

CALCULATED SOLUBILITIES OF RADIOELEMENTS AT 25°C IN J-13 WELL WATER

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INTRODUCTION

The equilibrium solubilities of stoichiometric minerals that contain radioactive elements in groundwater characteristic of Yucca Mountain, Nevada, can provide thermodynamically based source-term concentrations for performance assessment transport calculations. Radioelement concentrations calculated in this manner represent maximum equilibrium concentrations for the given conditions. Concurrent equilibrium coprecipitation (solid solution) of radioelements in solids composed dominantly or partially of other species and/or sorption of radioelements on solid surfaces would lead to equal or lower total aqueous solution concentrations for the radioelements. Thus solubilities of stoichiometric radioelement-bearing solids yield a degree of conservatism in models for radionuclide source concentrations. Furthermore, accurate thermodynamic models offer a secure basis for extrapolation over the long time scales of repository evolution.

Despite these favorable characteristics, a number of uncertainties and limitations must be recognized. Thermodynamic data are uncertain for both mineral dissolution reactions and critical aqueous speciation reactions. Although a comprehensive evaluation of the thermodynamic data base is beyond the scope of this study, selected comparisons to other recently developed solubility estimates and data bases reveal important discrepancies among them. The thermodynamic data for the computations reported here are derived from the composite data base associated with the EQ3/6 software package (data0.com.R7, 29-oct-90) developed at Lawrence Livermore National Laboratory partially in support of the Department of Energy high-level nuclear waste disposal program (e.g. Wolery, 1979; 1983; Wolery et al., 1990). The EQ3/6 data were extensively revamped for the program release that occurred in late 1990, and some important differences between it and earlier versions are noted with respect to radioelement solubilities.

The results of equilibrium analyses may also be invalidated by metastable supersaturations, which can persist indefinitely in low-temperature water-rock systems. Primary nuclear waste forms are sufficiently unstable thermodynamically that their dissolution can generate aqueous solutions that are supersaturated with respect to the most stable radioelement-bearing solids. Slow nucleation and/or growth rates for these solids, particularly at low temperatures, can sustain the supersaturated conditions. In this case minimum equilibrium solubilities do not give conservatively low radioelement concentrations. Similarly, colloidal and microbial concentrations of radioelements are not accounted in equilibrium solubility computations.

Finally, the detailed geochemical environment at Yucca Mountain, on which equilibrium solubilities depend, is incompletely constrained. The bulk chemical composition of J-13 well water extracted from the saturated-zone aquifer in the Topopah Spring unit is used as a reference for the calculations presented here (Table 1). Water in the unsaturated near-field environment at Yucca Mountain is expected to differ substantially from the J-13 composition, although details of the differences are incompletely understood. One likely difference is the equilibrium CO₂ pressure, which may be lower in the unsaturated zone. Therefore, two variations on the J-13 water chemistry are examined in this report which have different equilibrium partial pressures of CO₂, and correspondingly different values of pH. One water with a near-neutral pH of 6.9 corresponds to a CO₂ pressure of 10^{-1.81} bar, which is calculated

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based on the analytical data for J-13 water. The other with a slightly alkaline pH of 8.55 corresponds to the atmospheric CO₂ pressure of 10^{-3.5} bar. Equilibrium aqueous speciations of the two waters at 25°C using EQ3 (Table 1) indicate supersaturations with respect to many minerals, notably aluminosilicates, silica minerals, and ferric oxides/ hydroxides. These supersaturations are partially realistic, especially with respect to silica concentrations in excess of quartz solubility, which is common in low-temperature geochemical systems. Errors in the chemical analyses of aluminum and iron in J-13 water (e.g. due to inclusion of colloidal material) may be responsible for many additional predicted supersaturations. Despite these uncertainties, solution compositions retaining supersaturations are employed in the computations of radioelement solubilities reported here. This has a potentially nonconservative effect. For example, if a species concentration is modeled to be greater than its true concentration, and that species combines with a radioelement to form a solubility controlling mineral, then the calculated radioelement concentration (solubility) would be unrealistically diminished.

Solubilities at 25°C of uranium, lead, strontium, americium nickel, neptunium, plutonium, radium, tin, and thorium have been computed. These have been selected from radionuclides in nuclear waste identified by Kerrisk (1985) with potential to violate environmental or safety standards in a Yucca Mountain repository. The species cesium, iodine, and carbon have not been examined, because stoichiometric mineral solubilities for these elements are large. Individual radioelement solubilities were examined separately; i.e., no coupled effects among radioelements were considered, which is generally conservative with regard to radioelement concentrations. The one or two most stable solid phases in the EQ3 data base were identified for each radioelement, and the J-13 water variants were equilibrated with these phases in separate calculations to constrain the radioelement concentrations. Solubility controlling solid phases, radioelement concentrations, and dominant radioelement bearing aqueous species are summarized in Table 2 for each simulation.

DISCUSSION OF RESULTS

Uranium.

The calcium uranyl silicate, haiweeite, and the uranyl silicate, soddyite, are calculated to be the most stable uranium solids. Total uranium concentrations are 2.2x10⁻⁹ and 5.3x10⁻⁸ molal at equilibrium with the two minerals, respectively, in the low pH (high CO₂ pressure) solution, and 1.7x10⁻¹⁰ and 1.4x10⁻⁷ molal, respectively, for the high pH variation. Uranyl carbonate anions are the dominant uranium aqueous species. Haiweeite solubility decreases, and soddyite solubility increases with increasing pH. Strong aqueous uranyl phosphate complexes, which existed in prior versions of the EQ3 data base and which had a dominant effect on simulated aqueous uranium chemistry, are absent from the data0.com.R7 version. Schoepite (UO₃•2H₂O) and tyuyamunite (calcium uranyl vanadate) are somewhat more soluble than haiweeite and soddyite in the simulations.

Nguyen et al. (1991) recently published results of solubility studies at 30°C for four uranyl silicates: soddyite, uranophane, Na-boltwoodite, and Na-weeksite. Their data are theoretically compatible with the EQ3/6 data with regard to standard states and aqueous species properties. However, the stoichiometries adopted by Nguyen et al. for uranophane and Na-boltwoodite differ from those in the EQ3/6 data base. Weeksite data from Nguyen et al. are unreliable because soddyite crystallized in the solubility experiments. Hence, only the data for soddyite can be reasonably compared. The measured values for the equilibrium constant for soddyite reported by Nguyen et al. differ significantly from the values consistent with the EQ3/6 data base. These values are compared in Table 3. A potentially serious ambiguity in the Nguyen et al. data is the interpretation of the stoichiometry of the minerals. Ideal

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stoichiometries were assumed in the thermodynamic interpretation of their experimental data. However, chemical analyses of the solids reported by Nguyen et al. indicate significant deviations from these stoichiometries. The Nuclear Energy Agency has recently prepared a comprehensive evaluation of uranium chemistry which should be consulted in future evaluations of uranium solubility.

Lead.

Lead solubility is controlled by cerussite (PbCO_3) or plattnerite (PbO_2). In the lower pH solution the divalent lead cation is the dominant aqueous species, and cerussite solubility yields a total lead concentration of 6.2×10^{-8} molal. In the higher pH solution, PbOH^+ is the dominant aqueous species, and both plattnerite and cerussite solubilities yield lead concentrations of about 1.2×10^{-8} molal. Plattnerite precipitation requires oxidation of aqueous species of divalent lead. A strong lead carbonate aqueous species in former versions of the EQ3 data base dominated aqueous lead chemistry, but it has been eliminated from the data0.com.R7 compilation. These complexes may be important because they increase lead solubilities, and the aqueous environment at Yucca Mountain is rich in carbonate. Data for their stability should be carefully examined.

Strontium.

The carbonate strontianite is the stable solid controlling strontium solubility. Sr^{2+} is the main aqueous species, and the total strontium concentrations decrease from 4.3×10^{-5} to 1.1×10^{-6} with increasing pH for the two J-13 variants. These concentrations should provide reliably conservative limits because strontium would be readily incorporated (coprecipitated/exchanged) in secondary phases, such as zeolites, clays, and calcite, which would lead to lower aqueous concentrations.

Americium.

The solid AmOHCO_3 is calculated to control the solubility of americium at 6.9×10^{-8} and 5.7×10^{-9} molal in the lower and higher pH solutions, respectively. Americium carbonate ions are the dominant aqueous species. The solid $\text{Am}(\text{OH})_3$ is calculated to have a much greater solubility at the higher pH.

Nickel.

The spinel mineral trevorite (NiFe_2O_4) is calculated to have a low solubility. However, data in the EQ3/6 data base for ferrite minerals such as trevorite have recently been criticized as giving anomalously low solubilities (Jordi Bruno, oral communication, Natural Analogs Working Group Meeting, 1990). The anomalously high iron content of J-13 water also contributes to the low calculated solubility of nickel controlled by trevorite, hence values for trevorite have been omitted from Table 2. The solubility of the nickel silicate Ni_2SiO_4 is strongly pH dependent, yielding nickel concentrations that decrease from 9.3×10^{-6} to 5.0×10^{-9} molal between pH 6.9 and 8.5. The Ni^{2+} cation is the dominant aqueous species.

Neptunium.

The solubility of NpO_2 is calculated to be 9.9×10^{-6} molal in the lower pH solution and 5.6×10^{-7} molal in the higher pH solutions. The NpO_2^+ species dominates the aqueous neptunium chemistry in the lower pH solution, but the significance of the $\text{NpO}_2\text{CO}_3^-$ species increases with increasing pH, and is slightly more concentrated than NpO_2^+ in the higher pH solution. In the higher pH solution the solubility

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of amorphous $\text{NpO}_2(\text{OH})$ is calculated to be 1.3×10^{-4} molal.

Plutonium.

Crystalline PuO_2 controls the solubility of plutonium at 1.5×10^{-11} molal at pH 6.9 and 5.6×10^{-13} molal at pH 8.5 in the simulated waters. $\text{PuO}_2(\text{CO}_3)_2^{2-}$ is the dominant aqueous species at the higher pH and accounts for about four percent of the plutonium at the lower pH. Plutonium fluoride complexes constitute over ninety percent of aqueous plutonium at pH 6.9.

Radium.

Solid radium sulfate fixes the radium concentration at 3.2×10^{-7} molal in both model solutions. Ra^{2+} is the sole aqueous species of radium in the data base.

Tin.

Tin oxide (SnO_2) is at equilibrium with 2.7×10^{-8} molal $\text{Sn}(\text{OH})_4$ (the only significant aqueous species of tin) in both simulated solutions.

Thorium.

Thorianite (ThO_2) controls the thorium solubility at 9.2×10^{-16} molal in both solutions. A much high solubility of 5.7×10^{-7} molal is calculated for the solid $\text{Th}(\text{OH})_4$. Aqueous $\text{Th}(\text{OH})_4$ is the only significant species of thorium in solution.

CONCLUSIONS

This report offers one component of the comprehensive evaluation of radioelement solubilities that will be required to characterize the source term for performance assessments of the Yucca Mountain repository. The rigor of thermodynamic theory for reliable predictions and the instability of spent nuclear fuel in the Yucca Mountain environment compel this analysis. However, important uncertainties in this examination are the details of the geochemical environment, the likely deviations from chemical equilibrium, and the uncertainties in the thermodynamic data base. Critical evaluation of these factors should be undertaken.

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Table 1. Analytical composition of J-13 well water, and calculated equilibrium aqueous speciations at 25°C. Concentrations are given in units of molality.

Aqueous Species	Analytical Composition	Equilibrium Speciation (Dominant species)	
		log pCO ₂ = - 1.81	log pCO ₂ = -3.5
HCO ₃ ⁻	2.34E-3	2.03E-3	1.82E-3
CO ₂ (aq)		5.29E-4	
CO ₃ ²⁻			3.62E-5
Na ⁺	2.0E-3	1.99E-3	1.99E-3
SiO ₂	1.1E-3	1.10E-3	9.96E-4
H ₃ SiO ₄ ⁻			5.76E-5
HSiO ₃ ⁻			4.16E-5
Ca ²⁺	2.9E-4	2.80E-4	2.69E-4
CaCO ₃			1.26E-5
SO ₄ ²⁻	1.9E-4	1.82E-4	1.82E-4
CaSO ₄		3.96E-6	3.81E-6
Cl ⁻	1.8E-4	1.80E-4	1.80E-4
NO ₃ ⁻	1.6E-4	1.60E-4	1.60E-4
K ⁺	1.4E-4	1.40E-4	1.40E-4
F ⁻	1.1E-4	1.09E-4	1.10E-4
Mg ²⁺	7.2E-5	6.85E-5	6.70E-5
MgSO ₄		1.97E-6	1.93E-6
MgCO ₃			1.42E-6
Li ⁺	8.6E-6	8.59E-6	8.59E-6
Al ³⁺	1.1E-6		
AlO ₂ ⁻		7.19E-7	1.10E-6
AlF ₃		1.45E-7	
AlF ₂ ⁺		1.20E-7	
Al(OH) ₃		9.39E-8	
HPO ₄ ²⁻	1.1E-6		
CaP ₂ O ₇ ²⁻		3.40E-7	2.37E-7
MgP ₂ O ₇ ²⁻		2.10E-7	2.13E-7
Fe ³⁺	7.2E-7		
Fe(OH) ₃		5.04E-7	6.26E-7
Fe(OH) ₂ ⁺		2.15E-7	
Fe(OH) ₄ ⁻			8.78E-8
V ⁴⁺	5.7E-7		
H ₂ VO ₄ ⁻		2.30E-7	1.44E-8
VO ₃ OH ²⁻		1.78E-7	4.94E-7
VO ₂ (OH) ₂ ⁻		1.43E-7	8.95E-9
HVO ₄ ²⁻		1.92E-8	5.32E-8
Ti ⁴⁺	5.4E-7		
Ti(OH) ₄		5.40E-7	5.40E-7
Sr ²⁺	4.7E-7	4.48E-7	4.42E-7
SrHCO ₃ ⁺		1.20E-8	1.07E-8
SrSO ₄		9.82E-9	9.72E-9
Ba ²⁺	1.9E-8	1.87E-8	1.86E-8

(Continued on next page)

Table 1 (continued).

Aqueous Species	Analytical Composition	Equilibrium Speciation (Dominant species)	
		log pCO ₂ = - 1.81	log pCO ₂ = -3.5
Mn ²⁺	1.8E-8	1.70E-8	3.24E-9
MnSO ₄		4.21E-10	
MnO ₄ ⁻			1.22E-8
MnCO ₃			2.37E-9
pH	6.9	6.9	8.55
log(fO ₂ /bar)	-0.85	-0.85	-0.85

Data taken from Department of Energy (1988) and Daniels et al. (1982) (for Sr, Ba, Ti, P, and V).

TABLE 2. CALCULATED SOLUBILITIES OF RADIOELEMENTS IN VARIANTS OF J-13 WELL WATER AT 25°C.

Radioelement	Water	Solubility (molal)	Aqueous Species (percent)	Mineral Phase (composition)
Nickel	pH 6.9	9.26×10^{-6}	Ni ²⁺ (98.52) NiSO ₄ (1.44)	Ni ₂ SiO ₄
Nickel	pH 8.5	4.96×10^{-9}	Ni ²⁺ (98.39) NiSO ₄ (1.45)	Ni ₂ SiO ₄
Nickel	pH 8.5	2.98×10^{-5}	Ni ²⁺ (98.40) NiSO ₄ (1.43)	Busenite (NiO)
Strontium	pH 6.9	4.34×10^{-5}	Sr ²⁺ (95.24) SrHCO ₃ ⁺ (2.55) SrSO ₄ (2.08)	Strontianite (SrCO ₃)
Strontium	pH 8.5	1.10×10^{-8}	Sr ²⁺ (94.05) SrHCO ₃ ⁺ (2.27) SrSO ₄ (2.07) SrCO ₃ (1.51)	Strontianite (SrCO ₃)
Tin	pH 6.9 and 8.5	2.70×10^{-8}	Sn(OH) ₄ (100)	Cassiterite (SnO ₂)
Lead	pH 6.9	6.17×10^{-8}	Pb ²⁺ (85.17) PbOH ⁺ (14.41)	Cerussite (PbCO ₃)
Lead	pH 6.9	2.97×10^{-8}	Pb ²⁺ (85.17) PbOH ⁺ (14.40)	Plattnerite (PbO ₂)
Lead	pH 8.5	1.22×10^{-8}	Pb(OH) ⁺ (79.01) Pb ²⁺ (10.54) PbO (10.35)	Plattnerite (PbO ₂)

TABLE 2, CONTINUED.

Radioelement	Water	Solubility (molal)	Aqueous Species (percent)	Mineral Phase (composition)
Lead	pH 8.5	1.25×10^{-8}	Pb(OH) ⁺ (79.01) Pb ²⁺ (10.54) PbO (10.35)	Cerussite (PbCO ₃)
Radium	pH 6.9 and 8.5	3.23×10^{-7}	Ra ²⁺ (100)	RaSO ₄
Thorium	pH 6.9 and 8.5	9.16×10^{-15}	Th(OH) ₄ (100)	Thorianite (ThO ₂)
Thorium	pH 6.9 and 8.5	5.68×10^{-7}	Th(OH) ₄ (100)	Th(OH) ₄
Uranium	pH 6.9	2.16×10^{-9}	UO ₂ (CO ₃) ₂ ²⁻ (86.02) UO ₂ (CO ₃) ₃ ⁴⁻ (5.38) UO ₂ (OH) ₂ (4.29) UO ₂ CO ₃ (4.16)	Haiweeite (Ca(UO ₂) ₂ (Si ₂ O ₅) ₃ •5H ₂ O)
Uranium	pH 6.9	5.28×10^{-8}	UO ₂ (CO ₃) ₂ ²⁻ (85.94) UO ₂ (CO ₃) ₃ ⁴⁻ (5.38) UO ₂ (OH) ₂ (4.28) UO ₂ CO ₃ (4.16)	Soddyite (UO ₂) ₂ SiO ₄ •2H ₂ O
Uranium	pH 8.5	1.66×10^{-10}	UO ₂ (CO ₃) ₃ ⁴⁻ (69.51) UO ₂ (CO ₃) ₂ ²⁻ (27.92) UO ₂ (OH) ₂ (1.72)	Haiweeite (Ca(UO ₂) ₂ (Si ₂ O ₅) ₃ •5H ₂ O)
Uranium	pH 8.5	1.38×10^{-7}	UO ₂ (CO ₃) ₃ ⁴⁻ (69.47) UO ₂ (CO ₃) ₂ ²⁻ (27.92) UO ₂ (OH) ₂ (1.72)	Soddyite (UO ₂) ₂ SiO ₄ •2H ₂ O

TABLE 2, CONTINUED.

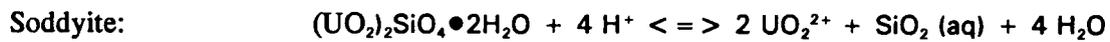
Radioelement	Water	Solubility (molal)	Aqueous Species (percent)	Mineral Phase (composition)
Neptunium	pH 6.9	9.93×10^{-6}	NpO ₂ ⁺ (96.25) NpO ₂ CO ₃ ⁻ (2.71) NpO ₂ OH (0.90)	NpO ₂
Neptunium	pH 8.5	5.55×10^{-7}	NpO ₂ CO ₃ ⁻ (43.63) NpO ₂ ⁺ (38.87) NpO ₂ OH (16.16) NpO ₂ (CO ₃) ₃ ⁴⁻ (0.77)	NpO ₂
Neptunium	pH 8.5	1.34×10^{-4}	NpO ₂ CO ₃ ⁻ (43.39) NpO ₂ ⁺ (39.12) NpO ₂ OH (16.16) NpO ₂ (CO ₃) ₃ ⁴⁻ (0.76)	NpO ₂ OH (amorphous)
Plutonium	pH 6.9	1.50×10^{-11}	PuO ₂ F ₃ ⁻ (76.88) PuO ₂ F ₂ (7.93) PuO ₂ F ₄ ²⁻ (6.69) PuO ₂ (CO ₃) ₂ ²⁻ (4.34) PuO ₂ ⁺ (3.56)	PuO ₂
Plutonium	pH 6.9	6.58×10^{-7}	PuO ₂ F ₃ ⁻ (76.55) PuO ₂ F ₂ (8.02) PuO ₂ F ₄ ²⁻ (6.55) PuO ₂ (CO ₃) ₂ ²⁻ (4.54) PuO ₂ ⁺ (3.72)	PuO ₂ (OH) ₂
Plutonium	pH 8.5	5.63×10^{-13}	PuO ₂ (CO ₃) ₂ ²⁻ (93.32) Pu(OH) ₅ (3.01) PuO ₂ ⁺ (2.14) PuO ₂ F ₃ ⁻ (1.06)	PuO ₂

TABLE 2, CONTINUED.

Radioelement	Water	Solubility (molal)	Aqueous Species (percent)	Mineral Phase (composition)
Plutonium	pH 8.5	2.59×10^{-8}	PuO ₂ (CO ₃) ₂ ²⁻ (93.32) Pu(OH) ₅ ⁻ (3.01) PuO ₂ ⁺ (2.14) PuO ₂ F ₃ ⁻ (1.06)	PuO ₂ (OH) ₂
Americium	pH 6.9	6.88×10^{-8}	AmCO ₃ ⁺ (88.09) Am(CO ₃) ₂ ⁻ (6.84) AmOH ²⁺ (1.70) AmF ²⁺ (1.64) Am ³⁺ (1.13)	AmOHCO ₃
Americium	pH 8.5	5.66×10^{-8}	Am(CO ₃) ₂ ⁻ (74.74) AmCO ₃ ⁺ (24.17) AmOH ²⁺ (0.52)	AmOHCO ₃
Americium	pH 8.5	1.26×10^{-6}	Am(CO ₃) ₂ ⁻ (74.73) AmCO ₃ ⁺ (24.19) AmOH ²⁺ (0.52)	Am(OH) ₃

TABLE 3. Comparison of Equilibrium Constants for Soddyite Dissolution

Reaction



Logarithm (base 10) of the equilibrium constant

	25°C EQ3/6	30°C Nguyen et al. (1991).
Soddyite	.3939	5.74