties and the formation of polymeric species (Baes and Mesmer, 1976; Gianguzza et al., 2004; Merkel and Planer-Friedrich, 2005). The uncertainties was illustrated in two independent publications of Nuclear Energy Agency (NEA), (Fuger et al., 1992) and International Atomic Energy Agency (IAEA), (Langmuir, 1978; Fuger et al., 1992; Grenthe et al., 1992) in 1992. These studies resulted in significantly different conclusions about equilibrium constants, resulting in very important differences in the predicted concentrations of various soluble species as a function of total uranium concentration at neutral and basic pH values (Merkel and Planer-Friedrich, 2005).

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Among the proposed sets of thermodynamic data (Langmuir, 1978; Fuger et al., 1992; Grenthe et al., 1992), the species and constants proposed by Langmuir (1978) and by Grenthe et al. (1992) have been widely used. Other investigators have suggested the formation of additional soluble species that were not reported by Langmuir (1978) or Grenthe et al. (1992), or have adopted modified values for constants, especially for the second hydrolysis constant (Fuger et al., 1992; Waite et al., 1994; Giammar and Hering, 2001,

2004). There are also differences in reported solubility constants for solid phases of uranyl (hydr)oxides. For example, Waite et al. (1994) used β - $\text{UO}_2(\text{OH})_2$ ($\log^*K_{\text{sp}} = 4.93$), cited from Grenthe et al. (1992), and Giammar and Hering (2001) used two solid phases with different \log^*K_{sp} of 4.70 (from Diaz Arocas and Grambow, 1998) or 5.20 (from Silva, 1992) to model their results. Some of the more commonly used suites of species and constants are presented in Table 1.

Table 1 – List of reported U(VI) species

Reference	Langmuir (1978)	Grenthe et al. (1992) (NEA)	Fuger et al. (1992) (IAEA)	NIST (1998)	Waite et al. (1994)	Baes and Mesmer (1976) ^a
Number of species other than UO_2^{2+}	6	17	9	13	14	4
Aqueous species	$\log^*\beta^0$					
UO_2OH^+	-5.78	-5.20	-5.76	-5.90	-5.2	-5.8
$\text{UO}_2(\text{OH})_2^0$	—	≤ -10.30	-13.00	—	-12.0	—
$\text{UO}_2(\text{OH})_3^-$	—	-19.20	—	—	-20.0	—
$\text{UO}_2(\text{OH})_4^{2-}$	—	-33.00	—	—	-33.0	—
$(\text{UO}_2)_2\text{OH}^{3+}$	—	—	-4.06	—	—	—
$(\text{UO}_2)_2(\text{OH})_3^+$	—	-2.70	—	—	-2.8	—
$(\text{UO}_2)_2(\text{OH})_2^{2+}$	-5.62	-5.62	-5.54	-5.57	-5.63	-5.62
$(\text{UO}_2)_3(\text{OH})_4^{2+}$	—	-11.90	—	-11.79	-11.9	(-11.75) ^b
$(\text{UO}_2)_3(\text{OH})_5^+$	-15.63	-15.55	-15.44	-15.59	-15.56	-15.63
$(\text{UO}_2)_3(\text{OH})_7^-$	—	-31.00	—	—	-31.0	—
$(\text{UO}_2)_4(\text{OH})_6^{2-}$	—	—	—	-20.48	—	—
				(I = 0.5 M)		
$(\text{UO}_2)_4(\text{OH})_7^-$	—	-21.90	—	-24.28	-21.9	—
				(I = 0.1 M)		
$\text{UO}_2(\text{CO}_3)^0$	10.06	9.68	10.0	9.6	9.7	—
$\text{UO}_2(\text{CO}_3)_2^{-2}$	16.98	16.94	17.0	16.9	17.0	—
$\text{UO}_2(\text{CO}_3)_3^{-4}$	21.40	21.60	21.6	21.6	21.63	—
$(\text{UO}_2)_3(\text{CO}_3)_6^{-6}$	—	54.00	53.4	54.0	—	—
$(\text{UO}_2)_2(\text{OH})_3\text{CO}_3^{-1}$	—	-0.94	—	-0.9	-1.18	—
${}^c(\text{UO}_2)_3(\text{OH})_3\text{CO}_3^{+1}$	—	0.57	—	0.7	—	—
$(\text{UO}_2)_{11}(\text{OH})_{12}(\text{CO}_3)_6^{-2}$	—	35.92	—	34.0	—	—
Solid phases	$\log^*K_{\text{sp}}^0$					
$\text{UO}_2(\text{OH})_2 \cdot \text{H}_2\text{O}(\text{c})$ (schoepite)	5.39 ^d	—	—	5.99	—	—
α - $\text{UO}_3 \cdot 0.9\text{H}_2\text{O}$	—	5.00	—	—	—	—
β - $\text{UO}_2(\text{OH})_2$	—	4.93	—	—	4.93	—
β - $\text{UO}_2(\text{OH})_2(\text{c})$	5.55	—	—	—	—	—
$\text{UO}_3 \cdot 2\text{H}_2\text{O}(\text{cr})$	—	4.81	—	—	—	—
$\text{UO}_3(\text{am})$ (gummite)	10.40	—	—	—	—	—
α - UO_3	—	8.63	—	—	—	—
β - UO_3	—	8.30	—	—	—	—
γ - UO_3	—	7.70	—	—	—	—
γ - $\text{UO}_3(\text{c})$	7.69	—	—	—	—	—
$\text{UO}_2(\text{OH})_2(\text{c})$	—	—	—	—	—	5.6 ^e

The sets of constants from Langmuir (1978) and Grenthe et al. (1992) were used to construct solubility lines in Fig. 1.

^a No carbonato complexes reported.

^b Apparent constant that reproduces data at high $[\text{Cl}^-]$.

^c Grenthe et al. (1992) denoted this species as $(\text{UO}_2)_3\text{O}(\text{OH})_2(\text{HCO}_3)^{+1}$.

^d The Gibbs free energies of formation of this solid are -390.4 and -391.1 kcal/mole, in Langmuir (1978) and Chen et al. (1999), respectively.

^e Crystalline structure was not identified in Baes and Mesmer (1976).

The significant differences in predicted solubility using the constants in Langmuir (1978) versus Grenthe et al. (1992) are demonstrated in Fig. 1. The shape differences are due to the presumption of different soluble species, different formation constants, and different polymeric content. The positional changes (greater or less solubility overall) are largely due to the use of different solubility constants (K_{sp}), with some changes in shape due to the changing ratio of polymeric to monomeric species as a function of total dissolved concentration (Fig. 1).

Bruno et al. (1995) observed that solubility was less than reported for schoepite (defined $UO_2(OH)_2$ in their research) when co-precipitated with Fe(III) (hydr)oxide. Duff et al. (2002) reported precipitation of uranate (γ - UO_3) or schoepite (defined $UO_2(OH)_2 \cdot 2H_2O$ in their work) depending on the U(VI) mole % in co-precipitates with Fe(III). Murakami et al. (1997, 2001) examined U(VI)–Fe(III) co-precipitates that were aged for 100 days at 25 °C and pH 5.3, using Scanning and Transmission Electron Microscopy. U(VI) was discovered on the surface of HFO and goethite/hematite as discrete, nm-sized particles of dehydrated schoepite. They reported that the solution was undersaturated with respect to schoepite. Ohnuki et al. (1997) extracted U(VI) that had been precipitated or sorbed on HFO. Extractable U(VI) decreased with aging time and with crystallinity of the ferric oxide minerals.

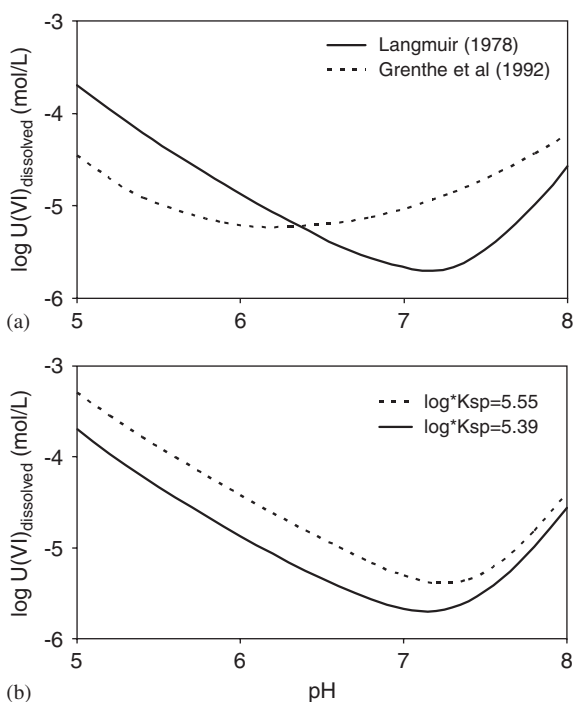


Fig. 1 – (a) Predicted U(VI) solubility based on two thermodynamic databases: solid line from Langmuir (1978) with schoepite ($\log^*K_{sp} = 5.39$); dotted line from Grenthe et al. (1992) with β - $UO_2(OH)_2$ ($\log^*K_{sp} = 4.93$). (b) Effect of different K_{sp} values on U(VI) solubility using formation constants from Langmuir (1978) for soluble species.

The objectives were the following: (1) measure the solubility of $UO_3 \cdot nH_2O^1$ at $10^{-3.5}$ atm of CO_2 as a function of time up to 48 days, degree of initial supersaturation, pH (5.9, 6.8, and 7.8), and addition of hydrous ferric oxide (HFO) or hematite (α - Fe_2O_3), and (2) use the experimental results to critically evaluate thermodynamic constants for hydrolysis and solubility of U(VI). The experiments also dealt with sorption but the focus of this paper is on solubility and selection of hydrolysis constants.

2. Materials and methods

All chemicals were reagent grade or better. Chloride was not used due to possible interference with kinetic phosphorescence analysis (KPA-11, ChemChek, Inc.) for U(VI). Samples for KPA analysis and calibration standards (0–20 ppb as U(VI)) were prepared in 0.01 M HNO_3 to minimize matrix effects (Brina and Miller, 1992, 1993; Sowder et al., 1998). Diluted URAPLEX[®] (ChemChek, Inc.) was prepared fresh before analysis. Experiments were conducted in 0.01 M $NaNO_3$ ionic medium. U(VI) stock (425 mM in 1.0 M HNO_3) was prepared from uranyl acetate. Working U(VI) stocks of lower concentrations were prepared in 0.01 or 0.1 M HNO_3 . For experiments with an added solid phase, 0.1 mM of Fe(III) as HFO or hematite (α - Fe_2O_3) was added.

To prepare HFO, 20 mM $Fe(NO_3)_3$ was slowly titrated to pH 7 with NaOH at room temperature. Gel-like precipitates immediately formed. The pH of the HFO suspension was repeatedly adjusted to 7 during 4 days. Na^+ and NO_3^- were removed using at least seven decants followed by addition of deionized (DI) water to the original volume; each decant replaced more than 90% of the supernatant with DI water. The Fe(III) concentration was analyzed using 1,10-phenanthroline after reduction to Fe(II). Hematite was synthesized by adding $FeCl_3$ to boiling 2 mM HCl to achieve 20 mM Fe(III) (Raming et al., 2002). This was kept at 100 °C for 5 days. To decrease residual $[Fe(III)_{dissolved}]$ and $[H^+]$, the liquid phase of the suspension was slowly removed using ultrafiltration, with constant replacement of permeate by DI water. Nearly monodispersed hematite particles (~ 100 nm) were identified using transmission electron microscope. Mössbauer spectroscopy measurement for the HFO and hematite confirmed that no impurity was present within the method detection limit (~ 1 mol% as Fe).

Water was prepared by adjusting pH of DI water to 5.9, 6.8, or 7.8 with NaOH during 2 days while bubbling with water-saturated air ($P_{CO_2} = 10^{-3.5}$ atm). Pre-carbonated water, $NaNO_3$ stock solution (1.0 M), and HFO or hematite stock (20 mM as Fe(III)) were added to reactor bottles to $\sim 90\%$ of desired volume. The reactors were kept equilibrated with air for 1 day. Just before addition of the U(VI), sufficient 0.01 or 0.1 M NaOH was added to compensate for the acidity of the U(VI) stock solution. The pH was then adjusted while bubbling with air. Then the final volume was obtained by adding DI water and monitoring mass with an analytical balance. The

¹ According to Finch et al. (1998), $n = 2.25$ for schoepite, $n \approx 2$ for metaschoepite, $n < 2$ for “dehydrated schoepite”.

pH of each reactor was frequently measured between sampling days and adjusted as needed.

The filtrate (0.2 μm) was preserved in and diluted with 0.01M nitric acid. Permeation coefficients (fraction of dissolved U(VI) that passed through the filter in the absence of any solid phase) were measured using the range of pH and reaction times. $[UO_2^{2+}]_{aq}$ was defined as filtered [U(VI)] divided by the permeation coefficient.

X-ray diffraction (XRD) analyses were performed on selected samples using a Scintag Pad V X-ray diffractometer with CuKα source. Data points were acquired every 0.02°2θ at a rate of 2.0°2θ/min from 5° to 70°2θ. Wet samples were mounted on slide glass as slurry and dried at room temperature.

3. Results and discussion

Experimental results for the sorption and precipitation conditions are shown in Fig. 2. The data were plotted as $\log [UO_2^{2+}]_{removed}$ vs. $\log [UO_2^{2+}]_{aq}$ diagrams, where $[UO_2^{2+}]_{aq}$ was the dissolved U(VI) concentration and $[UO_2^{2+}]_{removed}$ was the concentration of U(VI) that was incorporated into a solid phase through sorption and precipitation. $[UO_2^{2+}]_{removed}$ was

defined as the difference between total added concentration and $[UO_2^{2+}]_{aq}$.

The analysis that follows is focused on the precipitation zones, i.e., where $[UO_2^{2+}]_{aq}$ becomes constant for equilibrium conditions (longer aging times) and for a given pH, as defined by $*K_{sp}$. The vertical arrows in Fig. 2 represent the predicted $[UO_2^{2+}]_{aq}$ in equilibrium with schoepite for that pH, based on formation and solubility constants and species defined in Langmuir (1978). The experiments in the top row of Fig. 2 did not contain ferric (hydr)oxide and were initially supersaturated with respect to schoepite. $[UO_2^{2+}]_{aq}$ decreased over time to approximately the solubilities predicted using the constants in Langmuir (1978). The experiments with HFO (middle row in Fig. 2) or hematite (bottom row in Fig. 2) represent some conditions that were initially undersaturated with respect to schoepite and other conditions that were initially supersaturated with respect to schoepite. For supersaturated conditions, $[UO_2^{2+}]_{aq}$ decreased over time to approximately the predicted solubility, based on constants in Langmuir (1978).

Samples with low to intermediate initial supersaturation (Fig. 3(a) and (b)) contained schoepite (Powder Diffraction File number (PDF#) 29-1376 (JCPDS, 1994) and metaschoepite (PDF #43-0364). Schoepite was not detected for the highest initial supersaturation (Fig. 3(c)); sodium uranium oxide hydrate

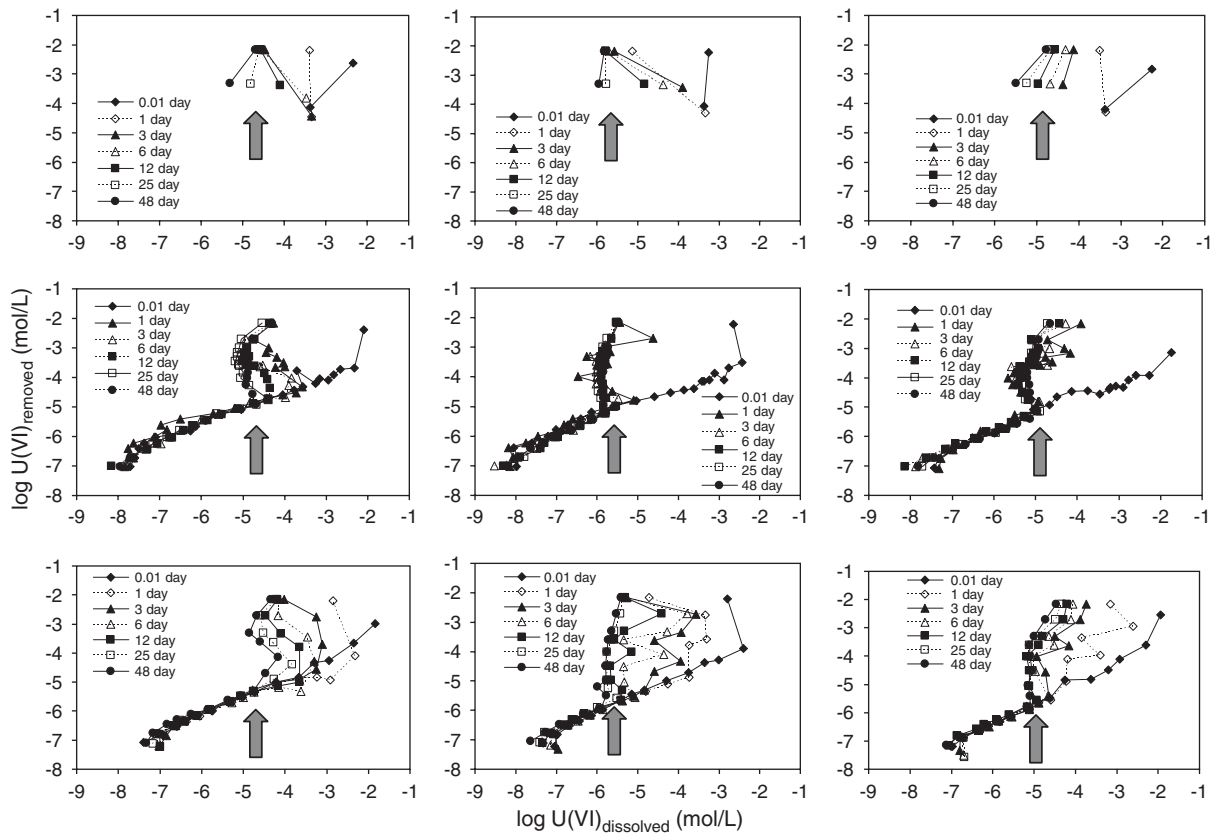


Fig. 2 – Log [U(VI)] in a solid phase compared to log [U(VI)] dissolved as a function of time (0.01–48 days) for pH 5.9 (left column), pH 6.8 (middle column), and pH 7.8 (right column), and with no Fe(III) phase (top row), HFO (middle row), or hematite (bottom row). Arrows show predicted solubility using formation constants from Langmuir (1978) with $\log *K_{sp} = 5.39$ for schoepite.

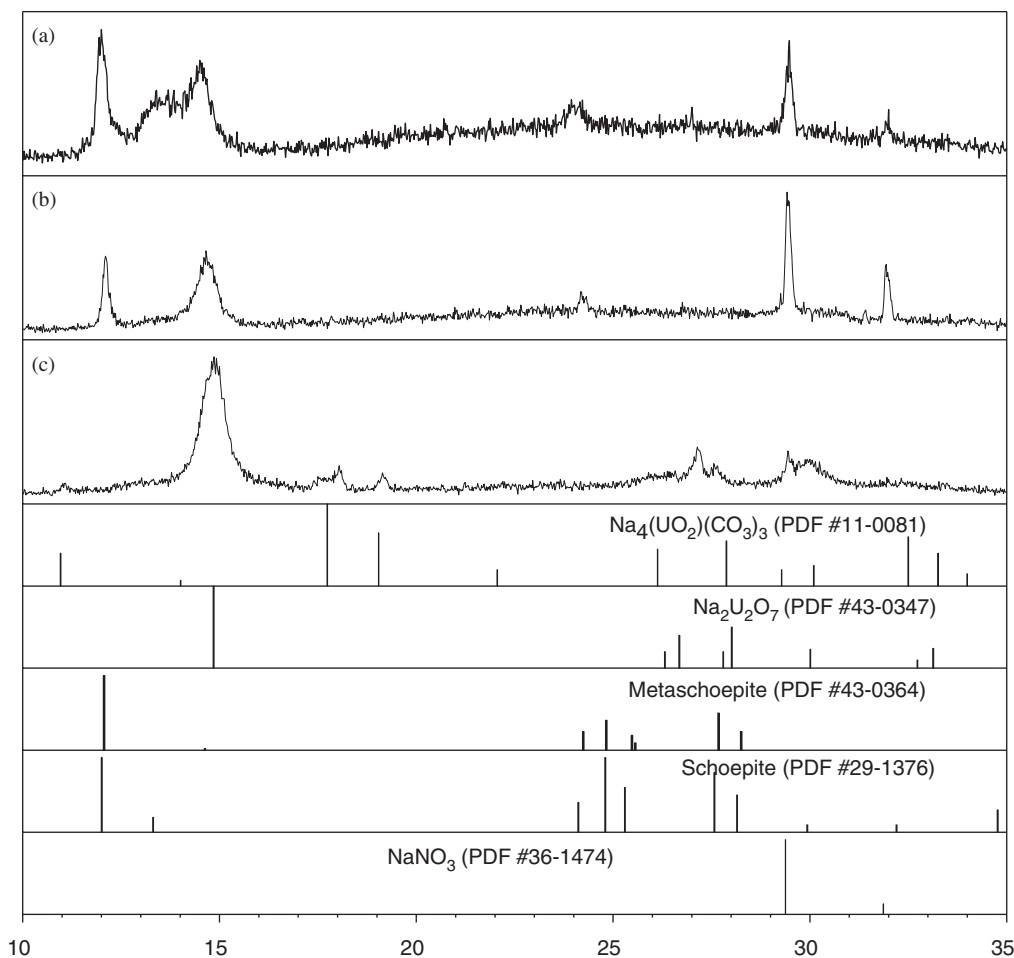


Fig. 3 – X-ray diffraction patterns for precipitates formed in the presence of HFO. Well-defined schoepite was identified for low initial supersaturation (a) and intermediate initial supersaturation (b) and was not observed for the highest initial supersaturation (c).

(PDF #43-0347) was observed and could have been produced by transformation of amorphous U(VI) (hydr)oxide (Giammar and Hering, 2004). Mixed precipitates of U(VI) and Fe(III) (Bruno et al., 1995; Duff et al., 2002) were not identified by XRD analysis. The XRD results are consistent with the observation that solubility was higher for the largest initial supersaturation, analogous to the tendency to precipitate HFO (rather than hematite) or amorphous $\text{Al}(\text{OH})_3$ (rather than gibbsite) when the initial degree of supersaturation is large (Feitknecht and Schindler, 1963; Schindler, 1967). The Ostwald step rule has been used to explain the formation of amorphous oxides of Fe(III) or Al(III) (Morse and Casey, 1988; Steefel and van Cappellen, 1990). If the surface tension between the stable solid phase and the solvent is high, then the formation of a more soluble phase with lower surface tension can be favorable. A critical nucleus size must be exceeded, for a given degree of supersaturation, before precipitation of the eventually more stable phase is thermodynamically favorable (Steefel and van Cappellen, 1990). Several investigators (Christ and Clark, 1960; Christ, 1965) reported that schoepite has poly types with different extents of hydration ($\text{UO}_3 \cdot x\text{H}_2\text{O}$). Christ and Clark observed dehydration of schoepite over several months under a water-saturated atmosphere at room tem-

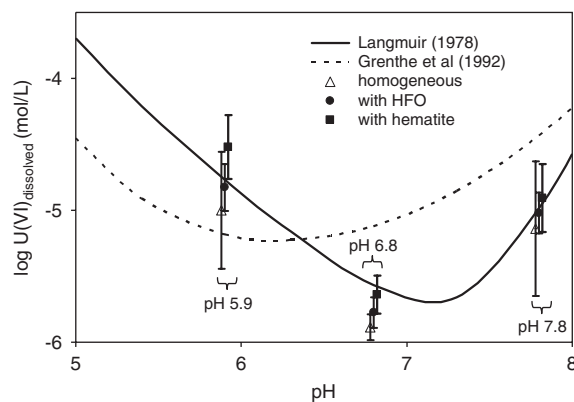


Fig. 4 – Measured solubility (mean \pm standard deviation) at 48 days compared to predicted solubility. Data include all initially supersaturated condition. All data were obtained at pH 5.9, 6.8, and 7.8.

perature. Sowder et al. (1999) noticed that re-hydration of synthetic schoepite resulted in reduced crystallinity. Dawson et al. (1956) reported inter-conversions of $\text{UO}_3 \cdot n\text{H}_2\text{O}$ as a function of temperature and the degree of hydration. Finch

and coworkers experimentally confirmed the intergrowth of three different types of schoepite (schoepite, metaschoepite, and dehydrated schoepite) (Finch et al., 1997, 1998). Giammar and Hering (2004) reported complete conversion of synthetic metaschoepite to clarkeite-like sodium uranyl oxide hydrate or a cesium uranyl oxide hydrate.

The measured solubilities of U(VI) after 48 days for the nine sets of initial conditions (three pH values and homogeneous, HFO, or hematite) are plotted in Fig. 4. There was no statistical differences at $p = 0.05$ due to different initial solid phases, although average solubility was always highest for hematite and lowest for the homogeneous condition. The solubility of uranyl after 48 days was closest to the predicted values using the speciation model from Langmuir (1978) with $\log^*K_{sp} = 5.39$ (solid line in Fig. 4).

All data on 48 days that showed initial supersaturation were averaged and then compared to predicted solubilities using three sets of formation constants and five reported values for \log^*K_{sp} (Fig. 5(a), (c), and (e)). Solubility predicted using Langmuir (1978) best described the experimental results

of this study. Predicted soluble speciation in equilibrium with the solid phases are presented in Fig. 5(b), (d), and (f). The dominant dissolved species between pH 5 and 8 were as follows: $(UO_2)_3(OH)_5^+$, $UO_2CO_3(aq)$, and $UO_2(CO_3)_2^{2-}$ based on Langmuir (1978); UO_2^{+2} , $UO_2(OH)_2^\circ$ and $(UO_2)_2(OH)_3(CO_3)^{-1}$ based on Grenthe et al. (1992); and UO_2^{+2} , UO_2OH^+ , and $(UO_2)_2(OH)_3(CO_3)^{-1}$ based on Waite et al. (1994).

The predicted speciation of uranyl is shown in Fig. 6 for $U(VI)_{total\ dissolved} = 1\ \mu M$ and $P_{CO_2} = 10^{-3.5}\ atm$, $25^\circ C$. $(UO_2)_3(OH)_5^+$ was still a dominant dissolved species based on the constants in Langmuir (1978) and UO_2^{+2} , $UO_2(CO_3)^\circ$, and $UO_2(CO_3)_2^{2-}$ were also important species. $UO_2(OH)_2^\circ$ dominated over most of the pH range of this study based on the constants in Grenthe et al. (1992), and $(UO_2)_2(OH)_3(CO_3)^{-1}$ accounted for over 20% of dissolved U(VI) for $pH \sim 7.5$. Application of the constants in Waite et al. (1994) indicated that UO_2^{+2} , UO_2OH^+ , $(UO_2)_2(OH)_3(CO_3)^{-1}$, and $UO_2(CO_3)_3^{-4}$ were dominant species from pH 5 to 8. Predicted concentrations of all dissolved species are listed in Table 2. The predicted concentrations of UO_2^{+2} for identical pH and total U(VI) varied

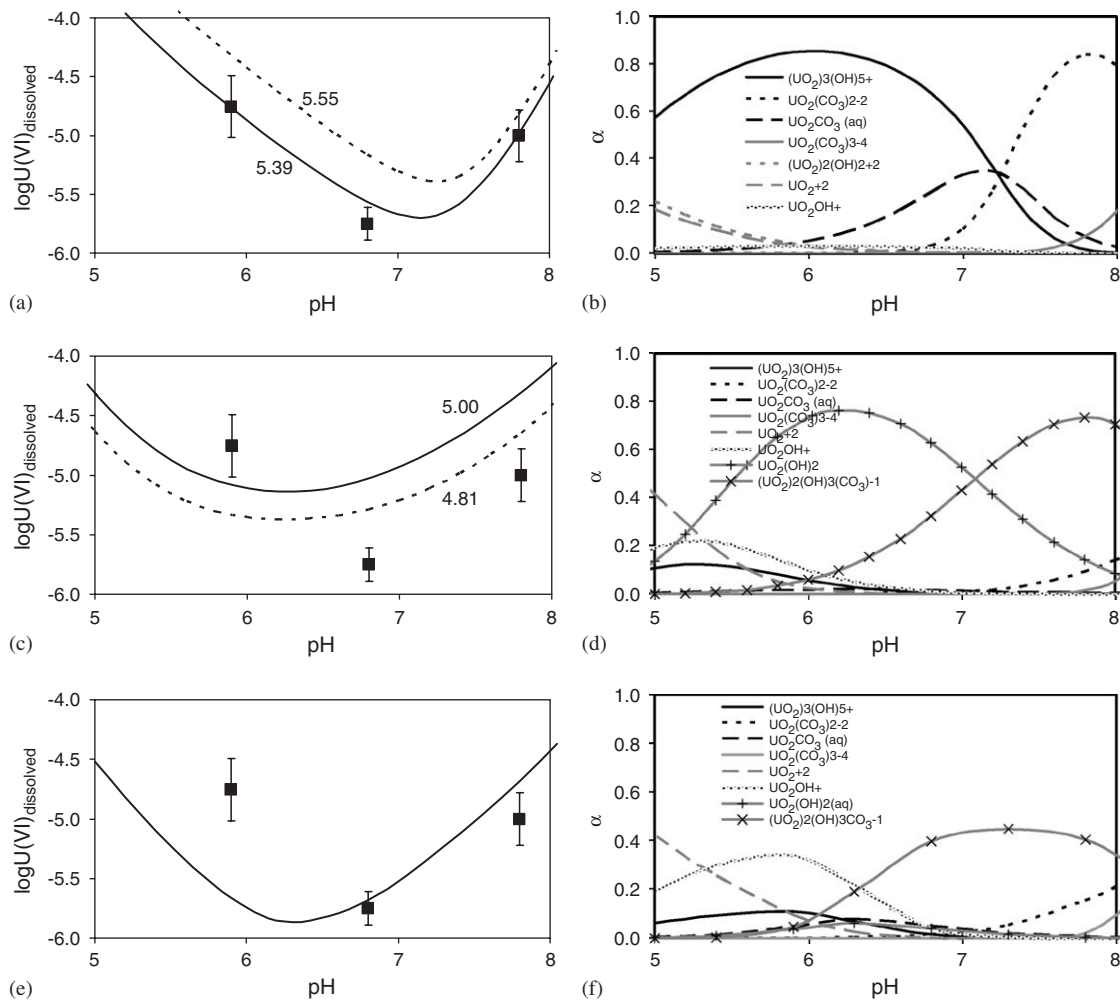


Fig. 5 – Average of all 48 day results for initially supersaturated conditions versus predicted solubility (left) and predicted soluble speciation in equilibrium with the solid phases (right): (a) and (b) were based on constants from Langmuir (1978); (c) and (d) were based on Grenthe et al. (1992); (e) and (f) were based on Waite et al. (1994). Two values of \log^*K_{sp} values in (a) and (b) represent the range reported by those authors.

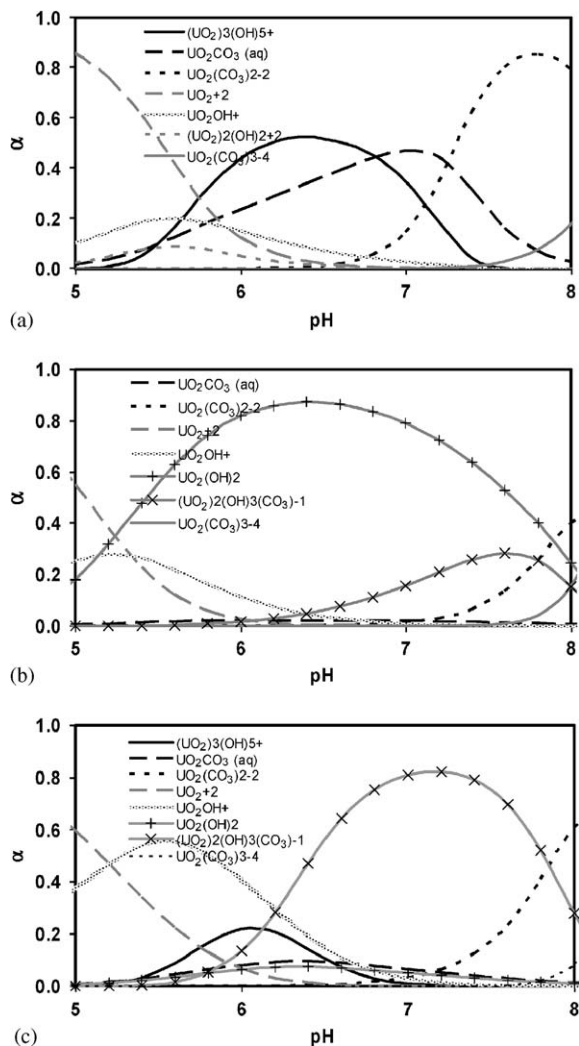


Fig. 6 – Predicted speciation versus pH for U(VI)_{total} = 10⁻⁶ M and P_{CO₂} = 10^{-3.5} atm: (a) cationic trimer and carbonate monomers are major species at neutral pH using Langmuir (1978); (b) dihydroxo monomer and anionic mixed ligand dimer dominate using Grenthe et al. (1992); (c) anionic mixed-ligand dimer dominates using Waite et al. (1994).

by more than an order of magnitude. The effect on the predicted environmental reactivity of U(VI) is significant, e.g., the Nernst potential for the U(VI)/U(IV) couple is proportional to $1/2 \log[\text{UO}_2^{2+}]$. One strategy for decreasing the mobility of uranium in groundwater is to reduce U(VI) to relatively insoluble uraninite UO_{2(s)} addition of Fe(II), organic substrate, or other reducing agents. For the pH and total U(VI) condition illustrated by in this example, reduction of U(VI) to a selected concentration would require three times the concentration of Fe²⁺ if calculated with the constants in Grenthe et al. (1992) compared to the constants in Langmuir (1978). Electrostatic models for predicting sorption of U(VI) onto hydrous metal oxides require calculation of sorbate speciation (Dzombak and Morel, 1990), i.e., it may be presumed that UO₂²⁺, UO₂(OH)⁺, carbonate, or polymeric species are sorbed (Hsi and Langmuir, 1985). The large differences in predicted U(VI) speciation could lead to significant differences in identifica-

Table 2 – Predicted fractional distributions of dissolved U(VI) species at pH = 6.8, U(VI)_{total} = 10⁻⁶ M, P_{CO₂} = 10^{-3.5} atm, and I = 0.01

Reference	Langmuir (1978)	Grenthe et al. (1992)	Waite et al. (1994)
UO ₂ ²⁺	5.85e-3	6.35e-4	1.55e-3
UO ₂ OH ⁺	4.49e-2	1.85e-2	4.53e-2
UO ₂ (OH) ₂ ⁰	—	8.36e-1	4.07e-2
UO ₂ (OH) ₃ ⁻	—	7.38e-3	2.85e-3
UO ₂ (OH) ₄ ²⁻	—	1.01e-9	2.45e-9
(UO ₂) ₂ OH ³⁺	—	5.63e-9	5.56e-8
(UO ₂) ₂ (OH) ₂ ²⁺	4.33e-3	5.09e-5	3.09e-4
(UO ₂) ₃ (OH) ₄ ²⁺	—	6.70e-7	1.41e-5
(UO ₂) ₃ (OH) ₅ ⁺	4.52e-1	6.94e-4	1.43e-2
(UO ₂) ₃ (OH) ₇	—	9.81e-6	2.07e-4
(UO ₂) ₄ (OH) ₇ ⁺	—	6.91e-6	5.57e-4
UO ₂ (CO ₃) ⁰	4.38e-1	1.98e-2	5.07e-2
UO ₂ (CO ₃) ₂ ²⁻	5.46e-2	5.41e-3	1.51e-2
UO ₂ (CO ₃) ₃ ⁴⁻	4.91e-5	8.45e-6	2.21e-5
(UO ₂) ₃ (CO ₃) ₆ ⁶⁻	—	8.58e-15	—
(UO ₂) ₂ (OH) ₃ CO ₃ ⁻¹	—	1.12e-1	3.99e-1
(UO ₂) ₃ (OH) ₃ CO ₃ ⁺¹	—	7.57e-10	—
(UO ₂) ₁₁ (OH) ₁₂ (CO ₃) ₆ ⁻²	—	1.67e-81	—

There is nearly an order of magnitude difference in predicted [UO₂²⁺] and larger variations for polymeric species.

tion of modeling parameters for surface complexation. Predictions of the concentrations of U(VI) polymers were very different. Use of the constants in Langmuir (1978) resulted in significant [(UO₂)₃(OH)₅⁺] even for low total dissolved U(VI); the dominant polymeric species was (UO₂)₂(OH)₃(CO₃)⁻¹ using the constants in Grenthe et al. (1992). Assumption of an anionic versus cationic polymer would result in different sorption behavior due to electrostatic terms. Polymeric species tend to sorb more strongly probably due to multiple attachment sites for a single species when adsorption energy per site exceeds entropy decreases (Stumm, 1992). Au et al. (1998, 1999) addressed this issue in detail when describing adsorption of organic polymers on oxide surfaces. Similar differences in speciation are predicted for lower U(VI) concentrations, e.g. for the maximum contaminant level for uranium in drinking water of 0.13 μM (30 ppb) (EPA, 2000).

4. Conclusions

The following conclusions were derived from this work.

1. Precipitation of UO₃·nH₂O was fastest in the presence of hydrous ferric oxide (HFO) and slower with hematite or without initial addition of a solid phase (homogeneous).
2. Solubility at 48 days was similar for HFO, hematite, or homogeneous conditions (no statistical difference at p = 0.05) although the mean values for solubility increased slightly in the order homogeneous < hematite < HFO.
3. An amorphous phase formed for the highest initial supersaturation conditions, consistent with the Ostwald step

rule. Solubility was up to a factor of ten higher and crystalline schoepite was not observed for the highest initial degree of supersaturation.

4. The solubility data were compared with several published sets of thermodynamic constants for soluble and solid species of U(VI), and especially with sets of constants described by Langmuir (1978), Grenthe et al. (1992), and Waite et al. (1994). The solubility results that are reported in this paper were represented most accurately by using the hydrolysis constants from Langmuir (1978) with schoepite ($\log^*K_{sp} = 5.39$) as the solubility limiting phase for low to intermediate initial degree of supersaturation.
5. The predicted concentrations of monomeric and polymeric species differed considerably when using the different sets of formation constants, e.g., predicted activity of UO_2^{2+} for 10^{-6} M total U(VI), pH 6.8, and $P_{CO_2} = 10^{-3.5}$ atm differed by more than a factor of ten depending on the suite of thermodynamic constants that were used.
6. The substantial differences in predicted speciation are significant with respect to oxidation–reduction potential, complexation, sorption, or precipitation of U(VI).

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