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Summary. Interpretation and modeling of recent experimental data [1] yield thermodynamic constants for the distribution of trace Np(V) between aqueous solutions and uranophane. These data indicate that neptunyl is relatively excluded from the uranyl mineral structure, but the interpretation depends on uncertain aqueous speciation and thermodynamic properties as a function of temperature. Despite Np exclusion, the low calculated solubility of uranophane at 25°C under conditions relevant to the proposed nuclear waste repository at Yucca Mountain, Nevada, leads to Np concentrations at equilibrium with a Np-bearing uranophane solid solution that are low compared to concentrations invoked as solubility limits in Yucca Mountain performance assessments.

Introduction

Spent nuclear fuel alteration under oxidizing conditions at the high level nuclear waste repository at Yucca Mountain, Nevada, will produce secondary uranyl minerals (e.g., [2,3,4,5,6,7,8]). Much speculation attends the role of these minerals in sequestering trace

radionuclides. For example, Burns et al. [9] provided crystallographic data suggesting that ions of actinide elements would substitute for uranyl ions in secondary uranyl minerals. Murphy and Codell [10] modeled incorporation of radionuclides in secondary schoepite, arbitrarily assigning their proportions relative to uranium to be the same as in the spent fuel. Then, adopting a source term model for radionuclide release controlled by schoepite solubility, they showed that modeled repository performance was substantially improved compared to cases based on empirical spent fuel dissolution rates. Chen et al. [11] used data from spent fuel alteration studies under conditions resembling those at Yucca Mountain (e.g., [12]) to speculate that the Np/U ratio in releases from spent fuel corresponded to the ratio in the fuel and to infer that the Np/U ratio in secondary uranyl products was the same. Promising reports of preferential Np incorporation in secondary dehydrated schoepite in spent fuel alteration tests [13] were shown later to be incorrect [14]. Despite this interest, investigations of the thermodynamic, kinetic, and solid solution properties of uranyl minerals are currently inadequate to predict reliably their effects on repository performance at Yucca Mountain.

Experimental Incorporation of Np in Uranyl Minerals

Burns et al. [1] synthesized uranophane, Na-compreignacite, β-$UO_2(OH)_2$, and metaschoepite containing neptunyl in variable trace amounts in solid solution at 75°C to 100°C. These crucial data apparently reflect solid-aqueous exchange equilibria and show that the Np/U ratio for each solid phase was proportional to the total aqueous Np(V) concentrations in the starting solutions. The synthesis studies revealed that Np

incorporation was limited in metaschoepite and in β-$UO_2(OH)_2$, and that Np solid solution in uranophane and in Na-compreignacite was substantially greater [1].

Aqueous Np concentrations in the synthesis experiments ranged to near 500 ppm [1]. Steady-state total Np concentrations in oxidizing solubility studies range from 10^{-5} to 10^{-3} M (about 2 to 200 ppm) under oxidizing, near neutral pH conditions relevant to Yucca Mountain [15,16]. In contrast, performance assessment studies for the Yucca Mountain repository adopt Np solubility limits at approximately 0.1 to 1 ppm (4×10^{-7} to 4×10^{-6} M) at pH 7 to 8 [17]. These limits are based on model water compositions and calculated NpO_2 and Np_2O_5 solubilities, and they provide reasonable upper bounds to empirical Np concentrations in spent fuel dissolution studies (e.g., [18]), which were not solubility experiments.

The maximum initial aqueous Np concentration in the Burns et al. [1] Np-bearing uranophane synthesis experiments was about 350 ppm (1.5×10^{-3} M). The corresponding Np/U ratio in synthetic uranophane was reported to be about 400 ppm (0.4 mg Np/g U+Np). In contrast, the Np/U ratio in spent nuclear fuel is larger, approximately 1000 ppm at 200 years after discharge in fuel with a burnup of 45 GWd/tHM. If the proportionality between the Np content of uranophane crystals and the aqueous Np concentration observed by Burns et al. [1] was valid for Yucca Mountain conditions, then the Np/U ratio in uranophane would be about 1 ppm for the nominal aqueous Np solubility limit of 1 ppm. This value is three orders of magnitude lower than the Np/U ratio in spent fuel suggesting that sequestration of Np in uranophane would provide an insignificant sink. However, this interpretation neglects the dependence of the Np

distribution on differences in aqueous speciation and temperature between the experiments and Yucca Mountain.

Interpretation of Aqueous Solutions and Solution-Solid Equilibria

Distribution coefficients typically relate the ratio of concentrations of trace to host elements in the solid to the ratio of the total concentrations of these elements in the aqueous phase. This approach is practical, but neglects aqueous speciation and nonideal mixing in both phases, and it cannot be applied outside the range of experimental conditions for which the data are determined. Alternatively, predictive thermodynamic and kinetic relations apply generally to solid solution-aqueous solution relations (e.g., [19,20,21]). A thermodynamic interpretation and predictive application of trace element distribution data from the Np-uranophane synthesis experiments of Burns et al. [1] could help validate their conclusion that "likely incorporation of Np^{5+} into the structure of uranophane ... could have a profound impact on the long-term mobility of Np in the [Yucca Mountain] repository ...." However, this contention is subject to substantial uncertainty because of important differences between the experimental conditions and the likely conditions at Yucca Mountain, and because of the minimal experimental coprecipitation of Np adduced above.

Complete aqueous solution compositions were not reported for the Np-bearing uranyl mineral synthesis experiments [1], but they can be estimated based on mass balance and thermodynamic controls. Reagents used to synthesize Np-bearing uranophane and corresponding calculated total molalities of individual components are given in Table I. The amount of added perchloric acid was calculated to match the

reported pH, and all concentrations were adjusted accordingly. Complete dissolution of reagents and no mineral precipitation were assumed to calculate an equilibrium aqueous speciation model for the starting solution at 25°C using PHREEQC [22]. Incomplete dissolution of reagents or precipitation, as suggested by the cooling model presented below, could affect these results.

The resulting model solution is dominated by acetate and acetate complexes. Data for aqueous mono-, di-, and tri-acetate complexes of uranyl ions and monoacetate complexes for neptunyl ions were taken from Martel and Smith [23]. Enthalpies of reaction are available only for uranyl acetate complexes, not neptunyl complexes. Other aqueous species data were taken from the LLNL (v8.R6) data base except as noted.

Experimental synthesis of Np-bearing uranophane was conducted at 100°C [1]. An equilibrium model for the aqueous solution at 100°C was generated using the component masses from the 25°C solution model (Table I) and adjusting the pH to achieve charge balance. A batch PHREEQC model was then used to simulate precipitation at 100°C of Np-bearing uranophane with the Np/U ratio reported in the experimental study using thermodynamic data described below. The principal aqueous species in the resulting solution are given in Table II. The quantity of Np-bearing uranophane precipitated in the model was 0.141 moles/kg H_2O. The total Np(V) concentrations in the model solutions were 1.27×10^{-3} m at 25°C and 1.22×10^{-3} m at 100°C. This result is supported qualitatively by the observation by P.C. Burns (personal communication) that only a small fraction of Np precipitated.
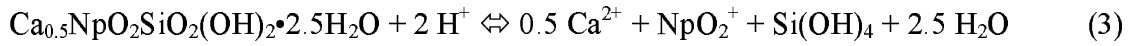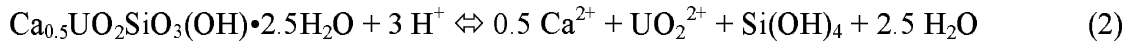
The thermodynamic properties of the Np-bearing uranophane were based on the reported composition of the synthetic phase containing 400 ppm Np/(U+Np) and the equilibrium mass action relation for the exchange reaction

$$Ca_{0.5}UO_2SiO_3(OH) \cdot 2.5H_2O + NpO_2^+ + H^+ \Leftrightarrow Ca_{0.5}NpO_2SiO_2(OH)_2 \cdot 2.5H_2O + UO_2^{2+} \quad (1)$$

   Uranophane   Np-uranophane

The stoichiometry of the Np-uranophane is inferred from the likely substitution of NpO_2^+ for UO_2^{2+} and coupled protonation of structural oxygen. The Np distribution thus depends on pH as well as on the hydrolysis and complexation of aqueous uranyl and neptunyl. The exchange reaction (1) is the difference between two dissolution reactions

$$Ca_{0.5}UO_2SiO_3(OH) \cdot 2.5H_2O + 3\ H^+ \Leftrightarrow 0.5\ Ca^{2+} + UO_2^{2+} + Si(OH)_4 + 2.5\ H_2O \quad (2)$$

$$Ca_{0.5}NpO_2SiO_2(OH)_2 \cdot 2.5H_2O + 2\ H^+ \Leftrightarrow 0.5\ Ca^{2+} + NpO_2^+ + Si(OH)_4 + 2.5\ H_2O \quad (3)$$

The equilibrium constant (K_x) for the exchange reaction (1) is written

$$K_x = K_{Ur}/K_{Np\text{-}Ur} = (a_{Np\text{-}Ur})(a_{UO_2^{2+}})/[(a_{Ur})(a_{NpO_2^+})(a_{H^+})] \quad (4)$$

where a stands for activity, Ur and Np-Ur denote the uranophane and Np-uranophane endmembers, respectively, of the solid solution, and K_{Ur} and $K_{Np\text{-}Ur}$ stand for the equilibrium constants for dissolution reactions (2) and (3). Reported experimental data provide a value at 25°C for log K_{Ur} = 5.41 [8,24,25]. Using an estimated standard enthalpy for the uranophane dissolution reaction (2), -65.1 kJ/mole [8], the 100°C value of log K_{Ur} = 3.12 is obtained from the van't Hoff equation. Assuming an ideal solid solution, a_{NpUr} and a_{Ur} equal the reported experimental mole fractions of the components, 4×10^{-4} and $1 - 4 \times 10^{-4}$ = 0.9996, respectively. Values for K_{NpUr} and K_x were then obtained by iteratively fitting the mole fractions of the solid components and the aqueous uranyl,

neptunyl, and hydrogen ion activities provided by the equilibrium batch precipitation model at 100°C. Log K_{Np-Ur} = 4.50 and log K_x = -1.38 were obtained for 100°C.

The standard state enthalpy of formation of the hypothetical Np-uranophane endmember at 25°C can be estimated by summing structural component enthalpies in their stoichiometric proportions for CaO, H_2O (structural), and H_2O (hydration) from [26], SiO_2 from [27], and the standard state enthalpy of formation of Np_2O_5(cr) from [28]. For $Ca_{0.5}NpO_2SiO_2(OH)_2 \cdot 2.5H_2O$, the estimated $\Delta H_f°_{Np-Ur}$ = -3394.5 kJ/mole. At 25°C the standard enthalpy for the dissolution reaction (3) can be estimated from

$$\Delta H°_{Np-Ur} = 0.5 \Delta_f H°_{Ca^{2+}} + \Delta_f H°_{NpO2^+} + \Delta_f H°_{Si(OH)4} + 2.5 \Delta_f H°_{H2O} - \Delta_f H°_{Np-Ur} = -26.7 \text{ kJ/mol} \quad (5)$$

using standard enthalpies of formation for the aqueous species from [28]. The corresponding standard enthalpy of the exchange reaction (1) at 25°C is -38.4 kJ/mole, making use of the standard enthalpy estimated by a similar method for the uranophane dissolution reaction (2) from [8].

The derived equilibrium constant for the Np-uranophane dissolution reaction (3) at 100°C was extrapolated to 25°C using the van't Hoff relation assuming a constant standard enthalpy of reaction, yielding log $K_{Np-Ur,298}$ = 5.44. The corresponding equilibrium constant for the exchange reaction (1) at 25°C is log $K_{x,298}$ = -0.03 using the experimental value of log $K_{Ur,298}$ = 5.41 [8,25].

Burns et al. [1] reported that the Np-bearing uranophane produced in their experiments was accompanied by crystals of Na uranyl acetate, which were subsequently removed by washing. Temperature dependent solubility data [29] were interpreted to provide values of log K_{NaUAc} = -2.55 and $\Delta H°_{NaUAc}$ = 20.44 kJ/mole for the reaction

$$NaUO_2(CHCOO)_3 \Leftrightarrow Na^+ + UO_2(CHCOO)_3^- \quad (6)$$

Using these data, our 100°C model indicates that the experimental solution was undersaturated with respect to $NaUO_2(CHCOO)_3$, so its precipitation did not affect the aqueous speciation. The 100°C model solution and Np-bearing uranophane precipitate were reequilibrated in a PHREEQC model at 25°C. The low temperature solution became supersaturated in Na uranyl acetate, which explains its presence in the products of the synthesis experiment.

Discussion of Uncertainties

A primary objective of this study is to address the uncertainty associated with applying the experimental Np coprecipitation data from Burns et al. [1] to conditions at the Yucca Mountain repository. A thermodynamic approach is deemed to be the most robust method for making such an extrapolation even if some thermodynamic data must be estimated at this time. Burns et al. [1] reported that their analytical data are expected to be accurate within about 10 percent, with uncertainties in Np concentrations up to 15 percent and mostly less than 5 percent based on duplicate analyses. As far as possible, thermodynamic data used in this analysis are taken from the most recent NEA compilation [28] with uncertainties evaluated in that report. Estimates of standard state enthalpies of formation for uranophane and Np-uranophane make use of U and Np data from that compilation. The PHREEQC data base used in the aqueous speciation and reaction path calculations for this study incorporates the NEA data.

Parallel assumptions were made in estimations of the standard state enthalpies of formation for uranophane [8] and for Np-uranophane, which limits uncertainty in the

estimated standard enthalpy for the exchange reaction between them. However, uncertainties are associated with the inferred stoichiometry of the exchange reaction. The assumption of constant standard enthalpy for the exchange reaction between 25°C and 100°C permits a thermodynamically based extrapolation of the higher temperature experimental data to the relevant temperature for the Yucca Mountain repository. Neglecting the temperature dependence of the standard enthalpy of exchange should introduce small errors relative to other uncertainties reiterated below.

Speciation of aqueous neptunyl is uncertain in acetic acid solutions at elevated temperature. Notably absent is the enthalpy of dissociation for aqueous $NpO_2(CH_3COO)$. To examine the possible significance of this uncertainty, using the enthalpy of dissociation of aqueous $UO_2(CH_3COO)^-$ for the neptunyl acetate complex would result in a difference of about 25 percent in the derived value of K_x.

Results reported in this paper, including estimated thermodynamic data, are model dependent, and important remaining uncertainties are recognized in our interpretation. Nevertheless, we conclude that the thermodynamic approach in this paper presently permits the most robust extrapolation the experimental coprecipitation data [1] to conditions relevant to the Yucca Mountain repository.

Application to the Yucca Mountain High-Level Nuclear Waste Repository

Potential sequestration of Np in uranophane by solid solution can be evaluated by modeling equilibrium among representative Yucca Mountain waters and Np-bearing uranophane using the thermodynamic ion exchange data estimated above. Repository chemistry will be controlled eventually by the ambient geochemical system with added

masses of iron, uranium, and other materials including radionuclides. Stable mineral

assemblages are likely to include uranophane as an alteration product of spent nuclear

fuel.

The ambient groundwater chemistry in the unsaturated zone at Yucca Mountain is

generally dilute, oxidizing, slightly alkaline, rich in silica and bicarbonate, and variable in

major ion concentrations (e.g., [30,31]). Sampling and analysis of pore water from the

hydrologically unsaturated zone are challenging, and reported data are subject to

reinterpretation (e.g., [32]). Perched water also occurs at Yucca Mountain, and it may

reflect the chemistry of relatively mobile fracture water. Two unsaturated zone water

chemistries representative of Yucca Mountain are given in Table III. The pore water data

were reinterpreted following the approach of Browning et al. [32], which imposes

equilibrium aqueous speciation, electroneutrality, and equilibrium CO_2 fugacity based on

gas phase measurements, and results in adjustments to the reported pH and bicarbonate

concentration. Equilibrium aqueous speciation for the perched water included small

adjustment of the reported bicarbonate value to achieve charge balance. Speciation

calculations were performed with EQ3NR, v7.2c with the data0.cmp.v8.R6 data base

(e.g., [33]) and the uranophane data noted above.

Table IV summarizes model aqueous uranium and neptunium speciation in Yucca

Mountain groundwaters (Table III) at equilibrium with Np-bearing uranophane having a

Np/U ratio of 10^{-3}. This value corresponds to the Np/U ratio in spent nuclear fuel and it is

thus a reasonable upper limit to the Np content of secondary uranophane that may form

by alteration of spent nuclear fuel. The resulting equilibrium model indicates that

neptunyl is relatively excluded from the uranophane structure. For experimental

conditions at 100°C, the calculated aqueous neptunyl/uranyl free ion ratio is 58 (Table II), the calculated total aqueous Np/U ratio is 0.04, and the experimentally observed Np/U ratio in coexisting uranophane was $4x10^{-4}$ [1]. For modeled conditions at Yucca Mountain at equilibrium with Np-bearing uranophane, the aqueous neptunyl/uranyl free ion ratio is calculated to be near 10^5 for a Np/U ratio in coexisting uranophane of 10^{-3}. Total aqueous Np/U concentration ratios are much smaller than free neptunyl/uranyl ion ratios primarily because of strong carbonate complexation of aqueous uranyl in the Yucca Mountain waters and because of uranyl acetate complexation in the experimental studies. For the Yucca Mountain models, the total aqueous Np/U ratios are $5x10^{-3}$ to $8x10^{-3}$ for perched and pore waters, respectively. These values are within an order of magnitude of the ratio of Np/U in coexisting uranophane (10^{-3}).

Despite relative Np exclusion from the uranophane structure, the low calculated solubility of uranophane containing trace Np under ambient conditions at Yucca Mountain results in total aqueous Np concentrations near 10^{-9} molal ($2x10^{-4}$ ppm) (Table IV). This value is orders of magnitude lower than the solubility limits for Np in Yucca Mountain performance assessment models [17].

Conclusions

Experimental synthesis data for Np coprecipitation in uranophane [1] are crucially important for evaluation of Np sequestration in the proposed nuclear waste repository at Yucca Mountain. Thermodynamic interpretations of experimental results are necessary before they can be used to guide repository performance evaluations. Uncertainties in

aqueous acetate chemistry, particularly at elevated temperature, complicate the interpretation of the experimental results.

Experimental data [1] show that NpO_2^+ is relatively excluded from the uranophane structure, and this same general conclusion is reached in our thermodynamic extrapolation of the experimental data to Yucca Mountain conditions. Nevertheless, the low calculated solubility of uranophane under Yucca Mountain conditions leads to low aqueous Np concentrations at equilibrium with uranophane containing trace amounts of Np in solid solution. Neptunium coprecipitation in uranophane could be an effective process for long term nuclear waste isolation at Yucca Mountain under ambient geochemical conditions.

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Table I. Reported [1] Reagents and Quantities in Np-bearing Uranophane Synthesis Experiment and Calculated Component Concentrations in Initial Solution

Reagent	Reported Quantity	Component	Molality
$UO_2(CH_3COO)_2.2H_2O$	5 mL at 0.2 M	Na^+	0.239
$Na_2SiO_3.9H_2O$	0.227 g	SiO_2	0.119
$Ca(CH_3COO)_2.H_2O$	0.282 g	Ca^{2+}	0.239
Np(V)	$\approx$ 350 ppm*	CH_3COO^-	0.777
$HClO_4$	1 M to make	UO_2^{2+}	0.149
	pH 5.4 solution	NpO_2^+	1.27×10^{-3}
*prior to addition of acidifying $HClO_4$ solution,		$HClO_4$	0.238
from a stock solution of 13.75 mg Np(V)		pH	5.4
dissolved in 3.626 mL of 1 M $HClO_4$			

Table II. Principal Aqueous Species and Concentrations (Molal Except pH) in the Model Solution at 100°C at Equilibrium with Np-bearing Uranophane

CH_3COOH	3.56×10^{-1}	NpO_2^+	8.10×10^{-4}
CH_3COO^-	1.48×10^{-1}	NpO_2CH_3COO	3.40×10^{-4}
$Ca(CH_3COO)_2$	6.23×10^{-2}	$UO_2CH_3COO_3^-$	2.30×10^{-2}
$CaCH_3COO^+$	4.78×10^{-2}	$UO_2CH_3COO_2$	7.40×10^{-3}
Ca^{2+}	6.88×10^{-2}	$UO_2CH_3COO^+$	2.21×10^{-4}
Cl^-	2.30×10^{-1}	UO_2OH^+	1.59×10^{-5}
Na^+	2.14×10^{-1}	UO_2^{2+}	1.39×10^{-5}
$NaCH_3COO$	1.79×10^{-2}	pH	4.37
SiO_2	3.71×10^{-4}	Ionic strength	4.41×10^{-1}

Table III. Predominant Equilibrium Species in Unsaturated Zone Waters from Yucca Mountain (Molal Concentrations Except pH) (Interpreted from Data in [30])

	Pore Water UZ14.144.8-145.2	Perched Water UZ14B387.68m
AlO_2^-	no data	2.21×10^{-4}
Br^-	no data	5.01×10^{-6}
Ca^{2+}	1.51×10^{-3}	7.33×10^{-4}
$CaSO_4$	8.22×10^{-5}	8.42×10^{-6}
Cl^-	2.17×10^{-3}	2.34×10^{-4}
HCO_3^-	1.93×10^{-3}	2.44×10^{-3}
$CO_2(aq)$	3.47×10^{-5}	3.99×10^{-5}
K^+	3.56×10^{-4}	1.12×10^{-4}
Mg^{2+}	4.36×10^{-4}	1.05×10^{-4}
$MgSO_4$	4.84×10^{-5}	2.44×10^{-6}
Na^+	2.08×10^{-3}	1.73×10^{-3}
SO_4^{2-}	9.21×10^{-4}	1.57×10^{-4}
$SiO_2(aq)$	1.34×10^{-3}	8.42×10^{-4}
$HSiO_3^-$	1.84×10^{-5}	1.27×10^{-5}
NO_3^-	3.53×10^{-4}	2.72×10^{-4}
pH	8.05	8.10

Table IV. Uranium, Neptunium, Uranyl, and Neptunyl in Model Yucca Mountain Groundwaters (Molal Concentrations)

	Pore Water	Perched Water
U(total)	1.07×10^{-7}	3.15×10^{-7}
$UO_2(CO_3)_3^{4-}$	5.94×10^{-8}	1.81×10^{-7}
$UO_2(CO_3)_2^{2-}$	4.41×10^{-8}	1.28×10^{-7}
$UO_2(OH)_2$	2.61×10^{-9}	5.00×10^{-9}
UO_2^{2+}	6.44×10^{-15}	8.73×10^{-15}
Np(total)	8.55×10^{-10}	1.60×10^{-9}
NpO_2^+	5.72×10^{-10}	9.47×10^{-10}
$NpO_2CO_3^-$	2.08×10^{-10}	5.05×10^{-10}
NpO_2OH	7.26×10^{-11}	1.39×10^{-10}