Solubility Evaluation for Yucca Mountain TSPA-SR

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ABSTRACT

A systematic evaluation of radionuclide solubility has been conducted for the Yucca Mountain Project. The conventional thermodynamic approach was employed and geochemical model calculations were used to estimate radionuclide solubilities for the base case. The study uses the computer code EQ3/6 as the major geochemical modeling tool. The water composition and environmental conditions are based on the results of in-package chemistry and in-drift chemistry studies. Field observations, laboratory measurements, and thermodynamic and kinetic considerations are utilized to ensure the resulting solubilities are conservative. Fourteen radioelements have been studied (U, Np, Pu, Th, Am, Ac, Tc, I, C, Cs, Sr, Ra, Pa, and Pb) and their solubilities are presented as either functions of environmental conditions or statistical distributions. Alternative solubility models for Np and Pu were also developed. These alternative models are based on measurements of spent fuel dissolution experiments rather than conventional thermodynamic considerations. Comparison of the Np and Pu base case models with their alternative models suggests that they are needed in order to advance our understanding about the behaviors of Np and Pu during the process of spent fuel corrosion.

INTRODUCTION

U.S. Department of Energy (DOE) has prepared a total system performance assessment (TSPA) for a site recommendation (SR) for Yucca Mountain, Nevada. This location is under consideration for the disposal of high-level radioactive waste. The solubility limits of radioelements make up a fundamental input to TSPA-SR. In previous TSPAs, solubility values from an expert elicitation were used. To meet the acceptance criteria set forth by U.S. Nuclear Regulatory Commission, a systematic solubility evaluation based on geochemical model calculations has been conducted [1,2]. This paper gives a brief summary of this effort.

The conventional approach of solubility evaluation assumes that the solubility of an element is controlled by a pure solid phase, called the solubility-controlling phase (SCP). The solubility is the concentration of the element in solution which is in equilibrium with the SCP under conditions of concern. This conventional approach, used in this study, is well established and the approach has been a standard practice in the nuclear waste management community for over two decades. It yields bounding values on solubility limits that are used for the base case TSPA evaluation, so they are sometimes called base case models.

On the other hand, it is well recognized that the concentrations of most radioelements released through spent fuel dissolution may be so low (except for U) as to prevent formation of their own pure phases [3,4]. The basic assumption used by conventional solubility models that the existence of pure radionuclide phases controls their solubility limits (except U) may not reflect reality. Consequently, the solubility limits obtained may be several orders of magnitude higher than the concentrations measured in spent fuel dissolution experiments [2]. This observation calls for alternative, more realistic, solubility models. We have developed such alternative models for two important elements, Np and Pu. In the following discussion, the base case models will be presented first, followed by the alternative Np and Pu models.

BASE CASE MODELS

The base case solubility models build on three sets of information: (1) in-package physical-chemical conditions, including pH, partial pressure of oxygen (f_{O_2}), partial pressure of carbon dioxide (f_{CO_2}), and ionic strength (I); (2) designation of the solubility-controlling phases for the element of concern; and (3) thermodynamic parameters describing the stability of aqueous species and solid phases. The geochemical modeling tool used for this study is EQ3/6 [5].

The major composition of the water was assumed to be J-13 Well water [6], with f_{O_2} assumed equal to the atmospheric value (0.2 bars), and f_{CO_2} ranging from $1.0E-4$ to $3.2E-3$ bars.

Designation of the SCP for an element is of key importance because the result can affect the calculated solubility by orders of magnitude. The specific pure phase chosen, in order of preference, was based on (1) geologic field observations, (2) experimental observation, or (3) crystallochemical arguments. For radioelements found almost exclusively in anthropogenic systems, such as Pu and Np, experimental observations were relied on. In those cases where information could not be obtained from field observations or experimental studies, crystallochemical arguments were used. Specifically, it was conservatively assumed that the most amorphous and hydrated (hence, most soluble) oxide of the particular radioelement controlled the solubility.

Results

The solubility limits of 14 elements are evaluated and presented in different ways, depending on the degree of understanding and details of analysis. Some are given as a function of environmental conditions, while others are presented as a statistical distribution; still others are given as bounding values.

Uranium (U) U solubility was calculated by assuming schoepite ($UO_3 \cdot 2H_2O$) to be the SCP. Schoepite was chosen because (1) it forms during degradation of commercial spent nuclear fuel (CSNF) in J-13 Well water; (2) field observations show that it can persist for more than 10^4 yr. [7]; (3) it is more soluble than other secondary uranyl minerals observed in laboratory experiments and natural analogs. Based on the solubility values calculated using EQ3NR, a seven-term regression equation as a function of pH, f_{CO_2} , and temperature was developed:

$$\log[U] = 7.9946 - 2.6963 pH + 0.4292 pH^2 - 1.6286 \log f_{CO_2} + 0.0095T + 0.4161 pH \times \log f_{CO_2} - 0.0051 pH \times T - 0.0022 \log f_{CO_2} \times T \quad (1)$$

where [U] is uranium solubility (mg/L), f_{CO_2} is CO_2 fugacity (bar), T is the temperature (Kelvin).

Neptunium (Np) There has been lengthy discussion about Np-bearing phase(s) that could form under the repository conditions. Thermodynamically, NpO_2 is the stable phase [8]. However, it has not been observed in solubility experiments, except for high temperature ones. It is believed that a kinetic barrier prevents NpO_2 from precipitating at low temperatures.

This study selected the relatively soluble Np_2O_5 as the Np SCP for the base case, because it was observed in precipitates in over-saturation experiments in J-13 Well water [9]. Based on EQ3NR results, Np solubility was derived as a function of environmental conditions:

$$\log[Np] = 6.7645 - 0.3268 \times \log f_{CO_2} - 0.1165 \times \log f_{CO_2}^2 - 0.6136 \times pH - 0.0040 \times pH^4 + 5.41E-4 \times pH^5 + 7.67E-4 \times \log f_{CO_2} \times pH^3 + 4.24E-3 \times \log f_{CO_2}^2 \times pH^2 + 4.10E-5 \times \log f_{CO_2} \times pH^5 \quad (2)$$

where [Np] is the solubility of Np (mg/L).

Plutonium (Pu) Despite numerous studies of Pu solubility, the stability fields of Pu solids remain somewhat uncertain. Solids precipitated from two over-saturation experiments [9,10] have a dark green color, which is characteristic of Pu(IV) solid phases. X-ray diffraction data match the data reported for PuO₂. However, the diffuse and broad X-ray diffraction peaks suggest poor crystalline structures. Precipitates formed at higher temperatures have a sharper X-ray pattern than solids precipitated at lower temperatures. It appears that the solubility-controlling phase(s) in those laboratory experiments are "plutonium hydroxides and/or plutonium colloids, aging towards PuO₂·xH₂O" [9]. The value of X should vary from 0 to 2. Moreover, Rai observed that Pu hydroxide gradually converted to anhydrous crystalline material [11]. Therefore, it is reasonable to assume that over geological time, plutonium hydroxides will convert to PuO₂(c).

α-decay damage of Pu solids complicates the selection of the controlling mineral for Pu solubility calculation. It was reported that in 1,300 days, PuO₂(c) converted to a less crystalline form [11] having properties between those of true crystalline PuO₂ and amorphous hydroxide, and this phase would control Pu solubility over time. Since no thermodynamic properties for this less crystalline material have been reported, PuO₂·2H₂O(am) was conservatively chosen as the controlling solid for Pu solubility. A function of environmental conditions was developed based on EQ3NR modeling results:

$$\log[Pu] = -5.5294 + 0.2433 \times \log f_{CO_2}^2 + 0.0544 \times \log f_{CO_2}^3 + 7.0457 \times pH - 1.6520 \times pH^2 + 0.1296 \times pH^3 + 0.0106 \times pH^3 \times \log f_{CO_2} + 0.0104 \times pH^2 \times \log f_{CO_2}^2 \quad (3)$$

where [Pu] is Pu solubility (mg/L).

Thorium (Th) The calculation assumes ThO₂(am) is the solubility-controlling mineral. The result is presented as a function of environmental conditions.

$$\log[Th] = 503.12 + 0.55175 \times \log f_{CO_2} + 9.8348e - 2 \times (\log f_{CO_2})^2 - 1160.6 \times pH + 144.18 \times pH^2 - 9.1823 \times pH^3 + 0.23630 \times pH^4 + 2.0397e-3 \times \log f_{CO_2} \times pH - 11132/pH + 9868.7/pH^2 \quad (4)$$

where [Th] is the solubility of Th (mg/L).

Americium (Am) AmOHCO₃ was chosen as the Am SCP based on the studies of Nitsche [10], which identified AmOHCO₃ as the solid phase precipitated from J-13 Well water. The following function is derived based on EQ3NR calculations:

$$\log[Am] = 58.0335 - 18.9422 \times pH + 1.4744 \times pH^2 - 6.0032 \times \log f_{CO_2} - 0.7005 \times \log^2 f_{CO_2} + 0.1162 \times pH^2 \times \log f_{CO_2} + 0.1146 \times pH \times (\log f_{CO_2})^2 \quad (5)$$

where [Am] is the solubility of Am (mg/L).

Actinium (Ac) Am is considered as an analog for Ac. Thus, Eq. (5) is also applicable for Ac, with a small difference in the constant term, which is from their different atomic weights.

Technetium (Tc), Carbon (C), Iodine (I), Cesium (Cs), and Strontium (Sr) It is assumed that under the assumed oxidizing repository conditions, no solubility-controlling solids exist for Tc, C, I, Sr, and Cs. Therefore, their solubility is arbitrarily set to 1.0 mol/L so that in TSPA their release would be modeled to be controlled by the waste inventory and the dissolution rate of the waste matrix.

Radium (Ra), Lead (Pb), and Protactinium (Pa) Assuming RaSO₄(s) as the SCP for Ra, EQ3 calculations over a pH range from 6 to 9 predict its solubility ranging from 1.1E-6 to 2.3E-6 mol/L. According to Marani [12], Pb solubility in carbonate containing waters ranges from 5.0E-9 to 8.0E-7

mol/L. A log-uniform distribution ranging from $1.0\text{E-}10$ to $1.0\text{E-}5$ mol/L is proposed for Pb solubility. The stable oxidation state of Pa in water is the +5 state. Due to lack of data for Pa(V) species, model calculations are not very meaningful. Based on the measured solubility reported by Berry [13], a log-uniform distribution for Pa solubility is recommended with a minimum of $1.0\text{E-}10$ mol/L and a maximum of $1.0\text{E-}5$ mol/L.

ALTERNATIVE MODELS

An Alternative Np Model

The aforementioned base case model for Np solubility assumes Np_2O_5 is the SCP. However, Np_2O_5 has not been identified in spent fuel dissolution experiments, nor have other Np pure phases. Moreover, Np concentrations measured in spent fuel experiments are several orders of magnitude lower than the Np concentrations measured in Np_2O_5 solubility experiments. It is likely that in reality, Np release from spent nuclear fuel is not controlled by Np_2O_5 or other Np pure phases, but by a different mechanism.

Based on an analysis of the crystal-chemical properties of the U-O, Np-O, and Pu-O bonds, Burns [14] predicted that "the substitutions $\text{Pu}^{6+} \leftrightarrow \text{U}^{6+}$ and $(\text{Np}^{5+}, \text{Pu}^{5+}) \leftrightarrow \text{U}^{6+}$ are likely to occur in most U^{6+} structures." Later, Buck [15] confirmed the prediction by TEM analyses of corrosion products of spent fuel vapor corrosion tests. In that study, Np was found incorporated into dehydrated schoepite. Therefore, it is reasonable to assume that Np will not be totally released into the aqueous phase during the period of spent fuel dissolution. Instead, some of the Np may be segregated into the secondary schoepite.

The alternative model discussed below examines the Np behaviors in water solutions based on the measured Np and U concentration data from spent fuel dissolution experiments [16,17,18]. **Concentrating Factor of Np** Denoting the ratio of Np to U in solution as $(\text{Np}/\text{U})_{\text{soln}}$ and in spent fuel as $(\text{Np}/\text{U})_{\text{fuel}}$, then, we define the concentrating factor of Np, which measures the degree of Np being concentrated in solution compared to the spent fuel with which it is in contact, as

$$F_c = \frac{(\text{Np}/\text{U})_{\text{soln}}}{(\text{Np}/\text{U})_{\text{fuel}}} \quad (6)$$

Re-arranging Eq. (6) yields

$$[\text{Np}] = F_c (\text{Np}/\text{U})_{\text{fuel}} [\text{U}] \quad (7)$$

where $[\text{Np}]$ and $[\text{U}]$ denote the concentrations of Np and U in solution, respectively.

Eq. (7) can be used to estimate Np concentrations using U concentration, provided that F_c can be obtained through experiments.

Estimation of F_c for Np Using Data from Fuel Experiments Unsaturated spent fuel dissolution tests are described in detail in the literature [16,17]. The concentrations of several radionuclides in the leachate are measured and reported by Finn [18].

There are 46 Np and U concentration datasets available from the high-drip rate and low-drip rate tests, from which the F_c of Np can be calculated. Fig. 1 is the histogram of $\log F_c$. $\log F_c$ has a near normal distribution, with a mode around 0.0 (i.e., F_c with a mode of 1.0). The fact that the mean of $\log F_c$ is very close to 0.0 and it has a mode of 0.0 indicates that the Np/U values in the solutions are very close to the Np/U values in the fuels. In other words, there is a congruent relation between U and Np. The congruent relation between U and Np partitioning between spent fuel and liquid phase has also been observed in other spent fuel dissolution experiments. For example, by analyzing

PNNL's Series 2 and Series 3 steady-state test results, Sassani [8] noticed that "The data suggest that Np enters the aqueous phase congruently with uranium as the fuel dissolves." Bruno [19] has also observed the congruent relation between Np and U in spent fuel dissolution experiments in the Spanish Nuclear Waste Program. Therefore, it is reasonable to conclude that the congruent relation

between U and Np is not a coincidence.

There are several perceivable explanations for this congruent relationship. A simple one is that this is the result of congruent dissolution of fuel matrix with little effects of secondary phases. Another explanation is that Np and U behave congruently not only in the dissolution process, but also in the process of secondary phase precipitation. The third one is that U and Np form their own solid phases, and the U and Np solubility controlled by them respectively would have a ratio equal to the ratio of U to Np in the fuel. Since it is observed that large amount of secondary uranium minerals formed [20], the first explanation does not hold. As

Figure 1. Histogram of F_c on a log scale. It appears that $\log F_c$ has a mode around 0.0 (i.e., F_c with a mode of 1.0).

stated earlier, no Np pure phases have been observed in fuel dissolution experiments, thus, the third hypothesis is unsubstantiated (though it is possible that the amount of Np pure phase is so small so that it is below the detective limit). Therefore, based on current evidence, only the second explanation stays. In other words, incorporation of Np into uranyl minerals is the most reasonable explanation for the observed congruent relationship between U and Np. It indicates the strong similarity of geochemical behaviors of U(VI) and Np(V).

It is worthwhile to analyze the variation of F_c with time. Fig. 2(a) shows F_c in high-drip tests as a function of time. The low-drip rate results are shown in Fig. 2(b). The solid lines are tests with ATM-103 fuel, while the dashed lines are tests for ATM-106 fuel. They show that in those four tests, F_c of Np fluctuates around 1.0.

Moreover, in all four tests, the highest F_c occurs in the first sample, and then F_c decreases and reaches the lowest value within 2 years. In other words, the largest variations in F_c occur in the first 2 years, and decrease with time. This suggests that Np and U congruency will become more dominant as time increases and the spikes of F_c s observed in the first 2 years are transient phenomena. As our focus is long-term performance, the transient phenomenon can be neglected.

The concentration data for ANL's vapor-tests are not yet available, so we cannot perform the same analysis on them. However, the ratio of fractional release rates of Np to that of U in vapor-tests exhibits remarkably similar behavior as to F_c in high and low drip tests. Thus, it appears that Np release is also strongly correlated with U release in the vapor-tests.

Figure 2. (a) F_c s of Np in ANL's high-drip rate tests as a function of time. F_c of Np fluctuates around 1.0 and appears to damp to 1.0 as time increases; (b) F_c s of Np in ANL's low-drip tests. It demonstrates the same behaviors as seen in (a), in low-drip rate tests, the variations of F_c s are smaller than in high-drip rate tests.

It was argued that "important differences between the complexation behaviors of NpO_2^+ and UO_2^{2+} in Si-saturated carbonate groundwaters" may exist [20]. However, the similar behaviors of F_c in vapor, low-drip, and high-drip tests do not support that speculation. In fact, it strongly suggests the opposite, i.e., the similarity between Np and U does not change with water composition or water contact modes.

Excluding those data points measured for times less than 2 years, a subset ($n=28$) of the four drip test data was obtained. The mean (μ) of $\log F_c$ is close to 0.0 (0.058), with a standard deviation (σ) of 0.485. The upper and lower limits of $\log F_c$ at a confidence level of 95.5% ($\mu \pm 2\sigma$) are 1.027 and -0.912 respectively. Converting back to the linear variable F_c , it has the mean equal to 1.142, and 95% confident limits are 10.653 and 0.122, respectively.

Results As discussed above, F_c is around 1.0, with an uncertainty range of about 2 orders of magnitude. Therefore, it is proposed that F_c have a geometric mean of 1.0, ranging from 0.1 to 10.0. The ratio of $(\text{Np}/\text{U})_{\text{fuel}}$ can be calculated from the waste inventory. Note that in order to have long-term predictive capability, the effect of Pu-241 and Am-241 decay to $(\text{Np}/\text{U})_{\text{fuel}}$, which increases $(\text{Np}/\text{U})_{\text{fuel}}$ by a factor of 3.78, should be considered. Otherwise, the calculated Np solubility could be erroneous and non-conservative.

Using Eq. (1) for $[\text{U}]$, then according to Eq. (7), Np solubility is

$$\log[\text{Np}] = 5.2806 - 2.6963 \times pH + 0.42918 \times pH^2 - 1.6286 \times \log f_{\text{CO}_2} + 9.5352e-3 \times T + 0.41613 \times pH \times \log f_{\text{CO}_2} - 5.1148e-3 \times pH \times T - 2.1621e-3 \times \log f_{\text{CO}_2} \times T + \log F_c \quad (8)$$

where $[\text{Np}]$ is the Np solubility in mg/L, $\log F_c$ has a normal distribution, with a mean of 0, and a standard deviation of 0.5.

It is necessary to mention two Np solubility models developed in the past based on the notion of Np incorporation into uranium minerals. One is the Murphy and Codell Model [21], which uses schoepite solubility to control the release of all the radioelements by equivalently assuming $F_c = 1$ for them. (In contrast, this model provides the statistical basis for F_c of $\text{Np} = 1$.) Another model is a mechanistic model developed for TSPA-VA (viability assessment) [22,23] using the reactive-transport code AREST-CT, which calculates Np concentration by accounting for chemical reactions, including spent fuel dissolution and secondary phase formation and destruction, and fluid flow through a waste package.

Table 1 lists the results of this empirical Np model by applying Eq. (8) to the expected environmental conditions of the proposed repository, along with several corroborating data supporting this model. The range of Np concentrations measured in the Spanish Nuclear Waste Program [21], listed in Row 3, is from $1.0\text{E-}9$ to $1.0\text{E-}7$ mol/L, which is within the range of this model. The fourth and fifth rows are measured steady-state Np concentrations for PNNL's Series 2 and Series 3 tests [24,25]. They are very close to the mean of this model. Note that no in-growth adjustment for Pu-241 and Am-241 decay has been done to these tests, otherwise, the agreement would be even closer. The last row is the Np concentration given by AREST-CT simulations [22,23],

Table 1. Np Result and Corroborating Data

Np Concentration (mol/L)	Maximum	Minimum	Average
This Alternative Model	6.85E-06	7.50E-11	7.31E-09
Measured Np Concentrations by Bruno	$\sim 1.0\text{E-}7$	$\sim 1.0\text{E-}9$	
PNNL Series 2			2.00E-09
PNNL Series 3			1.26E-09
AREST-CT Model	1.00E-06	1.00E-09	3.16E-08

breached waste package. In order to have a more precise picture of the reality and repository performance, it is necessary to advance our mechanistic understandings about the behaviors of Np and Pu during the process of spent fuel corrosion.

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