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Civilian Radioactive Waste Management System
Management and Operating Contractor

Constraints on Solubility-Limited Neptunium Concentrations for Use in Performance Assessment Analyses

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Prepared for:

U.S. Department of Energy
Yucca Mountain Site Characterization Office
P.O. Box 30307
North Las Vegas, NV 89036-0307

Prepared by:

TRW
1180 Town Center Drive
Las Vegas, Nevada 89134

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Prepared by: David C. Sassani Date: 01/23/98

and: Eric R. Siegmann Date: 1/26/98

Reviewed by: S. David Sevougian Date: 1/26/98

Approved by: Robert W. Andrews, Performance Assessment Manager Date: 1/26/98

1.0 INTRODUCTION

There have been two coupled methods used for constraining the aqueous concentration of dissolved radionuclides in each of the Total System Performance Assessments (TSPA), from 1991 through 1995, for the potential repository at Yucca Mountain, Nevada. This conceptual model combines far-from equilibrium dissolution of the waste form with the imposition of equilibrium mineral saturation-limits, or solubility-limits, to constrain the source-term of dissolved radionuclides. The first limit is provided by the model of the waste-form dissolution rate (this includes spent fuel and glass, but because spent fuel is projected to be about 90% of the anticipated radionuclide mass-inventory, it will be the focus of this discussion). The spent-fuel dissolution model includes effects of alteration of the original UO_{2+x} in spent fuel to more oxidized forms. The second limit is based on the solubility of solid phases containing the element of interest. Within the TSPA analyses, this limit is modeled stochastically using distributions of solubility-limited dissolved concentrations for each element considered. The solubility-limited aqueous concentration of an element is then split among its isotopes based on their relative abundances. (Note: the isotope ^{237}Np represents virtually all of the Np in spent fuel so that solubility-limited concentrations are directly applicable without need to distribute the dissolved concentration among its isotopes.) Within TSPA calculations, the aqueous radionuclide concentrations resulting from these two constraints are compared and the lower value is used to represent the source-term concentration of that radionuclide.

Between the 1991 and 1993 TSPA analyses, incorporation of new project data resulted in revisions to both dissolution rates and solubility limits. These changes resulted in higher calculated Np releases. As discussed below, the data upon which the revised solubility constraints are based probably represent ***metastable*** equilibrium between the aqueous fluids and ***metastable*** Np-phase(s) (i.e., Na-neptunyl carbonate hydrates and Np_2O_5—Nitsche et al., 1993, 1994). In addition, at the relevant conditions the calculated ***stable*** Np-phase NpO_2 corresponds to Np concentrations many orders of magnitude lower than these metastable phases. However, simply using the calculated NpO_2 solubilities to constrain the solubility-limited Np concentration may be objected to on grounds that kinetic barriers could prevent the formation of the NpO_2 phase.

Therefore, in the analysis below, the applicability of the various phase constraints for aqueous Np concentrations has been evaluated through synthesis of project data from the dissolution-rate studies, the solubility studies, and thermochemical calculations. The results indicate that, for *J-13-like fluids*, NpO_2 solubility is the more appropriate constraint because source-term concentrations should not reach levels high enough for the metastable phases observed in the Nitsche et al., (1993, 1994) studies to form.

Below is presented a background summary of the constraints utilized in each of the TSPA analyses (Section 1.1), a summary of Np concentration constraints that are derived from spent fuel dissolution studies (Section 2), a discussion of the applicability of the data used in TSPA-1995 to constrain Np concentrations for the case of J-13-like fluid compositions (Section 3), and a preliminary strategy for revisions to the solubility constraints on Np concentrations to be used in future Total System Performance Assessments (Section 4).

1.1 Background on Neptunium Constraints Used in Previous TSPA Analyses

1.1.1 Total System Performance Assessment for 1991

The analysis performed in 1991 (TSPA-91, Barnard et al., 1992) calculated ^{237}Np releases based on a solubility-limited source-term for ^{237}Np. To represent the solubility-limited concentrations (in units of moles/liter, M), TSPA-1991 used a log-uniform distribution with a minimum of -10.23, a maximum of -7.72, and an expected value of -8.48. This distribution was generated from a selected nominal value for Np concentration of 5.9×10^{-9} M. This nominal value was the highest steady-state value observed in the spent-fuel studies of Wilson (1987, 1990a, 1990b; Jardine, 1991). A variability range of 2 orders of magnitude below, and 0.5 orders of magnitude above, was applied to this nominal value to generate the final distribution (Barnard, 1991, p. 4-30).

1.1.2 Total System Performance Assessments for 1993

Two sets of TSPA analyses were performed in 1993 (Wilson et al., 1994; and Andrews et al., 1994). Both of these analyses incorporated new project data for constraining the dissolved concentration of Np in the source-term. In one case (Wilson et al., 1994), the distribution for solubility-limited Np concentrations (M) was taken directly as that given by an elicitation of project experts. The project-expert elicitation distribution for Np (Gauthier, 1993, Wilson et al., 1994) is based on the Nitsche et al. (1993, 1994) studies of solubility-limited Np concentrations, which are discussed in Section 3.1.3. The distribution was given as log beta with a minimum value of -8, a maximum value of -2, an expected value of -4, and a coefficient of variation of 0.2 (Gauthier, 1993, Wilson et al., 1994). In the other TSPA-1993 analysis (Andrews et. al., 1994), the Nitsche et al. (1993, 1994) studies were used also to develop additional constraints on Np concentration as functions of temperature and pH. In both of these cases, the solubility-limited Np concentrations were raised by about 2 to almost 6 orders of magnitude over those used in TSPA-1991.

In addition to raising the solubility-limited Np concentrations, these TSPA-1993 analyses also incorporated modified waste-form alteration/dissolution rate models. These revised dissolution-rate models were based on the flow-through experiments of Gray et al. (1992), which are applicable for far-from equilibrium conditions for the dissolution reaction. Because these rates represent far-from equilibrium conditions, the reaction rates are higher than for close-to equilibrium conditions. These far-from equilibrium dissolution rates provide conservative bounds for the dissolution-rate limited aqueous release of radionuclides into dilute, J-13-like fluids. In contrast to the TSPA-1991 analysis, these models incorporated functional dependence on the system parameters of temperature, pH, and dissolved carbonate (Wilson et al., 1994; Andrews et al., 1994).

Even though the solubility-limited Np concentrations were raised for TSPA-1993 analyses, the combination with modified dissolution rates resulted in solubility-limited source-terms for ^{237}Np because of transport limitations. Because of such high solubility-limited Np concentra-

tions, and the inclusion of greater-than-10,000 year time frames, Np was a major contributor to the total long-term release in TSPA-1993.

1.1.3 Total System Performance Assessment for 1995

The peak doses at long-times in the 1995 Total System Performance Assessment analyses were caused mainly by the isotope of Neptunium, ^{237}Np (M&O, 1995), as was the case in TSPA-1993 (Wilson et al., 1994; Andrews et al., 1994). This result was driven mainly by the high values for the solubility-limited concentrations of Neptunium used in those analyses as given by the project-expert elicitation (Gauthier, 1993, Wilson et al., 1994). The distribution for solubility-limited Np concentrations used in the TSPA-1995 study represents a minor modification (as recommended by the Solubility Working Group-SolWoG) of the original distribution given by the internal project elicitation.

The elicited project experts (Gauthier, 1993, Wilson et al., 1994) based the original log beta distribution on the range of values from the recent measurements of steady-state Np concentrations in both J-13 and UE-25p#1 ground waters (Nitsche et al., 1993; 1994) together with ongoing research at Los Alamos National Laboratory. In reviewing the proposed distributions, the SolWoG suggested that the minimum value be changed from 1×10^{-8} to 5×10^{-6} molar, but did not indicate how to adjust the coefficient of variation or the expected value (Dyer, 1993). In the TSPA-1995 analyses the distribution parameters were adjusted so that the shape of the modified distribution was similar to that of the original distribution, except for the lack of a tail at low values of log(Np concentration). The change made in TSPA-1995 makes the moderate values more probable at the expense of the probability of very low values of log(Np concentration). The parameters used for the modified distribution are a minimum of −5.3, a maximum of −2, an expected value of −3.85, and a coefficient of variation of 0.15 (slightly smaller than that for the original elicited distribution, M&O, 1995).

The revision to the spent-fuel dissolution-rate model in TSPA-1995 represents minor modifications and, thus, the TSPA-1995 dissolution rate equation is relatively consistent with the TSPA-1993 analyses. As was found in TSPA-1993, the TSPA-1995 results indicate that Np release is the dominant release/dose contributor at long time frames and, therefore, constraints on dissolved Np concentrations in J-13-like fluids warrant critical examination. Comparison of aqueous Np concentrations in J-13-like fluids derived from dissolution studies, solubility studies, and thermochemical calculations allows an assessment of the applicability of the dataset used to construct the distribution of Np solubility limits given by the project-expert elicitation.

2.0 WASTE FORM DISSOLUTION STUDIES SYNTHESIS

This section presents a synthesis of a number of spent-fuel dissolution-rate studies which have variable flow rates. The flow rates range from none (batch studies) to fast (flow-through studies). These studies have been used to constrain the dissolved concentrations of Neptunium in the resultant fluids. The Np concentration values derived from these studies are used in Section 3 to evaluate current solubility limits for Np used in total system performance assessments. In addition to variable flow rates, the dissolution-rate studies were done over a range of conditions such as temperature, fuel sample, and time. The effects of each of these variables on the dissolved radionuclide concentrations are discussed below for Neptunium.

2.1 Neptunium Considerations From Experimental Observations

Although neptunium is not considered a primary actinide of concern in terms of dose immediately after core discharge, its contribution to available dose grows with time because of its long half-life of 2.14×10^{6} years. Within nuclear fuel, ^{237}Np has an initial concentration of about 4×10^{-4} g/g fuel (see Sections 2.1.4 and 3.1.1 below) which grows with time as ^{241}Am, with a half life of 432 years, decays to ^{237}Np. The radioactivity conversion factor for ^{237}Np is 7.05×10^{-4} Ci/gram. In TSPA-1995, ^{237}Np contributes predominantly to the peak doses calculated for the 1,000,000 year time frame mainly due to high values of solubility-limited aqueous Np concentrations and low sorption in the geosphere (M&O, 1995).

As discussed in detail in Section 3, the project-elicited solubility limits are based on a set of solubility experiments that approached steady-state conditions from *oversaturation* and formed a highly *metastable* Np-bearing phase. That is, highly concentrated Np solutions were prepared using very soluble Np-salts and these were allowed to precipitate Np-solids from this highly unstable state, in order to try to identify upper limits on Np concentrations in J-13-like fluids. Aqueous Np concentrations measured in dissolution experiments are relevant directly to evaluating the applicability of such experimental results for a system which will approach its steady-state conditions from *undersaturation*. If spent-fuel dissolution cannot provide Np concentrations high enough to even approach saturation of the *metastable* phase (even over a large range of fluid-flow rates), then there is no reason to expect such a phase would form and control Np concentrations at longer time-frames.

The discussion below summarizes four sets of experiments that determined ^{237}Np dissolution rates from spent fuel into J-13 water. Two sets (Wilson, 1990a—Series 2; Wilson, 1990b—Series 3) are steady-state experiments in which the samples were immersed in water and the solution was sampled at various time intervals. In the third set (Finn, et. al, 1995), J-13 water was dripped on the samples every 3.5 days. A fourth set of experiments (Gray and Wilson, 1995) analyzed Uranium dissolution rates in a flow-through apparatus, but did not measure ^{237}Np directly. These four sets of tests are evaluated below to examine the relations between the different testing methods, and to derive additional constraints on the aqueous concentrations of Neptunium for J-13 -like fluids starting out at zero Np content. Values taken from these sources and the conversion methods used to derive corresponding dissolved Np

concentrations are shown in Tables 2-1a and 2-1b, and the derived values are summarized in Table 2-2.

2.1.1 Series 2 Steady-State Tests (Wilson, 1990a)

Spent fuel particles (2-3 mm range) with clad hulls were soaked in fused silica vessels and J-13 water at 25°C (Wilson, 1987, Wilson, 1990a). The particles had been soaked in distilled water during the Series 1 tests so that fission products from the gap and cracks had already been removed. The vessels were open to the hot-cell atmosphere. The samples are from the Turkey Point (TP) and the H. B. Robinson (HBR-same as ATM-101) reactors, both pressurized-water reactors (PWR). After each of five cycles, the fuel particles and equipment were washed to measure the amount of Np dissolved in the fluid.

Initially, Turkey Point (TP) samples had higher readings, 0.9 - 1.8 pCi/mL, than H. B. Robinson, but the rest of the data (cycles) for H. B. Robinson (HBR) ranged from 0.1 to 0.8 pCi/mL (Table 2-2). These lower values are at, or near, the detection limits given for ^{237}Np (0.2 pCi/mL or 0.3 ppb). The best estimate concentration (steady-state) at 25 °C is 0.4 pCi/mL (5.68×10^{-7} g/L; 2.4×10^{-9} M) based on an average of all the steady-state values in these cycles (Wilson, 1990a, Sec. 3.2.5). Filtration of the fluid samples showed no significant colloidal component. The data suggest that Np enters the aqueous phase congruently with uranium as the fuel dissolves. The derived values of dissolved Np from these tests are shown as Series 2 experiments in Table 2-2. For the last cycles of HBR and TP fuels, the values of 3.0×10^{-9} M and 1.6×10^{-9} M Np, respectively, are close to the best estimate concentration given above.

2.1.2 Series 3 Steady-State Tests (Wilson, 1990b)

Series 3 steady-state tests using Turkey Point and H. B. Robinson fuel (same as ATM-101) in J-13 water were performed in closed stainless steel containers and at temperatures of 25 °C and 85 °C (Wilson, 1990b). Fluid samples were filtered with 0.4 micron filters to see if any of the actinides were carried as colloids. As with the Series 2 tests, the fuel particles and equipment were washed to retrieve any material that had reprecipitated on them.

The solutions develop initial high concentrations of from 2 to 10 pCi/mL that decrease to ~0.2 to 1 pCi/mL in 200 days (Wilson, 1990b). After these early variations, ^{237}Np concentrations remain between 0.1 to 0.5 pCi/mL (Table 2-2). The best estimate concentration (steady-state) at is 0.2 pCi/mL (2.84×10^{-7} g/L; 1.2×10^{-9} M) based on an average of all the steady-state values in cycles 2 and 3 (Wilson, 1990b, p. 3.35). Wilson (1990b-Table 4.2) provides best estimate values for 25°C and 85°C of 1.3×10^{-9} M and 7.9×10^{-10} M , respectively. No clear relation to temperature or filtration was observed for the dissolved ^{237}Np concentrations. The derived values of dissolved Np from these tests are shown as Series 3 experiments in Table 2-2. For the last cycles, the values of 1.4×10^{-9} M (25°C HBR) and 8.1×10^{-10} M Np (85°C HBR), are close to the best estimate concentration given above. The derived value for TP at 85°C is 2.7×10^{-10} M, which is slightly lower.

In these experiments (Wilson 1990b), the ^{237}Np release fractions (which include *all* Np removed from the spent fuel, not just that remaining dissolved in the aqueous phase—i.e., R_{Np} is [released Np]/[initial Np in fuel]) in all experiments were close to those for uranium (R_{Np}/R_U = 1.14 to 1.55). This indicates that dissolution is approximately congruent in these tests. In addition, these values seem to have about the same temperature dependence as that for uranium release determined by Gray and Wilson (1995). The increase in temperature from 25 °C to 85 °C increases the R_{Np} by a factor of 2.21 (Wilson, 1990b), close to the value of 2.33 measured for uranium (Wilson, 1990b). Using Gray and Wilson's equation (Gray and Wilson, 1995, Equation 4.1) to estimate the uranium release fraction at 25°C and 85°C produces a ratio (R_{85}/R_{25}) of 2.35, which is only slightly different from those derived from the study of Wilson (1990b).

2.1.3 Drip Tests (Finn et al, 1995)

In the drip tests, two types of fuel particles (ATM-103 and ATM-106) were exposed to 0.75 mL of EJ-13 water (J-13 water equilibrated with tuff at the higher temperature of the experiment) every 3.5 days (0.214 mL/day) at a temperature of 90 °C (Finn et al., 1995). Liquids were collected at four time intervals and the concentrations of actinides were measured. The fuel was not washed, so any material that reprecipitated on the fuel surface was not measured. For the first interval ("first cycle" in Table 2-2), aqueous concentrations of 2 to 116 pCi/mL, or 1.2×10^{-8} M and 7.0×10^{-7} M respectively (Tables 2-1a and 2-2), were determined. These early values decrease at later times. For the last interval, aqueous concentrations of 0.027 to 0.17 pCi/mL were determined (Table 2-2). The Np concentrations derived from these are 1.6×10^{-10} M and 9.9×10^{-10} M Np (Tables 2-1b and 2-2)—somewhat consistent with those from batch tests discussed above. The average values for the entire time period of the drip tests are determined here to be 1.7×10^{-8} M for ATM-106 and 1.4×10^{-7} M for ATM-103.

2.1.4 Flow-Through Tests (Gray and Wilson, 1995)

Gray and Wilson (1995) performed uranium fuel dissolution tests in a fast-flowing apparatus (0.1 mL/min, or 144 mL/day) using J-13 water at 22 °C. The flow rate is so high that the extent of reaction is limited to the point that reactant compositions do not change and fluid concentrations remain far from saturation with the phase dissolving. This system ensures a far-from-equilibrium condition for the reaction being studied. Within these experiments, concentrations of ^{237}Np were not measured. However, assuming congruent dissolution of the fuel, the concentration of dissolved Np can be estimated from the measured value of U (see Table 2-1b) and the ratio of these elements in the fuel. The Np/U ratio in the fuel was calculated using the fission product inventory for 30 MWd/kgU as generated by the Radiological Database version CDB_R/v1.1 (M&O, 1993). The mass ratio is found to be 4.41×10^{-4} g Np/g U. Using this value to convert the observed U concentrations to Np concentrations results in 2.3×10^{-10} M Np (see Tables 2-1b and 2-2). This value is only about 20% of the 25°C values determined in the batch studies discussed above (Table 2-2).

For estimating the Np concentration in Gray and Wilson's (1995) dissolution experiments at 90°C, the temperature terms of their Equation 4.1 were used. The measured dissolution rate for 22°C was scaled upward to 90°C by evaluating the above equation at both temperatures and using the ratio (R_{90}/R_{22} = 2.62) as a multiplier on the value at 22°C. The resulting estimated value of 6.1×10^{-10} M Np is given in Table 3-1.

2.1.5 Comparison of Neptunium Concentrations

All four experimental studies summarized above were performed with J-13-like water and spent nuclear fuel. The fluid flow rates ranged from 0.0 (steady-state tests) to 0.144 L/d (flow-through tests). The temperatures of the experiments ranged from 22 °C to 90 °C. Values taken from these sources were converted into dissolved Np concentrations using the methods shown in Tables 2-1a and 2-1b for the first and last cycle results. Table 2-2 summarizes the concentrations of aqueous neptunium determined for the last test cycles. The averages and standard deviations for the Np activity concentrations data from all tests are also given in Table 2-2. In general, the concentrations are higher in the first cycle of any experimental study and decrease at later time. All four experimental studies give fairly consistent results for the latter cycles even though they encompass about four orders of magnitude difference in flow rate. The data suggest that temperature dependency is weak and there is only a slight, negative dependence on the flow rate. In the section below, the derived values are discussed and used to evaluate the applicability of the project expert elicited values for the case of J-13-like water compositions.

TABLE 2-1a. Derived dissolved Np concentrations from values measured in "first cycles" of dissolution studies.

Experiment	Value Used	Reference	Location in Reference	Conversion Multiplier	Np Concentration moles/Liter
Series 2, HBR, 25°C	112. pCi Np	Wilson, 1990a	Table 3.5, Row 2	[10^{-12}Ci/pCi / (7.05×10^{-4} Ci/g *237 g/m * 0.25L)]	2.7×10^{-9}
Series 2, TP, 25°C	112. pCi Np	Wilson, 1990a	Table 3.5, Row 2	[10^{-12}Ci/pCi / (7.05×10^{-4} Ci/g *237 g/m * 0.25L)]	2.7×10^{-9}
Series 3, HBR, 25°C	68. pCi Np	Wilson, 1990b	Table 3.7, Row 2	[10^{-12}Ci/pCi / (7.05×10^{-4} Ci/g *237 g/m * 0.25L)]	1.7×10^{-9}
Series 3, TP, 85°C	203. pCi Np	Wilson, 1990b	Table 3.7, Row 2	[10^{-12}Ci/pCi / (7.05×10^{-4} Ci/g *237 g/m * 0.25L)]	4.9×10^{-9}
Series 3, HBR, 85°C	68. pCi Np	Wilson, 1990b	Table 3.7, Row 2	[10^{-12}Ci/pCi / (7.05×10^{-4} Ci/g *237 g/m * 0.25L)]	1.6×10^{-9}
Drip, ATM-106, 90°C	7×10^{-8} total g Np	Finn et al, 1995	Table 2, Row 1	[1/[237 g/m *(113d-0d) * 2.14×10^{-4} L/d]]	$12.\times10^{-9}$
Drip, ATM-103, 90°C	4×10^{-6} total g Np	Finn et al, 1995	Table 2, Row 5	[1/[237 g/m *(113d-0d) * 2.14×10^{-4} L/d]]	$700.\times10^{-9}$

TABLE 2-1b. Derived dissolved Np concentrations from values measured in "last cycles" of dissolution studies.

Experiment	Value Used	Reference	Location in Reference	Conversion Multiplier	Np Concentration moles/Liter
Series 2, HBR, 25°C	124 pCi Np	Wilson, 1990a	Table 3.5, Row 2	[10^{-12}Ci/pCi / (7.05×10^{-4} Ci/g *237 g/m * 0.25L)]	3.0×10^{-9}
Series 2, TP, 25°C	67.5 pCi Np	Wilson, 1990a	Table 3.5, Row 2	[10^{-12}Ci/pCi / (7.05×10^{-4} Ci/g *237 g/m * 0.25L)]	1.6×10^{-9}
Series 3, HBR, 25°C	56.3 pCi Np	Wilson, 1990b	Table 3.7, Row 18	[10^{-12}Ci/pCi / (7.05×10^{-4} Ci/g *237 g/m * 0.25L)]	1.4×10^{-9}
Series 3, TP, 85°C	11.3 pCi Np	Wilson, 1990b	Table 3.7, Row 18	[10^{-12}Ci/pCi / (7.05×10^{-4} Ci/g *237 g/m * 0.25L)]	0.27×10^{-9}
Series 3, HBR, 85°C	33.8 pCi Np	Wilson, 1990b	Table 3.7, Row 18	[10^{-12}Ci/pCi / (7.05×10^{-4} Ci/g *237 g/m * 0.25L)]	0.81×10^{-9}
Drip, ATM-106, 90°C	8×10^{-10} total g Np	Finn et al, 1995	Table 2, Row 4	[1/[237 g/m *(581d- 482d) * 2.14×10^{-4} L/d]]	0.16×10^{-9}
Drip, ATM-103, 90°C	5×10^{-9} total g Np	Finn et al, 1995	Table 2, Row 8	[1/[237 g/m *(581d- 482d) * 2.14×10^{-4} L/d]]	0.99×10^{-9}
Flow, ATM-101, 22°C	125 ngU/ml	Gray and Wilson, 1995	Fig.A.44, 1/Flow = 10 min/mL	[10^{-9} g/ng*10^{3}mL/L*4.41×10^{-4} gNp/gU /237g/m][a]	0.23×10^{-9}

a) Note, this conversion assumes congruent dissolution of Np from the waste form.

TABLE 2-2. NEPTUNIUM CONCENTRATIONS IN J-13-LIKE WATER

Experiment	Temperature °C	Flow L/d	Fuel Type	First Cycle pCi/mL	Last Cycle pCi/mL	Last Cycle, Moles/L
Series 2	25	0	HBR	0.45	0.50	3.0 E-9
			TP	0.45	0.27	1.6 E-9
Series 3	25	0	HBR	0.27	0.22	1.4 E-9
	85	0	TP	0.81	0.045	0.27E-9
	85	0	HBR	0.27	0.14	0.81E-9
Drip	90	2.14E-4	ATM-106	2.0	0.027	0.16E-9
			ATM-103	116	0.17	0.99E-9
Flow	22	0.144	Series 3	—	0.039	0.23E-9
			Archive			
			ATM-101			
			Average	17.2	0.18	1.05E-9
			(If drop 116)	0.72		
			Std. Dev.	40.4	0.15	8.8E-10

3.0 CONSTRAINTS ON AQUEOUS NEPTUNIUM CONCENTRATIONS DERIVED FROM SPENT-FUEL DISSOLUTION STUDIES

This section provides an evaluation of the bounds used to calculate the dissolved concentration of Np in total system performance assessment (TSPA) models. The relevance of the current constraints is evaluated against data derived from spent-fuel dissolution-rate studies (discussed above in Section 2) and thermochemical equilibrium calculations. At the end of this section, suggestions are made for revisions to the current constraints on solubility-limited concentrations of Neptunium in J-13-like water used in TSPA-1995 (M&O, 1995). These revisions incorporate constraints from dissolution studies and should be used for cases representing J-13-like water compositions in sensitivity studies of TSPA-1995 and in further performance assessments (e.g., TSPA-VA).

3.1 Applicability of Current TSPA Solubility-Limited Np Concentrations in Light of Dissolution Studies Data on Aqueous Np Concentrations

Synthesis of data on dissolved Np concentrations derived from (a) spent-fuel dissolution studies, (b) oversaturation steady-state concentration studies, and (c) thermochemical calculations of phase equilibria is facilitated by assessing the conditions at which experimental measurements and calculations were performed (summarized in Tables 3-1 and 3-2). Seeming inconsistencies in the data are a common result of the fact that some of the experiments/calculations were done at different conditions and, therefore, are not all directly comparable. Because Np is a multivalent metal, the oxygen fugacity (or redox potential-Eh) is one primary variable to consider. In this preliminary analysis, a number of experimentally determined and calculated results are compared and sources of apparent discrepancies are evaluated semi-quantitatively based on the experimental and calculational conditions given in the source materials. This assessment is done to provide the context for using results from one study to constrain the applicability of another.

3.1.1 Comparison of Conditions

First, how do data from the drip tests (Finn et al., 1995—F95), the steady-state tests (Wilson, 1990a,b—W90), and the flow-through tests (Gray and Wilson, 1995—GW95) (all discussed above in Section 2) relate to each other? The complicated relations among these studies can be assessed by examination of the differences in experimental conditions. The F95 tests can be assumed reasonably to have equilibrated at atmospheric oxygen fugacities because of the high surface-area-to-volume ratio of water drops and the relative masses of the atmosphere to water involved in the drip tests (slow flow). Similarly, the fluids used by GW95 were set to atmospheric oxygen fugacities in the experimental flow-through apparatus. This constraint should remain throughout the experiment because of high flow rates and the very small extent of reaction experienced by any mass of fluid passing over the solid. It is reasonable to conclude that these two studies were conducted at relatively consistent oxygen fugacities set to atmospheric values. Because most of the other compositional variables of the fluids were similar (i.e., ~J-13), F95 and GW95 data should be fairly directly comparable in terms of

chemical conditions. However, in the case of the W90 batch tests, it is not clear if the steady-state tests were equilibrated to atmospheric oxygen fugacities.

Table 3-1. Summary of Np concentrations determined from spent fuel alteration/dissolution rate studies compared to the range of values provided by project-expert elicitation, which are based on the data of Nitsche et al. (1993, 1994). See text for discussion of conditions of Wilson (1990a,b) tests.

Study	C_{Np} M	Flow Rate L/d	Notes
Wilson, 1990a	2.3×10^{-9}	0 (batch)	25 °C Series #2, last cycle average
Wilson, 1990b	1.4×10^{-9}	0 (batch)	25 °C Series #3, last cycle HBR
Wilson, 1990b	5.4×10^{-10}	0 (batch)	85 °C Series #3. last cycle average
Jardine, 1991	5.9×10^{-9}	0 (batch)	85°C high value of Wilson (1990a,b)
Finn et al., 1995 ATM-106	1.6×10^{-10}	2.14×10^{-4}	90 °C, ATM-106 last cycle, J-13 water, $\log fO_2$ = atm
Finn et al., 1995 ATM-103	9.9×10^{-10}	2.14×10^{-4}	90 °C, ATM-103 last cycle, J-13 water, $\log fO_2$ = atm
Gray and Wilson, 1995	2.3×10^{-10}	1.44×10^{-1}	22 °C, J-13 water, $\log fO_2$ = atm (assumes congruent dissolution)
Gray and Wilson, 1995	6.1×10^{-10}	1.44×10^{-1}	90°C, J-13 water, $\log fO_2$ = atm (extrapolation of 22°C value using temperature dependence of Gray and Wilson, 1995--see text for discussion)
Project-expert elicitation* Range (based primarily on Nitsche et al. 1993, 1994)	5×10^{-6} to 1×10^{-2}	0 (batch)	oversaturation values, initial J-13 with added NaOH and $HClO_4$, metastable Na-NpO_2-CO_3-Hydrate and Np_2O_5 phases observed, 25, 60, & 90°C
Nitsche et al., 1993 Table VI	4.4×10^{-5} to 6.4×10^{-3}	0 (batch)	oversaturation values, initial J-13 with added NaOH and $HClO_4$, metastable Na-NpO_2-CO_3-Hydrate and Np_2O_5 phases observed, 25, 60, & 90°C
Nitsche et al., 1994 Table VI	7.0×10^{-6} to 2.9×10^{-3}	0 (batch)	oversaturation values, initial UE-25p#1 with added NaOH and $HClO_4$, metastable Na-NpO_2-CO_3-Hydrate observed, 25 & 60°C

*-Elicitation values given by project experts modified as recommended by the Solubility Working Group (see text for discussion).

Table 3-2. Summary of *calculated* Np concentrations in equilibrium with NpO_2 under various conditions.

Study	C_{Np}, M	Conditions
Wilson, 1990b; Wilson and Bruton, 1989	6.3×10^{-7}	EQ3/6 Calculated NpO_2 Solubility, 25°C, $\log fO_2$ = -0.7 (atm), $\log fCO_2$ = -3.5 (atm)
Wilson, 1990b; Wilson and Bruton, 1989	6.3×10^{-6}	EQ3/6 Calculated NpO_2 Solubility, 90°C, $\log fO_2$ = -0.7 (atm), $\log fCO_2$ = -3.5 (atm)
Wilson, 1990b; Wilson and Bruton, 1989	1×10^{-9}	EQ3/6 Calculated NpO_2 Solubility, 25°C, $\log fO_2$ = -12, $\log fCO_2$ = -3.5 (atm)
Wilson, 1990b; Wilson and Bruton, 1989	1×10^{-8}	EQ3/6 Calculated NpO_2 Solubility, 90°C, $\log fO_2$ = -12, $\log fCO_2$ = -3.5 (atm)
Janecky et al., 1994	3.2×10^{-11}	EQ3/6 Calculated NpO_2 Solubility, 25°C, "J-13" water w/Eh = 482 mV, and pH = 7, $\log fO_2$ = -22.5
Janecky et al., 1994	7.8×10^{-13}	EQ3/6 Calculated NpO_2 Solubility, 60°C, "J-13" water w/Eh = 325 mV, and pH = 7, $\log fO_2$ = -26.5
Janecky et al., 1994	4.7×10^{-12}	EQ3/6 Calculated NpO_2 Solubility, 90°C, "J-13" water w/Eh = 299 mV, and pH = 7, $\log fO_2$ = -23.2
Wolery et al., 1995	1×10^{-13}	EQ3/6 Calculated NpO_2 Solubility, 25°C, J-13 water w/Eh = 340 mV, and pH = ~7.4, $\log fO_2$ = -30.5

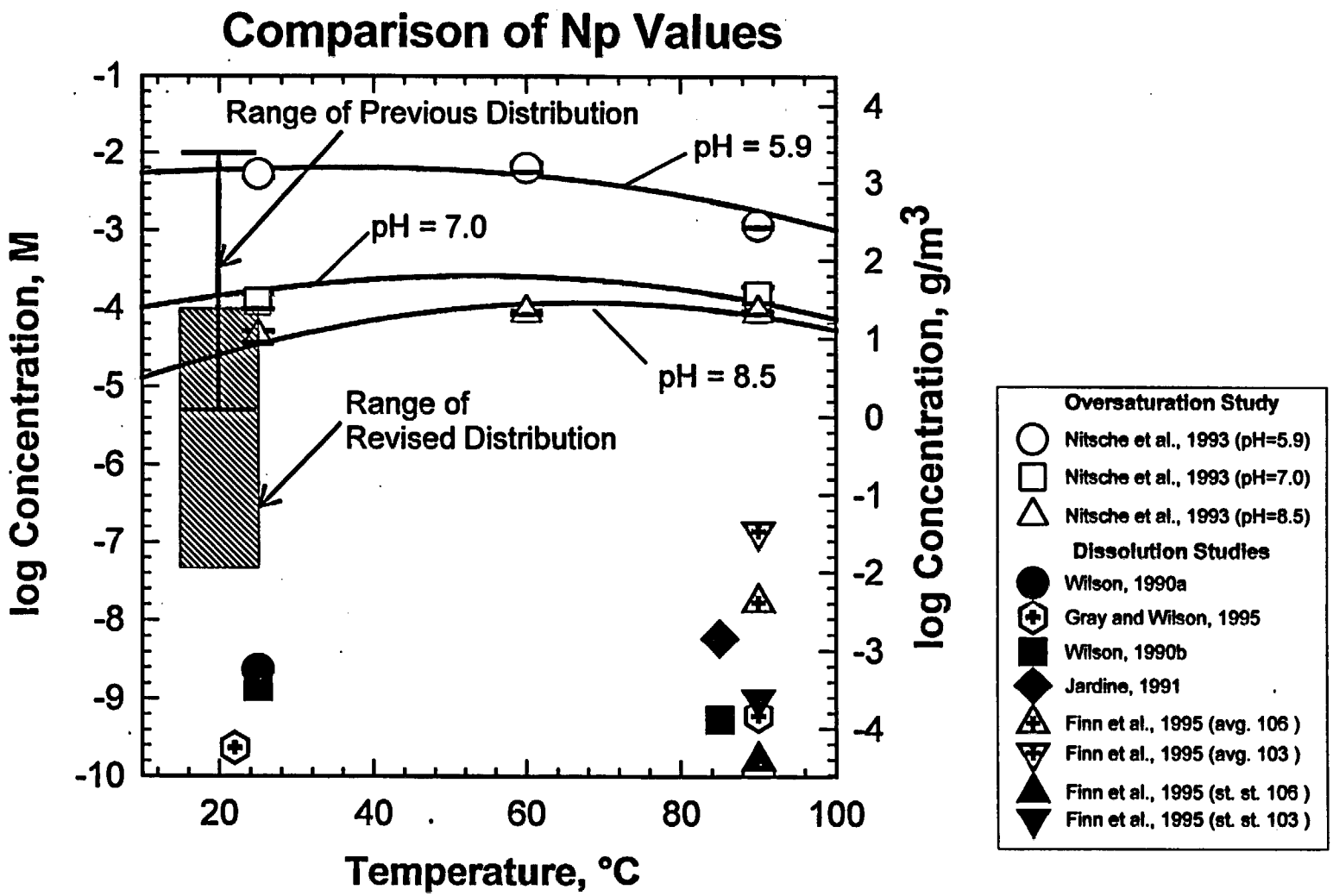

Figure 3-1. Comparison of the previous range of project elicited values (bar) based on the oversaturation measurements of Nitsche et al.(1993) with the values derived from spent fuel dissolution studies starting from undersaturation and the range of the revised (shading) distribution (st. st. = steady state; avg. = average of whole test time for Finn et al., 1995 study).

Because the W90 investigators did not set the oxygen fugacity, they compared their determinations with NpO_2 solubilities calculated both at $logfO_2$ values set to atmospheric (-0.7) and set to -12, as reported by Bruton and Shaw (1987) and Wilson and Bruton (1989). Whereas calculated NpO_2 solubilites at atmospheric conditions (Table 3-2) are much higher than the W90 determinations, values calculated at the lower oxygen fugacity are closer to the W90 measured values (Wilson, 1990b, Wilson and Bruton, 1989). It is interesting to note that their calculated values in equilibrium with atmospheric oxygen fugacities (Table 3-2) are about 2.5 to 3.7 orders of magnitude higher than Wilson's (1990) measured steady-state Np concentrations for the batch studies (Table 3-1). There is a second possible explanation for this discrepancy that does not preclude equilibration of the W90 tests at atmospheric oxygen fugacities.

Another possible explanation of the lower-than-expected values is that, instead of a *pure* NpO_2 controlling the Np concentration, Np exists as a trace component of dissolved NpO_2 in the structure of the uranium minerals forming. On average, the spent fuel waste form is about 0.01 to 0.1 mole % Neptunium. For example, the values for HBR fuel ATM-101 given by Barner (1985; Table F.1) are about 2 to 4×10^{-4} g NpO_2/g oxide (or about 0.02 to 0.04 mole % NpO_2). Bruton and Shaw (1987-Table 2) utilize an average spent fuel composition that has 0.14 mole % Np in its structure.

Assuming that NpO_2 is incorporated as an ideal solid solution into the precipitating Uranium phases in about the same proportion as it occurs in the waste form, the ~0.001 mole fraction of NpO_2 would set the activity of the NpO_2 component to about 0.001. This would result in a ~3 order-of-magnitude reduction to the dissolved Np concentration in equilibrium with pure NpO_2 at atmospheric oxygen fugacities. Using this factor to adjust the calculated values at atmospheric oxygen fugacities (Wilson, 1990b, Wilson and Bruton, 1989), provides reasonable matches to the values determined in Wilson (1990a,b). The possibility of incorporation of both Np and Am (which is similarly dilute in the experiment relative to equilibrium with a pure Am phase) as trace constituents in precipitating Uranyl phases was discussed by Wilson and Bruton (1989). In addition, Buck et al., (1997) report Np incorporation into dehydrated schoepite ($UO_3 \cdot 0.8H_2O$) that precipitates during the drip tests (Finn et al., 1995).

In addition, to the chemical conditions, flow rates were also variable among these studies and may account for some of the observed differences in the data. The current data derived form these studies only provides about a factor of 4 difference in Np concentration for flow rate changes of about 4 orders of magnitude. This effect is not very large and is not be fully quantified in this analysis.

3.1.2 Relative Stability of Np-oxides—NpO_2 and Np_2O_5

Assessing the relative stabilities of NpO_2 and Np_2O_5 at a given temperature and pressure involves only specifying the oxygen fugacity of the system because a reaction can be written between these phases as

$$Np_2O_{5(s)} \Leftrightarrow 2\,NpO_{2(s)} + 1/2\,O_{2(g)} \qquad \textbf{(3-1)}$$

which indicates that equilibrium between these two solids is an oxygen fugacity buffer. At any temperature and pressure, both solids would be stable at the equilibrium oxygen fugacity, only Np_2O_5 would exist above it, and NpO_2 would be the stable phase at oxygen fugacities below the equilibrium value. Given the thermochemical data for reactions among NpO_2, Np_2O_5, Np^{4+} and NpO_2^+ in the EQ3/6 data0.com.r2 datafile, the equilibrium constant for Reaction 3-1 (K_{3-1}) can be calculated as a function of temperature at 1 atmosphere pressure. For the following reactions,

$$NpO_{2(s)} + 4H^+ \Leftrightarrow Np^{4+} + 2\,H_2O_{(l)} \qquad \textbf{(3-2)}$$

$$Np_2O_{5(s)} + 2H^+ \Leftrightarrow 2\,NpO_2^+ + H_2O_{(l)} \qquad \textbf{(3-3)}$$

$$NpO_2^+ + 2H^+ \Leftrightarrow Np^{4+} + 1/2\,O_{2(g)} + H_2O_{(l)} \qquad \textbf{(3-4)}$$

values of the log equilibrium constants (log K) were taken from the EQ3/6 data0.com.r2 datafile (Table 3-3). The above reactions and their log K values have been combined (Reaction 3-3 plus 2 times Reaction 3-4 minus 2 times Reaction 3-2) to yield the equilibrium constant (K_{3-1}) for the oxygen fugacity buffer relation defined by the coexistence of these two solids (Reaction 3-1).

Table 3-3. Log of the equilibrium constants for Reactions 3-1 through 3-4 at 25, 60, and 100°C and 1 atmosphere.

Reaction Property	25°C, 1 atm	60°C, 1 atm	100°C, 1 atm
log K_{3-2}	-7.8	-7.6	-6.3
log K_{3-3}	9.5	8.0	6.0
log K_{3-4}	-9.8	-8.5	-6.6
log K_{3-1}	5.5	6.2	5.4

The equilibrium oxygen fugacity for Reaction 3-1 is given by the following relation

$$K_{3-1} = fO_2^{\frac{1}{2}} \tag{3-5}$$

and can be calculated from the log K_{3-1} values in Table 3-3 by taking the log of Equation 3-5 to get

$$\log fO_2 = 2 \log K_{3-1} \tag{3-6}$$

This results in values of log fO_2 of 11.0, 12.4, and 10.8 at 25°C, 60°C, and 100°C, respectively. These values are much greater than that for equilibrium with the atmosphere (log fO_2 = −0.7) suggesting that Np_2O_5 is metastable relative to NpO_2 under all natural conditions.

These values indicate that NpO_2 is stable relative to Np_2O_5 over the temperature range 25 to 100 °C below log oxygen fugacities of about 11 to 12. The source of these data in the EQ3/6 database is referenced as the Lemire (1984) AECL compilation/review of Np data. Without a technical review of the original sources of the thermochemical data, the accuracy of this dataset is uncertain. In order for Np_2O_5 to be a stable equilibrium phase at, or near, atmospheric oxygen conditions, there would have to be about 10 to 12 orders of magnitude inaccuracy in the values. Although this in not an unheard level of inaccuracy, it is a relatively large degree of error for this type of information. It appears that, unless there are very large errors in the thermochemical data, the Np_2O_5 phase should not be stable relative to NpO_2 under any natural conditions.

3.1.3 Discussion of Aqueous Np Concentration Limits

The range of solubility-limited Np concentrations used in TSPA-1995 is based primarily on the range of the data of Nitsche et al. (1993, 1994). These ranges are shown in Table 3-1 together with aqueous Np concentrations derived from the spent-fuel alteration/dissolution studies as discussed above. The project-elicited distribution range, the data from Nitsche et al., (1993), and the values derived in this study from the dissolution studies are shown in Figure 3-1. The dissolution studies represent a variety of water flow rates—high rates for the flow-through studies (Gray et al., 1992; Gray and Wilson, 1995), lower rates for the unsaturated dripping studies (Finn et al., 1995), and no flow for the batch studies (Wilson, 1990a, 1990b).

It appears clear from Figure 3-1 that the dissolved Np concentrations in the resultant fluids of these studies are *all* well below those of the metastable solubilities measured by Nitsche et al. (1993, 1994). These dissolution studies reached these lower concentrations in very short periods of time (at most a few years) relative to that expected for geological disposal. It does not seem likely that the metastable phases observed in the oversaturation experiments of

Nitsche et al. (1993, 1994) would form at all for the case of J-13-like water interaction with the waste form.

The *highest* value derived here from the spent-fuel studies (1.4×10^{-7} M see Section 2.1.3) is *only* about 3 percent of the *minimum* value in the current solubility-limit range (Table 3-1) for use in TSPA calculations. In addition, this highest value (1.4×10^{-7} M) is an average from F95 data that includes the measured values from *all* the cycles in the experiments. The values in the early portion of the tests were much higher than the later ones. As discussed above and shown in Table 2-2, the values were high in the first cycle from F95 (ATM-103) and decreased for the latter cycles to a value of 9.9×10^{-10} M, which is about 2 orders of magnitude *smaller* than the average given above. This indicates even further that it is highly unlikely that J-13 water reacting with spent fuel will achieve concentrations of Np high enough to even approach saturation of the metastable phases upon which the current solubility limits are based. The next highest value in Table 3-1 is that of 5.9×10^{-9} M given by Jardine (1991) as the high value reported by Wilson (1990a,b). This value is only 0.12% of the minimum value of the project-expert elicited range. Thermochemical analyses of the Nitsche et al (1993, 1994) studies have evaluated the degree of metastability in those tests.

The degree to which the fluids from the Nitsche et al (1993, 1994) studies were supersaturated with respect to NpO_2 was calculated by Janecky et al. (1994). The saturation state values calculated by Janecky et al., (1994) for pH of 7 were used here to derive corresponding equilibrium NpO_2 solubilities (Table 3-2). Comparing these values to the range of Np concentrations used by the project expert elicitation (Table 3-1), shows that NpO_2 is calculated to be about 5 to 10 orders of magnitude *supersaturated* in the Nitsche et al. (1993, 1994) studies, depending on the experimental conditions. Calculation of the stable Np phase and its solubility in J-13-like water at other conditions (Wilson and Bruton, 1989; Wilson 1990b; Wolery et al., 1995) has also shown that the dissolved Np concentration set by NpO_2 equilibrium is orders of magnitude lower than those observed for the metastable phases formed in supersaturation experiments (Nitsche et al., 1993, 1994).

The differences in the *calculated* NpO_2 solubilities (Table 3-2) appear to be due mainly to differences in the imposed oxygen fugacity (or Eh) in the various calculations. The highest calculated Np concentrations correspond to atmospheric oxygen fugacity settings, and the values decrease at more reduced conditions. Although the highest calculated value in Table 3-2 of 6.3×10^{-6} M is near the lower end of the range for the Nitsche et al. (1993) data, the redox conditions in the experiment were much lower than this such that direct comparison is inappropriate. The calculations of Janecky et al. (1994) were performed at the appropriate redox conditions measured in the Nitsche et al. (1993) tests and the corresponding calculated NpO_2 limited concentrations given in Table 3-2 are many orders of magnitude lower.

Using calculated NpO_2 solubilities (or values for NpO_2 as a solid solution component) for direct constraints on solubility limits for TSPA requires the assumption that kinetic inhibitions to precipitation would not be prohibitive on geologic time scales (i.e., one must assume that the a metastable phase does not precipitate and deter the systems approach to equilibrium). Although this is the case for any solubility limiting phase, this assumption is more difficult to

make in the case of Np. This difficulty comes from a theoretical standpoint. Because the aqueous Np is pentavalent and the Np in NpO_2 tetravalent, precipitation therefore requires a reduction of the aqueous Np. At low temperature, reduction reactions are generally slow reactions even at reduced conditions in hydrothermal bomb experiments.

In addition, metastably elevated silica concentrations in the Yucca Mountain ground water indicate that disequilibrium can persist on geologic time scales. However, for any metastable phase to first precipitate, the solution must become saturated (or even slightly supersaturated) with that phase. In the case of silica in Yucca Mountain ground waters, there are highly metastable silica-source phases, e.g., volcanic glass, that are dissolving and contributing higher than equilibrium concentrations to the fluid. Phases such as opal-CT and cristobalite, which are metastable relative to stable quartz, precipitate and impose silica concentrations that are about 2 to 3 times those of the equilibrium concentration (Duffy, 1993).

As discussed above, it appears that spent fuel dissolution studies in J-13-like water may have been able to (super)saturate with respect NpO_2 (or its corresponding solid-solution phase). However, *none* of the spent fuel dissolution studies resulted in Np concentrations apparently required to reach saturation of the metastable sodium-neptunyl-carbonate-hydrate phases or Np_2O_5 phases observed in the Nitsche et al. (1993, 1994) studies. These tests then indicate that metastabley high concentrations are not developed at laboratory time-scales and should not be expected over longer time frames. In addition, if the Np occurs in as a NpO_2 solid solution in the spent fuel, or as minute discrete NpO_2 solids, then nucleation kinetics should not be a major factor.

4.0 STRATEGY FOR FUTURE TOTAL SYSTEM PERFORMANCE ASSESSMENTS

This work represents a synthesis of Np concentrations as constrained by the spent-fuel alteration/dissolution studies and calculational studies of NpO_2 solubility with the conceptual framework of a performance assessment model that uses a far-from equilibrium dissolution rate combined with solubility-limited dissolved radionuclide concentrations. Based on the discussion in Section 3.1.3 above, it is recommended that the current distributions for solubility limited Np concentrations be shifted lower by two orders of magnitude with preservation of the "shape", or variance, of the distribution. This shifted range for the distribution is shown in Figure 3-1 for comparison to the range of the previous distribution and the values derived and discussed above.

Based on the values discussed above and shown in Figure 3-1, this is a relatively conservative adjustment, and still encompasses a large portion of the range provided by the project expert elicitation, even though there is little or no possibility that for J-13-like water these values will ever apply. For the beta distribution of $\log_{10}(Np)$ given in TSPA-95 (M&O, 1995-Table 6.3-1), this revision amounts to shifting the expected value of $\log_{10}(Np)$ (in mol/L) from -3.85 to -5.85, and the minimum and maximum values from -5.30 and -2.0, to -7.30 and -4.0, respectively. Because the variance, and thus the standard deviation, remain the same for the revised distribution, the coefficient of variation (i.e., the standard deviation divided by the mean) becomes 0.099. This adjustment is supported also by lower values measured for the

concentration of Np in J-13-like fluids in ongoing oversaturation studies at Los Alamos National Laboratory (LANL-Efurd et al., 1998). These tests were conducted under slightly different conditions than the Nitsche et al. (1993) study, but also have precipitated apparently metastable Np solids.

As fluid compositional scenarios are defined in the performance assessment near-field geochemistry model, all the solubility-limit distributions will need to be reevaluated and revised for each specific fluid-composition scenario. Assessing how solubility-limit distributions are changed by new data is facilitated by a well-defined paradigm for building the distribution. A suggested approach is to define, for each element, the stable, solubility-limiting phase for each specific fluid scenario. For the identified stable phase, its equilibrium dissolved radionuclide concentration would be used to constrain the expected value of the distribution. For the case of Np in J-13-like fluids, calculated or measured NpO_2 solubilities should be used for the expected value.

Construction of a distribution around such a value would entail encompassing sources of uncertainties associated with the identification of the stable solid phase and the derivation of the solubility-limited value, as well as conceptual uncertainties that are buried in this approach. These sources include (1) parameter uncertainty on the experimental measurements or the thermochemical data used to delineate the radionuclide concentration, (2) conceptual model uncertainties primarily regarding a) potential kinetic barriers to stable phase formation, b) potential misidentification of the actual stable phase(s), and c) incorporation of radionuclides as trace solid solutions in other phases. Some of the magnitudes of conceptual uncertainties could be assessed by constraints on solubility limits of metastable phases and natural analogues for geochemical behavior of radionuclides. The first of these three sources of conceptual error generally adds uncertainty at values greater than the expected value, whereas the latter two generally lead greater uncertainty lower than the expected value. Such distributions would also be used to incorporate uncertainty/variability in the fluid compositions, although major processes affecting water composition should be addressed via different water composition scenarios.

It is envisioned that improvements to future TSPA analyses would result from further analysis of the data from spent-fuel alteration/dissolution studies in order to derive relations between concentration and flow rate. These could then be used to define values of radionuclide concentrations for specific flow rates in conjunction with the source-term concentrations derived solely from the far-from equilibrium studies. Such limits would be specifically applicable to the water composition(s) and temperature(s) of the studies.

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