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

Je-Hun Jang, Brian A. Dempsey, William D. Burgos*

Environmental Engineering, 212 Sackett Bldg., The Pennsylvania State University, University Park, PA 16802, USA

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ABSTRACT

Solubility of $UO_3 \cdot nH_2O$ 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 $UO_3 \cdot nH_2O$.

1. Introduction

U(VI) exists predominantly as uranyl (UO_2^{2+}) for acidic conditions, and forms hydroxyl and carbonato 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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*Corresponding author. Tel.: +1 814 865 1226; fax: +1 814 863 7304.
E-mail address: jhjang2004@gmail.com (J.-H. Jang).

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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-$UO_2(OH)_2$ ($\log {}^*K_{sp} = 4.93$), 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
$UO_2(OH)_2^0$	—	⩽−10.30	−13.00	—	−12.0	—
$UO_2(OH)_3^-$	—	−19.20	—	—	−20.0	—
$UO_2(OH)_4^{-2}$	—	−33.00	—	—	−33.0	—
$(UO_2)_2OH^{3+}$	—	—	−4.06	—	—	—
$(UO_2)_2(OH)_3^+$	—	−2.70	—	—	−2.8	—
$(UO_2)_2(OH)_2^{2+}$	−5.62	−5.62	−5.54	−5.57	−5.63	−5.62
$(UO_2)_3(OH)_4^{2+}$	—	−11.90	—	−11.79	−11.9	(−11.75)[b]
$(UO_2)_3(OH)_5^+$	−15.63	−15.55	−15.44	−15.59	−15.56	−15.63
$(UO_2)_3(OH)_7^-$	—	−31.00	—	—	−31.0	—
$(UO_2)_4(OH)_6^{+2}$	—	—	—	−20.48 (I = 0.5 M)	—	—
$(UO_2)_4(OH)_7^+$	—	−21.90	—	−24.28 (I = 0.1 M)	−21.9	—
$UO_2(CO_3)^0$	10.06	9.68	10.0	9.6	9.7	—
$UO_2(CO_3)_2^{-2}$	16.98	16.94	17.0	16.9	17.0	—
$UO_2(CO_3)_3^{-4}$	21.40	21.60	21.6	21.6	21.63	—
$(UO_2)_3(CO_3)_6^{-6}$	—	54.00	53.4	54.0	—	—
$(UO_2)_2(OH)_3CO_3^{-1}$	—	−0.94	—	−0.9	−1.18	—
[c]$(UO_2)_3(OH)_3CO_3^{+1}$	—	0.57	—	0.7	—	—
$(UO_2)_{11}(OH)_{12}(CO_3)_6^{-2}$	—	35.92	—	34.0	—	—
Solid phases				$\log {}^*K_{sp}^0$		
$UO_2(OH)_2 \cdot H_2O(c)$ (schoepite)	5.39[d]	—	—	5.99	—	—
α-$UO_3 \cdot 0.9H_2O$	—	5.00	—	—	—	—
β-$UO_2(OH)_2$	—	4.93	—	—	4.93	—
β-$UO_2(OH)_2(c)$	5.55	—	—	—	—	—
$UO_3 \cdot 2H_2O(cr)$	—	4.81	—	—	—	—
$UO_3(am)$ (gummite)	10.40	—	—	—	—	—
α-UO_3	—	8.63	—	—	—	—
β-UO_3	—	8.30	—	—	—	—
γ-UO_3	—	7.70	—	—	—	—
γ-$UO_3(c)$	7.69	—	—	—	—	—
$UO_2(OH)_2(c)$	—	—	—	—	—	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 [Cl^-].

[c] Grenthe et al. (1992) denoted this species as $(UO_2)_3O(OH)_2(HCO_3)^{+1}$.

[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).