OFFICE OF CIVILIAN RADIOACTIVE WASTE MANAGEMENT
ANALYSIS/MODEL COVER SHEET

1. QA: QA

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Complete Only Applicable Items

2. ☒ Analysis — Check all that apply

Type of Analysis
☐ Engineering
☐ Performance Assessment
☒ Scientific

Intended Use of Analysis
☐ Input to Calculation
☒ Input to another Analysis or Model
☒ Input to Technical Document
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Describe use:
Input to Waste Form PMR

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Type of Model
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We made editorial changes to page 10+11 and the reference section on 4/28/00. ~~whe~~ We added a new citation for EQ3/6 and removed the reference LLNL1999 and replaced with CRWMS M+O 1998a.
Christine Stockman 4/28/00.

NM5507

FOR H. A. BENTON
4/28/00

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OFFICE OF CIVILIAN RADIOACTIVE WASTE MANAGEMENT
ANALYSIS/MODEL REVISION RECORD

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1. Page: 2 of: 43

2. Analysis or Model Title:

Pure Phases Solubility Limits – LANL

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00	Initial issue

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ACRONYMS AND ABBREVIATIONS

AMR	Analysis and Modeling Report
AP	administrative procedure
CRWMS	Civilian Radioactive Waste Management System
CSCI	Computer Software Configuration Item
DIRS	Data Input Reference System
DTN	data tracking number
LANL	Los Alamos National Laboratory
LLNL	Lawrence Livermore National Laboratory
M&O	Management and Operating Contractor
QAP	Quality Assurance Procedure
TSPA	Total System Performance Assessment
XRD	x-ray diffraction
YM	Yucca Mountain

1. PURPOSE

The natural and engineered system at Yucca Mountain (YM) defines the site-specific conditions under which one must determine to what extent the engineered and the natural geochemical barriers will prevent the release of radioactive material from the repository. Most important mechanisms for retention or enhancement of radionuclide transport include precipitation or co-precipitation of radionuclide-bearing solid phases (solubility limits), complexation in solution, sorption onto surfaces, colloid formation, and diffusion. There may be many scenarios that could affect the near-field environment, creating chemical conditions more aggressive than the conditions presented by the unperturbed system (such as pH changes beyond the range of 6 to 9 or significant changes in the ionic strength of infiltrated waters). For an extended period of time, the near-field water composition may be quite different and more extreme in pH, ionic strength, and CO_2 partial pressure (or carbonate concentration) than waters at some distance from the repository. Reducing conditions, high pH (up to 11), and low carbonate concentration may be present in the near-field after reaction of infiltrating groundwater with engineered barrier systems, such as cementitious materials. In the far-field, conditions are controlled by the rock-mass buffer providing a near-neutral, oxidizing, low-ionic-strength environment that controls radionuclide solubility limits and sorption capacities.

There is the need for characterization of variable chemical conditions that affect solubility, speciation, and sorption reactions. Modeling of the groundwater chemistry is required and leads to an understanding of solubility and speciation of the important radionuclides. Because experimental studies cannot be performed under the numerous potential chemical conditions, solubility limitations must rely on geochemical modeling of the radionuclide's chemistry. Fundamental thermodynamic properties, such as solubility products, complex stability constants, and redox potentials for radionuclides in different oxidation states, form the underlying database to be used for those calculations.

The potentially low solubilities of many radionuclides in natural waters constitute the first barrier for their migration from the repository into the environment. Evaluation of this effect requires a knowledge of the site-specific water chemistry and the expected spatial and temporal ranges of its variability. Quantitative determinations of radionuclide solubility in waters within the range of chemistry must be made. Speciation and molecular complexation must be ascertained to interpret and apply solubility results. The solubilities thus determined can be used to assess the effectiveness of solubility in limiting radionuclide migration. These solubilities can also be used to evaluate the effectiveness of other retardation processes expected to occur once dissolution of the source material and migration begin. Understanding the solubility behavior of radionuclides will assist in designing valuable sorption experiments that must be conducted below the solubility limit since only soluble species participate in surface reactions and sorption processes.

The present strategy for radionuclide solubility tasks has been to provide a solubility model from bulk-experiments that attempt to bracket the estimate made for this Analysis and Modeling Report (AMR) of water conditions on site. The long-term goal must be to develop a thermodynamic database for solution speciation and solid-state determination as a prerequisite for transport calculations and interpretation of empirical solubility data. The model has to be self-consistent and tested against known solubility studies in order to predict radionuclide solubilities over the continuous distribution ranges of potential water compositions for performance assessment of the site.

Solubility studies upper limits for radionuclide concentrations in natural waters. The concentration in the aqueous phase is controlled by the radionuclide-bearing solid phase and by the complexation reactions with ligands present in solution. Meaningful and acceptable thermodynamic data resulting from solubility and speciation data should meet the following criteria:

- Approach to equilibrium from both under- and over-saturation
- Accurate determinations of solution concentrations
- Well-characterized solubility controlling solid phase
- Knowledge of the nature (oxidation state, coordination environment) of the species involved in the equilibrium reactions under consideration.

1.1 OBJECTIVE

This report was developed in accordance with the Development Plan for *Waste Package Materials Department Analysis and Modeling Reports Supporting the Waste Form PMR* (CRWMS M&O 2000). It specifically addresses the item, "Pure Phase Solubility Limits: LANL" of the product development plan and is in compliance with procedure AP-3.10Q. In accordance with this document, the purpose of this AMR is to compile and evaluate available thermodynamic data on key radionuclides, namely neptunium, plutonium, technetium, and several elements of secondary priority. The various steps involved in the review process for thermodynamic data include:

1. Screening the open literature for experiments investigating the solubility and speciation of the radionuclides of interest
2. Evaluation of data for accuracy, internal consistency, technical acceptance, and quality assurance requirements
3. Extracting and formulating a set of thermodynamic data that can be used for solubility calculations. Formulating a set of thermodynamic data that can be used for solubility calculations by the Yucca Mountain Site Characterization Project (YMP).

The data will be implemented into the thermodynamic database to calculate solubility distributions and solubility limits for various scenarios.

1.2 PRIMARY TASKS

This report was developed in accordance with the Development Plan for *Waste Package Materials Department Analysis and Modeling Reports Supporting the Waste Form PMR* (CRWMS M&O 2000).

1. Compile and evaluate existing thermodynamic data for neptunium, plutonium, and technetium compounds relevant for conditions at Yucca Mountain.
2. Provide solubility distributions for radionuclides of secondary priority relevant for conditions at Yucca Mountain.
3. Document results and recommendations as either a model or analysis document per AP-3.10Q. If an abstracted model is developed, then documentation must be provided to ensure traceability and transparency of the method and processes used in the model (AP-3.10Q). Sensitivity analysis should be documented as analysis per AP-3.10Q.

2. QUALITY ASSURANCE

The Quality Assurance (QA) program applies to this analysis. All types of WPs were classified (per QAP-2-3) as Quality Level-1. CRWMS M&O (1999a, p. 7) in *Classification of the MGR Uncanistered Spent Nuclear Fuel Disposal Container System* is cited as an example of a WP type. The development of this analysis is conducted under activity evaluation *1101213FM3 Waste Form Analyses & Models - PMR* (CRWMS M&O 1999b), which was prepared per QAP-2-0. The results of that evaluation were that the activity is subject to the *Quality Assurance Requirements and Description* (DOE 2000) requirements.

3. COMPUTER SOFTWARE AND MODEL USAGE

The software package, EQ3/6, Version 7.2b, was approved for QA work by Lawrence Livermore National Laboratory (LLNL) and is identified as Computer Software Configuration Item (CSCI): UCRL-MA-110662 V 7.2b (CRWMS M&O 1998a). An installation and test report was written and submitted to Software Configuration Management (SCM), and the proper installation was verified before the runs described in this analysis were made. The implementation of the SCFT mode is covered by SCR LSCR198, and the Software Qualification Report (SQR) for Media Number 30084-M04-001. The SCFT addendum was installed on three of the Central Processing Units (CPUs) identified in block 16 of the SCR, and the installation and test reports were filed and returned to SCM before the calculations were run. All the EQ3 runs were performed on a Sandia National Laboratories system CPU (#S822733), a Dell 300 MHz Pentium II, located at 34 Monticello NE, Albuquerque, New Mexico.

The programs have been used only within the range of validation in accordance with AP-SI.1Q. The EQ3/6 calculations reported in this document used version 7.2b of the code, which is appropriate for the application, and were executed on Pentium series (including Pentium II) personal computers (PCs). Its present custodian, LLNL, has verified the EQ3/6 package. The source codes were obtained from SCM in accordance with the Management & Operating contractor (M&O) AP-SI.1Q procedure. The code was installed on the Pentium PCs according to an M&O-approved Installation and Test procedure (CRWMS M&O 1998b). This involves decompressing code executables, compiling the EQ3NR database, running several test cases, and comparing these to published results to confirm satisfactory code execution.

4. INPUTS

To calculate solubilities of radionuclides of secondary importance, J-13 groundwater (Harrar et al. 1990, pp. 4.2-4.3; DTN: LL980711104242.054, see Table 1) was used as input in EQ3 solubility calculations, though the pH was varied (see section 6), and occasionally, to maintain charge balance, chloride or sodium levels were allowed to deviate from J-13 groundwater values. This allowed drift is required for numerical conversion and does not materially affect the outputs of the secondary radionuclide solubility calculations. The specific partial pressures of CO_2 and O_2 of the ambient repository atmosphere are set to, respectively, $10^{-3.0}$ and $10^{-0.7}$ atm (DOE 1998). The oxygen partial pressure is equivalent to that in the atmosphere. The carbon dioxide pressure is higher and was chosen to reflect the observation that J-13 groundwater is in equilibrium with above-atmospheric carbon dioxide levels. The gas phase equilibria at the repository horizon are expected to be similar to that prevailing in the open atmosphere. EQ3 used as input the thermodynamic data file data0.com.R2 (DTN: MO9911SPATHD62.002). Output files (DTN: SN0003T0811199.007) have been submitted to the technical data management system. Occasionally, a more recent thermodynamic database–data0.com.V8.R6–is referred to for identification of aqueous species. Data0.com.V8.R6 has not been used in any calculations (DTN: LA9912WR831372.004).

Table 1. Chemical Composition of Reference Water

Variable	Composition (mg/L)	Source
Na	45.8	Harrar et al. 1990
Cl	7.14	Harrar et al. 1990
Si(aq)	28.5	Harrar et al. 1990
Ca	13.0	Harrar et al. 1990
K	5.04	Harrar et al. 1990
Mg	2.01	Harrar et al. 1990
Li	0.048	Harrar et al. 1990
F	2.18	Harrar et al. 1990
NO_3^-	8.78	Harrar et al. 1990
SO_4^{--}	18.4	Harrar et al. 1990
pH	6-9	varied

4.1 DATA AND PARAMETERS

The initial stage of calculating and predicting radionuclide solubilities begins with the compilation of a thermodynamic database. Data to be used may have been developed within the program or may be accessible through the open scientific literature. Data determined experimentally or calculated based on thermodynamic principles were compiled from the open literature that have been determined experimentally or have been calculated based on thermodynamic principles. Only data published in peer-reviewed internationally recognized journals were used. The data sources are identified in Tables 2, 3, and 4 of this document and are tracked in the Document Input Reference System (DIRS). The thermodynamic data for neptunium, plutonium, and technetium compounds have been submitted to the Technical Data Management System (TDMS) under the following respective data tracking numbers (DTNs):

- DTN: LAWR831372AN99.002 for Np
- DTN: LA9912WR831372.003 for Pu
- DTN: LAWR831372AN99.001 for Tc.

The detailed discussions of the evaluation of available literature data are included in the following:

- Letter Report on Neptunium Thermodynamic Database (Runde 1999a)
- Letter Report on Plutonium Thermodynamic Database (Runde 1999b)
- Letter Report on Technetium Thermodynamic Database (Runde 1999c).

Tables 2, 3, and 4, summarize the thermodynamic data that are recommended for use for solubility and stability calculations (described in the letter reports [Runde 1999a, b, c]) follow:

- Neptunium (DTN: LAWR831372AN99.002)
- Plutonium (DTN: LA9912WR831372.003)
- Technetium (DTN: LAWR831372AN99.001).

The plutonium and neptunium data resident in the most recent standard thermodynamic data file, data0.com.V8.R6 (DTN: LA9912WR831372.004) (dated December 1996 and available by anonymous file transfer protocol from LLNL), are taken from Lemire and Tremaine (1980, p. 368) and Lemire (1984, pp. 26-27, 29-31). Updated neptunium, technetium, and plutonium data as summarized in Tables 2, 3, and 4 respectively were incorporated into data0.com.V8.R6 (DTN: LA9912WR831372.004) by replacing pre-existing data. Note that data0.com.V8.R6 remains to be verified and was not used for any calculations in this analysis. The values of $\Delta_f G^o_{298}$ for water constituents and ligands (Johnson et al. 1992, pp. 932-943; Shock and Helgeson 1988, pp. 2026-2027) that were used to calculate the $\Delta_f G^o_{298}$ of Np, Pu, and Tc complexes and solids were extracted from the data0.com.V8.R6 data file (DTN: LA9912WR831372.004). These data were selected, rather than thermodynamic data available from other sources, to maintain internal consistency within the data file (see DTNs: LAWR831372AN99.002, LA9912WR831372.003, and LAWR831372AN99.001).

4.2 CRITERIA

This AMR complies with the DOE interim guidance (Dyer 1999). Subparts of the interim guidance that apply to this analysis are those pertaining to the characterization of the Yucca Mountain site (Subpart B, Section 15), the compilation of information regarding geochemistry and mineral stability of the site in support of the License Application (Subpart B, Section 21(c)(1)(ii)) and the definition of geochemical parameters and conceptual models used in the performance assessment (Subpart E, Section 114(a)).

The criteria used for evaluating, accepting, or rejecting data followed the procedures as outlined in Chapter II and Appendices B, C, and D in Grenthe et al. (1992, pp. 9-28, 683-715).

4.3 CODES AND STANDARDS

No specific codes and standards have been identified as applying to this work activity.

5. ASSUMPTIONS

No assumptions are made in this AMR.

6. ANALYSIS/MODEL

The solubility of most radionuclides depends on the solution speciation and on the solubility of the controlling radionuclide-bearing solid phase. Bulk solubility experiments can provide empirical data for a given set of chemical conditions. Since only few empirical data sets can be collected (most empirical solubility experiments are long-term experiments), only a limited amount of data can be collected over a limited range of conditions. Thus, the solubility and speciation behavior must be modeled for general conditions and potential variances based on a thermodynamic database for relevant radionuclide compounds. The model can be tested against the empirical bulk solubility data prior to performance assessment. Once the developed model and thermodynamic database are self-consistent and match well against known solubilities, the model can be used over a continuous distribution range of potential groundwater compositions to generate weighted solubility distributions for use in Total System Performance Assessment (TSPA).

The radionuclide species most relevant to natural waters of low to moderate ionic strength are the aqueous ions and oxide, hydroxide, and carbonate compounds in solution and solid state (Silva and Nitsche 1995, pp. 382, 384). Chloride, and nitrate solid phases and aqueous complexes are not important in low ionic strength waters (Spahiu and Puigdomenech 1998, p. 418). Thermodynamic data were compiled for the aqueous ions, oxides, hydroxides, fluorides, and carbonates, and calculated the Gibbs free energy of formation, $\Delta_f G^o_{298}$, from data corrected for ionic strength at standard conditions. Only data published in peer-reviewed journals are used for technical acceptance and accuracy evaluation. The specific ion-interaction theory (Grenthe et al. 1992, pp. 683-698) was used to correct ion activity coefficients for ionic strength since no Pitzer parameters were available for the relevant radionuclide species.

Thermodynamic data were compiled for the solution and solid states of Np, Pu, and Tc compounds. The Gibbs free energy of formation, $\Delta_f G^o_{298}$, was calculated from data corrected for ionic strength at standard conditions. The recommended data sets are summarized in Tables 2, 3, and 4. Only data published in peer-reviewed journals are used.

For the reaction of metal ions (M) with a ligand (L),

$$mM^{x+} + nL^{y-} \rightleftharpoons (M_mL_n)^{mx-ny} \qquad \text{(Eq. 1)}$$

the stepwise formation constant was used, $\beta_{l'}$ (or β_m), given by

$$\beta_{l'} = [ML_{l'}] / ([ML_{l'-1}][L]) \qquad \text{(Eq. 2)}$$

and the overall formation constant $\beta_{kl'm}$, defined by

$$\beta_{kl'm} = [ML_{l'}] / ([M][L]^{l'}) \qquad \text{(Eq. 3)}$$

The subscripts of β_{klm} define the number of the central metal ions (k) and the hydroxo (l') and (m) ligands. Because there is typically little information for polynuclear species, k equals 1 throughout this evaluation. Solubility products, K_s, are used for the reaction:

$$M_mL_n + n\,H^+ \rightleftharpoons mM^{x+} + nHL^{1-y}, \qquad \text{(Eq. 4)}$$

and K_{sp} refers to the dissolution reaction

$$M_mL_n \rightleftharpoons mM^{x+} + nL^{y-}. \qquad \text{(Eq. 5)}$$

Superscript zero (^{o}) indicates the thermodynamic standard state, which is defined as the stable state at 1 bar pressure and the temperature under consideration. In this paper, 25°C is considered as the standard-state temperature. The most fundamental relationships used for the calculations of the Gibbs free energy of a reaction from solubility products and formation constants are (Latimer 1952, pp. 8-9):

$$\Delta_fG^o_{298} = \Delta_fH^o_{298} - T\Delta S^o_{298} \qquad \text{(Eq. 6)}$$

and

$$\Delta_fG^o_{298} = -RT \bullet \ln K_{298}. \qquad \text{(Eq. 7)}$$

with R, the gas constant (8.3144 J/(Mol•K)) (Weast 1985) and T is the absolute temperature in K. Most thermodynamic data and free-energy data are reported for 25°C.

Table 2. Recommended Thermodynamic Data for Np(IV,V) Compounds

Reaction	**$\Delta_f G^\circ_{298}$ (kJ mol^{-1})**
NpO_2^+	-907.90±5.77
Np^{4+}	-491.10±9.49
$NpO_2^+ + 3\ H^+ = Np^{4+} + 0.25\ O_2 + 1.5\ H_2O$	---
$NpO_2^+ + OH^- =$ **$NpO_2OH(aq)$**	-1080.61±5.88
$NpO_2^+ + 2\ OH^- =$ **$NpO_2(OH)_2^-$**	-1247.33±5.84
$NpO_2^+ + 2\ OH^- + CO_3^{2-} =$ **$NpO_2(OH)_2(CO_3)^{3-}$**	-1791.01±7.36
$NpO_2^+ + OH^- + 2\ CO_3^{2-} =$ **$NpO_2(OH)(CO_3)_2^{4-}$**	-2155.41±6.71
$NpO_2^+ + CO_3^{2-} =$ **$NpO_2CO_3^-$**	-1463.34±5.84
$NpO_2^+ + 2\ CO_3^{2-} =$ **$NpO_2(CO_3)_2^{3-}$**	-2001.25±5.92
$NpO_2^+ + 3\ CO_3^{2-} =$ **$NpO_2(CO_3)_3^{5-}$**	-2523.46±5.80
$NpO_2^+ + F^- =$ **$NpO_2F(aq)$**	-1197.07±8.55
$NaNpO_2CO_3 \bullet 3.5H_2O(s)$ $= Na^+ + NpO_2^+ + CO_3^{2-} + 3.5H_2O$	-2591.02±5.86
$Na_3NpO_2(CO_3)_2(s)$ $= 3\ Na^+ + NpO_2^+ + 2\ CO_3^{2-}$	-2831.01±5.94
$KNpO_2CO_3(s)$ $= K^+ + NpO_2^+ + CO_3^{2-}$	-1795.97±5.80
$K_3NpO_2(CO_3)_2(s)$ $= 3\ K^+ + NpO_2^+ + 2\ CO_3^{2-}$	-2902.00±5.81
$NpO_2(OH)\ (am)$ $= NpO_2^+ + OH^-$	-1115.26±5.79
$NpO_2(OH)\ (cr)$ $= NpO_2^+ + OH^-$	-1119.31±5.84
$Np_2O_5\ (s)$ $+ 2\ H^+ = 2\ NpO_2^+ + H_2O$	-2023.30±12.41
$Np^{4+} + H_2O =$ **$NpOH^{3+}$** $+ H^+$	-726.00±10.30
$Np^{4+} + 4\ H_2O =$ **$Np(OH)_4(aq)$** $+ 4\ H^+$	-1382.74±11.08
$Np(OH)_4(am)$ $+ 4\ H^+ = Np^{4+} + 4\ H_2O$	-1431.26±9.65
$NpO_2(s)$ $+ 4\ H^+ = Np^{4+} + 2\ H_2O$	-1021.80±2.5
$Np^{4+} + 5\ CO_3^{2-} =$ **$Np(CO_3)_5^{6-}$**	-3324.64±11.26
$Np^{4+} + 4\ CO_3^{2-} =$ **$Np(CO_3)_4^{4-}$**	-2803.14±11.36
$Np^{4+} + F^- =$ **NpF^{3+}**	-823.94±9.55
$Np^{4+} + 2\ F^- =$ **NpF_2^{2+}**	-1144.10±9.74

DTN: LAWR831372AN99.002

NOTES: $\Delta_f G^\circ_{298}$ values for environmentally relevant Np(V) and Np(IV) compounds are bolded (DTN: LAWR831372AN99.002). The data are discussed in detail in the Runde (1999a) letter report.

The errors in Runde (1999a) have been corrected in this table.

Table 3. Recommended Thermodynamic Data for Pu(III,IV,V,VI) Compounds

Reaction	**$\Delta_f G^\circ_{298}$ (kJ mol^{-1})**
PuO_2^{2+}	-767.0±6.6
PuO_2^{+}	-857.5±6.7
Pu^{4+}	-477.8±3.4
Pu^{3+}	-578.6±3.3
$PuO_2^{2+} + OH^- = PuO_2OH^+$	-970.5±6.6
$PuO_2^{2+} + 2\ OH^- = PuO_2(OH)_2(aq)$	-1162±6.6
$PuO_2^{2+} + CO_3^{2-} = PuO_2CO_3\ (aq)$	-1348.6±6.8
$PuO_2^{2+} + 2\ CO_3^{2-} = PuO_2(CO_3)_2^{2-}$	-1906.9±6.8
$PuO_2^{2+} + 3\ CO_3^{2-} = PuO_2(CO_3)_3^{4-}$	-2449.1±6.8
$PuO_2^{2+} + F^- = PuO_2F^+$	-1075.1±6.8
$PuO_2^{2+} + 2\ F^- = PuO_2F_2(aq)$	-1371.6±7.3
$PuO_2^{+} + H_2O = PuO_2OH(aq) + H^+$	-1039.1±6.7
$PuO_2^{+} + CO_3^{2-} = PuO_2CO_3^-$	-1414.7±6.7
$PuO_2^{+} + 2\ CO_3^{2-} = PuO_2(CO_3)_2^{3-}$	-1951.2±8.8
$PuO_2^{+} + 3\ CO_3^{2-} = PuO_2(CO_3)_3^{5-}$	-2469.4±7.8
$Pu^{4+} + H_2O = PuOH^{3+} + H^+$	-712.2±4.1
$Pu^{4+} + 4\ H_2O = Pu(OH)_4 + 4\ H^+$	-1375±7
$Pu^{4+} + 5\ CO_3^{2-} = Pu(CO_3)_5^{6-}$	-3109.7±3.5
$Pu^{4+} + F^- = PuF^{3+}$	-809.9±6.5
$Pu^{4+} + 2\ F^- = PuF_2^{2+}$	-1131.2±6.7
$Pu^{3+} + H_2O = PuOH^{2+} + H^+$	-775.8±4.4
$Pu(OH)_3(s) = Pu^{3+} + 3\ OH^-$	-1200.1±5.7
$PuO_2 \bullet 2H_2O = Pu^{4+} + 4\ OH^-$ or $Pu(OH)_4(am) = Pu^{4+} + 4\ OH^-$	-1432±17
PuO_2© $+ 2\ H_2O = Pu^{4+} + 4\ OH^-$	-976.2±3.6
$PuO_2(OH)_2(s) = PuO_2^{2+} + 2\ OH^-$	-1211.2±9.1
$PuO_2(OH)(am) = PuO_2^{+} + OH^-$	-1065.6±7.5
$PuO_2CO_3(s) = PuO_2^{2+} + CO_3^{2-}$	1376.1±6.8

DTN: LA9912WR831372.003

NOTES: **$\Delta_f G^\circ_{298}$ values for environmentally relevant Pu(III,IV,V,VI) compounds are bolded (DTN: LA9912WR831372.003). The data are discussed in detail in the Runde (1999b) letter report.**

The errors in Runde (1999b) have been corrected in this table.

Table 4. Recommended Thermodynamic Data for Tc(IV) and Tc(VII) Compounds

Reaction or Species	$\Delta_f G°_{298}$ (kJ mol^{-1})
TcO_4^-	-637.2±7.6
$Tc(s) + 1.75\ O_2(aq) + 0.5\ H_2O = TcO_4^- + H^+$	0
$Tc^{3+} + O_2(aq) + 2\ H_2O = TcO_4^- + 4\ H^+$	92.4±10.5
$TcO^{2+} + 0.75\ O_2(aq) + 1.5\ H_2O = TcO_4^- + 3\ H^+$	-114.0±10.5
$TcO_4^{2-} + H^+ + 0.25\ O_2(aq) = 0.5\ H_2O + TcO_4^-$	-578.3±10.0
$TcO_4^{3-} + 2\ H^+ + 0.5\ O_2(aq) = 1.0\ H_2O + TcO_4^-$	-521.4±11.2
$HTcO_4(aq) = TcO_4^- + H^+$	-637.1
$(TcO(OH)_2)_2(aq) + 4\ H^+ = 2\ TcO^{2+} + 4\ H_2O$	-1172.2 ±14.2
$H_2TcO_4(aq) = TcO_4^{2-} + 2\ H^+$	-629.7±12.1
$HTcO_4^- = TcO_4^{2-} + H^+$	-628.0±10.5
$TcO(OH)_2(aq) + 2\ H^+ = TcO^{2+} + 2\ H_2O$	-567.5±7.1
$TcO(OH)^+ + H^+ = TcO^{2+} + H_2O$	-344.7±10.5
$TcO(OH)_3^- + H^+ = TcO(OH)_2(aq) + H_2O$	-742.52±7.10
$Tc(OH)_2CO_3(aq) = TcO(OH)_2(aq) + CO_2(g)$	-667.91±7.20
$Tc(OH)_3CO_3^- + H^+ = TcO(OH)_2(aq+)\ CO_2(g) + H_2O$	-857.95±7.20
$HTcO_4(s) = TcO_4^- + H^+$	-603.2±10.5
$KTcO_4(s) = TcO_4^- + K^+$	-932.7±7.6
$NaTcO_4(s) = TcO_4^- + Na^+$	-890.4±10.1
$CsTcO_4(s) = TcO_4^- + Cs^+$	-949.8±9.8
$Tc(OH)_2(s) + 3\ H^+ + 0.25\ O_2(aq) = Tc^{3+} + 2.5\ H_2O$	-460.3±3.8
$Tc(OH)_3(s) + 3\ H^+ = Tc^{3+} + 3\ H_2O$	-656.6±3.8
$Tc_2O_7(s) + H_2O = 2\ TcO_4^- + 2\ H^+$	-943.2±15.0
$Tc_3O_4(s) + 9\ H^+ + 0.25\ O_2(aq) = 3\ Tc^{3+} + 4.5\ H_2O$	-861.4±3.8
$Tc_4O_7(s) + 10\ H^+ = 2\ Tc^{3+} + 2\ TcO^{2+} + 5\ H_2O$	-1278.4±21.0
$TcO_2 \bullet 2H_2O(am) + 2\ H^+ = TcO^{2+} + 3\ H_2O$	-849.7±7.0
$TcOH(s) + 3\ H^+ + 0.5\ O_2(aq) = Tc^{3+} + 2\ H_2O$	-233.4±3.8
$TcS_2(s) + H_2O = TcO^{2+} + 2\ HS^-$	-229
$TcS_3(s) + 4\ H_2O = TcO_4^{2-} + 3\ HS^- + 5\ H^+$	-276
$Tc_2S_7(s) + 8\ H_2O = 2\ TcO_4^- + 7\ HS^- + 9\ H^+$	-594
$TcO_2(cr)$	-404±8

DTN: LAWR831372AN99.001

NOTES: $\Delta_f G°_{298}$ values for Tc(IV,VII) compounds are bolded (DTN: LAWR831372AN99.001). The data are discussed in detail in the Runde letter report (1999c).

6.1 EMPIRICAL SOLUBILITY DATA OF NEPTUNIUM AND PLUTONIUM IN YUCCA MOUNTAIN WATERS

Neptunium and plutonium are two of the radionuclides of concern in long-term emplacement of nuclear waste (Dozol and Hageman 1993, p. 1083). The uranium-oxide matrix of spent nuclear fuel contains approximately 0.025 percent neptunium as NpO_2 (Bruton and Shaw 1988, p. 490).

The solubilities of neptunium, plutonium, and americium have been studied in J-13 groundwater from YM. Nitsche et al. (1993, pp. 3-4), and Nitsche et al. (1995, pp. 3-4) studied neptunium, plutonium, and americium solubilities in YM waters (J-13 and UE25 p#1) as a function of pH and temperature. However, the experiments were continually titrated to maintain the pH and produced solutions with ionic strengths too high to describe the low ionic strength of YM waters accurately. As a result of the significantly increased sodium concentrations in the experiments, metastable sodium neptunyl(V) carbonates and Np_2O_5 were formed simultaneously, impeding the proper determination of upper neptunium solubility limits and the meaningful thermodynamic interpretation of the obtained data. In addition, there are inconsistencies of about one order of magnitude in the series of reported plutonium solubility values. These early experiments did, however, point to the prime importance of neptunium and plutonium in YM TSPA (CRWMS M&O 1994; Wilson et al. 1994), both because of the relatively high solubility and low sorption behavior of neptunium and the potential simultaneous existence of multiple oxidation states and, therefore, complicated solubility behavior of plutonium.

6.1.1 Neptunium Solubility

The average neptunium solubility generally decreased with increasing pH (Efurd et al. 1998, pp. 3895-3896) following the known trend of neptunium solubilities up to approximately pH 8 in carbonate-containing media (Neck et al. 1994, p. 298; Runde et al. 1996, p. 2070), and up to approximately pH 12 in carbonate-free systems (Neck et al. 1992, p. 27). Results of the neptunium solubility experiments from both over- and under-saturation converge to approximately the same steady-state concentrations (Table 5). At the conditions of these experiments, speciation model calculations indicate NpO_2^+, $NpO_2(OH)$, and $NpO_2CO_3^-$ as the predominant species in solution (Efurd et al. 1998, p. 3896). Further increase in pH would result in increasing neptunium solubility due to the formation of higher complexed anionic neptunium species in solution. With increasing temperature, a slight decrease in solubility is observed at pH 7 and 8.5, while at pH 6 the neptunium solubility remains approximately constant. The soluble neptunium concentrations are similar at pH 7 and 8.5, while at pH 6 the solubility is about one to two orders higher depending on the temperature. At pH 8.5, the neptunium concentrations were observed to decrease in the first 250 days, followed by an increase in concentration for the 25°C and 90°C oversaturation experiments (all other oversaturation experiments either showed the expected decreasing or constant concentration trend throughout the 450 days of the equilibration). Because the solid phase was not investigated during these events, this trend at pH 8.5 cannot be explained conclusively at the present time.

The neptunium precipitates formed were dark greenish-brown in color. X-ray diffraction (XRD) data showed only a few broad Bragg reflections for neptunium solids formed at low temperature, while increased temperature induced sharper peaks at 90°C. The powder patterns obtained are generally consistent with the reported data for both Np_2O_5 and Np_3O_8, with some additional peaks, which do not correspond to these solids (Efurd et al. 1998, p. 3896). The formation of the mixed oxide Np_3O_8 is not likely, and in fact, the existence of a Np_3O_8 phase has been discounted (Efurd et al., 1998, p. 3896). The observed diffraction patterns do not match other reported neptunium solids, and the existence of a sodium neptunyl carbonate could be excluded. It should also be noted that the reported X-ray powder pattern of Np_2O_5 was obtained from solids produced by the reaction of Np(V) in molten lithium perchlorate at 260°C in the absence of water. In contrast, hydrated Np(V) oxide would be expected to form in aqueous solution experiments. Thus, through comparison with the literature for neptunium solids and hydrated U(VI) hydroxide, the principal lines in the XRD of the neptunium precipitates are assigned to $Np_2O_5 \bullet xH_2O$. While the additional peaks are probably caused by intercalated water molecules and the further separation of the neptunium oxide layers, the presence of amorphous Np(V) hydroxide by XRD cannot be excluded (Efurd et al. 1998, p. 3896).

Efurd et al. (1998, p. 3896) used the solubility data in J-13 groundwater to calculate the solubility product of $Np_2O_5 \bullet xH_2O$. At pH 8.5, hydrolysis and carbonate complexation reactions dominate the speciation in solution with a species distribution of 31 percent NpO_2^+, 11 percent NpO_2OH, and 58 percent $NpO_2CO_3^-$ (Efurd et al. 1998, p. 3896). Thus, to avoid the combined uncertainties of their formation constants and the non-steady-state behavior at pH 8.5, only the solubility data at pH 6 and 7 were used. At pH 6 and 7 and low total carbonate, Np(V) hydrolysis and carbonate complexation are minimized (Neck et al. 1992, p. 29; Neck et al. 1994, p. 298), and NpO_2^+ is the predominant solution species (100 percent and 94 percent, respectively). From the undersaturation dataset, a mean thermodynamic solubility product log $K^\circ_s = 5.2 \pm 0.8$ was obtained for Equation 8 (Efurd et al. 1998, p. 3896):

$$Np_2O_5 \bullet xH_2O + 2\,H^+ \rightleftharpoons 2\,NpO_2^+ + x{+}1H_2O \qquad \text{(Eq. 8)}$$

The derived value agrees well with log $K_s = 5.5 \pm 1.9$ (calculated from free energy of formation value of -8±11 kJ/mol reported by Merli and Fuger (1994, p. 121)). However, both values imply a significantly lower logarithmic-thermodynamic-solubility product from the value of 9.5±2.6 (Lemire 1984, p. 29) previously present in data0.com.V8.R6 (DTN: LA9912WR831372.004), thereby lowering the calculated neptunium solubility by several orders of magnitude. The solubility product derived for $Np_2O_5 \bullet xH_2O$ is used to conservatively describe the solubility of Np_2O_5 which, because it possesses fewer water molecules, should possess lower solubility.

Table 5. Averaged ^{237}Np Concentrations in mol L^{-1} in J-13 groundwater

		pH 6	pH 7	pH 8.5
25°C	Oversaturation	$(6.5 \pm 1.1) \times 10^{-4}$	$(3.1 \pm 0.2) \times 10^{-5}$	$(1.5 \pm 0.6) \times 10^{-5}$
	Undersaturation	$(6.5 \pm 1.0) \times 10^{-4}$	$(2.9 \pm 0.7) \times 10^{-5}$	$(1.5 \pm 0.3) \times 10^{-5}$
	[Lit.]	$(5.3 \pm 0.3) \times 10^{-3}$	$(1.3 \pm 0.2) \times 10^{-4}$	$(4.4 \pm 0.7) \times 10^{-5}$
60°C	Oversaturation	$(9.4 \pm 1.2) \times 10^{-4}$	$(1.6 \pm 0.6) \times 10^{-5}$	$(1.7 \pm 0.9) \times 10^{-5}$
	Undersaturation	–	–	–
	[Lit.]	$(6.4 \pm 0.4) \times 10^{-3}$	$(9.8 \pm 1.0) \times 10^{-4}$	$(1.0 \pm 0.1) \times 10^{-4}$
90°C	oversaturation	$(9.1 \pm 1.8) \times 10^{-4}$	$(8.6 \pm 2.3) \times 10^{-6}$	$(5.8 \pm 2.5) \times 10^{-6}$
	undersaturation	$(8.7 \pm 0.9) \times 10^{-4}$	$(9.3 \pm 1.9) \times 10^{-6}$	$(5.9 \pm 2.1) \times 10^{-6}$
	[Lit.]	$(1.2 \pm 0.1) \times 10^{-3}$	$(1.5 \pm 0.4) \times 10^{-4}$	$(8.9 \pm 0.4) \times 10^{-5}$

NOTES: Data are measured as a function of pH and temperature from oversaturation (after 450 days equilibration) and undersaturation (after 151 days equilibration) (Efurd et al. 1998, p. 3896) and compared with literature data (Nitsche et al. 1993, p. 3). Uncertainties are given as one standard deviation.

6.1.2 Plutonium Solubility

The plutonium solubility was studied only from oversaturation (Table 6) (Efurd et al. 1998, pp. 3896-3898). In general, plutonium is about three orders of magnitude less soluble than neptunium, and pH does not affect the soluble concentration as much as seen in the neptunium solubility studies (Figures 1 and 2). Increasing temperature decreases the plutonium solubility below 10^{-8} mol L^{-1}. The plutonium concentrations at 60°C and 90°C are pH independent, while at 25°C they show higher variability. Note that the solutions were filtered through 4.1-nm pore size filters, and the solubility data include the possible presence of small-sized plutonium colloids. Thus, the listed plutonium solubility data are conservative with respect to the real solid-liquid phase equilibria with soluble molecular species.

The plutonium precipitates were dark green in color, which is characteristic of Pu(IV) solid phases. Most of the observed XRD peaks were diffuse and broad, indicating the existence of a poorly crystalline solid phase (Efurd et al. 1998, p. 3897). However, temperature increases the crystallinity of precipitates, and the powder diffraction patterns obtained for the solid formed at 90°C have sharper Bragg reflections than observed for the low temperature solids. The pattern matched the data for PuO_2 (Efurd et al. 1998, p. 3897). However, this result does not exclude the potential presence of aged Pu(IV) polymer and/or amorphous $Pu(OH)_4$. Indeed, a rising absorption tail below 500 nm is observed in the diffuse reflectance spectrum of a precipitate formed at 90°C (Efurd et al. 1998, p. 3897) along with absorption peaks at 469, 510, 577, 610 (broad), and 735 nm, consistent with a Pu(IV) colloid precursor to $PuO_2(s)$. To investigate the potential presence of a carbonate solid, the aged Pu(IV) solid was dissolved in 3 M HCl (Efurd et al. 1998, p. 3897). While the solid's color intensified to bright green with contact of the acidic solution, the solid dissolved only partially. The addition of HCl did not result in CO_2 gas evolution as would be expected if the solid were a carbonate salt. Interestingly, besides the expected Pu(IV) absorption at 469 nm, a Pu(VI) absorption peak was observed at 830 nm. Because oxidation of Pu(IV) to Pu(VI) did not occur during the time frame of this dissolution experiment (Efurd et al. 1998, p. 3897), the observed Pu(VI) must have originated from the solid. Impurities of Pu(VI) in the solid may have formed radiolytically. In addition, the formation of a higher Pu oxidation state in PuO_2 is consistent with results from previous studies on the instability of PuO_2 in the presence of water vapor and the transformation to a mixed-valence Pu(IV)/(VI) oxide layer at the solid surface (Efurd et al. 1998, p. 3897). However, due to the instability of Pu(VI) towards reduction at low ionic strength and relatively low redox potential (Langmuir 1997, p. 529), no significant influence of Pu(VI) impurities in the solid on the Pu bulk solubility is expected. Plutonium hydroxides and/or plutonium colloids, aging toward $PuO_2 \cdot xH_2O$, are therefore interpreted to be the solubility-controlling solids in these experiments. The formation of these solid phases was also reported previously in plutonium solubility measurements in YM water (Nitsche 1987, p. 124; Nitsche et al. 1992, p. 29; 1993, p. 4; 1995, p. 4). Different crystallinities of the Pu(IV) colloidal material, possibly caused by different ionic strength or aging time, result in varying solubilities. A higher degree of amorphous material might be the reason for the higher plutonium solubility as reported previously by Nitsche et al. (1993, p. 4) (Table 6).

Table 6. Averaged $^{239/240}Pu$ Concentrations in mol L^{-1} in J-13 groundwater

		pH 6	pH 7	pH 8.5
25°C	oversaturation	(4.7±1.1) x 10^{-8}	(2.4±1.2) x 10^{-8}	(9.4±1.6) x 10^{-9}
	[Lit.]	(1.1±0.4) x 10^{-6}	(2.3±1.4) x 10^{-7}	(2.9±0.8) x 10^{-7}
60°C	oversaturation	(9.0±2.0) x 10^{-9}	(8.2±0.7) x 10^{-9}	(6.2±1.8) x 10^{-9}
	[Lit.]	(2.7±1.1) x 10^{-8}	(3.7±0.9) x 10^{-8}	(1.2±0.1) x 10^{-7}
90°C	oversaturation	(4.3±2.1) x 10^{-9}	(3.6±1.1) x 10^{-9}	(4.2±1.1) x 10^{-9}
	[Lit.]	(6.2±1.9) x 10^{-9}	(8.8±0.8) x 10^{-9}	(7.3±0.4) x 10^{-9}

NOTES: Data are given in mol L^{-1} as a function of pH and temperature as measured from oversaturation (after 400 days equilibration) (Efurd et al. 1998, p. 3897) in comparison with literature data (Nitsche et al. 1993, p. 4). Uncertainties are given as one standard deviation.

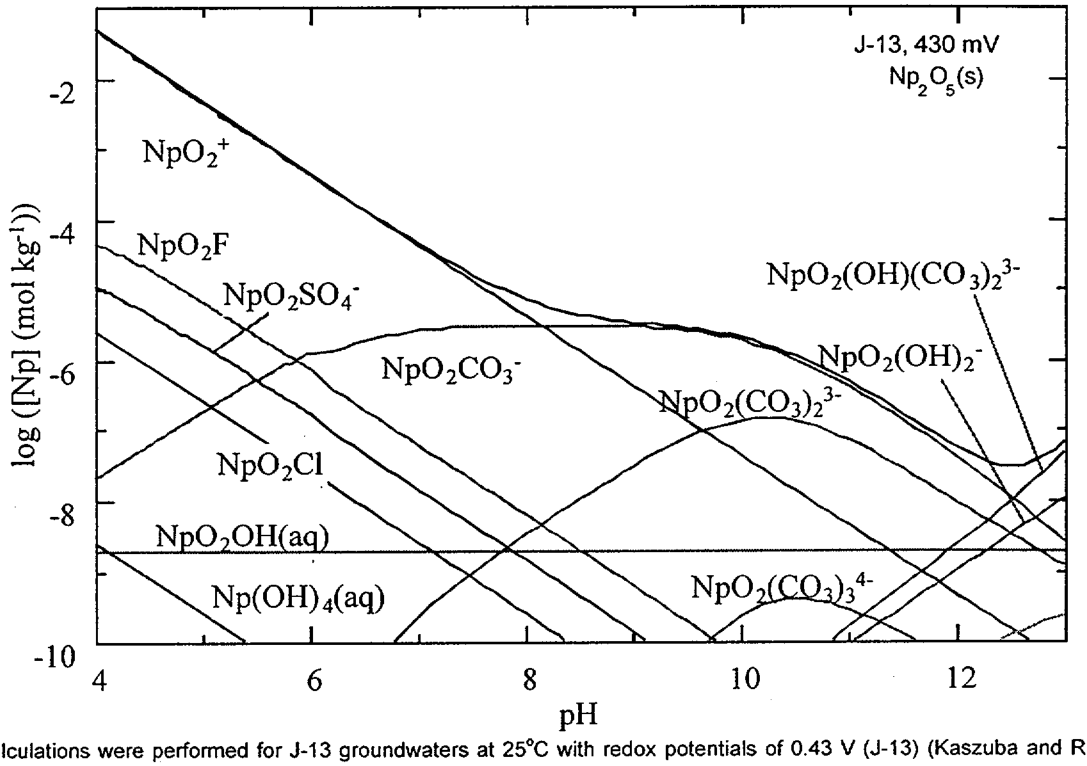
6.2 MODELING SOLUBILITY AND SPECIATION OF NEPTUNIUM AND PLUTONIUM IN J-13 GROUNDWATER

6.2.1 Stability and Solubility of Neptunium Solid Phases

Equilibrium thermodynamics predicts NpO_2 is the predominant stable solid for most Eh and pH conditions that span the stability range of J-13 waters (Efurd et al. 1998, p. 3898; Kaszuba and Runde 1999, p. 4430). To date, however, NpO_2 has not precipitated in solubility experiments conducted with natural waters (Efurd et al. 1998, p. 3898). Np(V) (Efurd et al. 1998, p. 3893) and amorphous Np(IV) solid phases (Rai et al. 1987, p. 36) precipitated instead. Thus, NpO_2 may be the thermodynamically stable neptunium solid phase for geologic, but not shorter, time scales. It is important, therefore, to understand the stability of the metastable phases because these solids will initially control soluble neptunium concentrations. In the absence of NpO_2, Np_2O_5, and $Np(OH)_4(am)$ are the stable solids in both groundwaters at oxidizing and reducing conditions, respectively.

Solubility curves calculated for the Np(V) solid phases, Np_2O_5, $NpO_2(OH)$ (aged), and $NaNpO_2CO_3{\bullet}3.5H_2O$, suggest that Np_2O_5, which typically either is hydrated or has adsorbed water, is the solubility-controlling phase in J-13 water (Figure 2; Kaszuba and Runde 1999, p. 4431; Efurd et al. 1998, p. 3896). Amorphous $NpO_2(OH)$ solid is less stable than its crystalline counterpart, which is a relationship consistent with fundamental thermodynamic principles. Efurd et al. (1998, p. 3898) first noted that the data of Lemire (1984, pp. 29-31) reversed this relationship. Despite the predominance of Np(V) carbonato complexes in aqueous solution of moderate to high pH (Figure 1), the Np(V) carbonate solid phase $NaNpO_2CO_3{\bullet}3.5H_2O$ is more soluble and, thus, less stable than Np_2O_5. The Np_2O_5 solubility curve displays a minimum at approximately pH 12 in contrast to the flat solubility curves modeled with the data of Lemire (1984, pp. 29-31) and Efurd et al. (1998, p. 3896). This minimum is due to the reduced importance of $NpO_2OH(aq)$ and the presence of mixed hydroxo carbonato species of Np(V) at high pH. The stability constant for $NpO_2OH(aq)$ is two orders of magnitude less than the value –8.9±0.1 reported by Lemire (1984, p. 30). Credible stability constants for mixed hydroxo carbonato species (letter report by Runde (1999a) and Supporting Information in (Kaszuba and Runde 1999) of Np(V) were not reported until recently (Kaszuba and Runde 1999, p. 4428). The decrease in soluble neptunium concentrations above pH 10 and the solubility minimum at pH 12 are important for effective nuclear-waste package design, such as including cement as an engineered barrier and the mixing of highly alkaline solutions with aquifers in release scenarios at nuclear-waste storage facilities.

An understanding of Np(V) alkali-carbonate solid-phase stability is important for evaluating neptunium geochemistry in waters more alkaline than J-13 groundwater. For the millimolar sodium and potassium content that characterizes J-13 groundwater, and many other natural waters, Np_2O_5 is the stable solid phase under oxidizing conditions and a wide range of pH (Figure 2) (Kaszuba and Runde 1999, pp. 4430-4431). Sodium concentrations must exceed approximately 0.05 molar at neutral pH to stabilize $NaNpO_2CO_3 \cdot 3.5H_2O$ (see experimental data of Efurd et al. 1998, p. 3898; Nitsche et al. 1993, pp. 2-3). At pH 10, a sodium content greater than 0.5 molar is required to stabilize $Na_3NpO_2(CO_3)_2$. High sodium concentrations characteristic of brines are required to stabilize $Na_3NpO_2(CO_3)_2$ at a more neutral pH (approximately 6 molar sodium at pH 8.5). In contrast to the sodium system, somewhat lower concentrations of potassium stabilize $KNpO_2CO_3$, but similar amounts of potassium stabilize $K_3NpO_2(CO_3)_2$ (approximately 1 molar potassium at pH 10 and 6 molar potassium at pH 8.5). Thus, Np(V) alkali-carbonate solid phases control soluble neptunium concentrations in waters containing molar quantities of sodium or potassium (Kaszuba and Runde 1999, p. 4431). Soluble neptunium concentrations in these alkaline waters are two to three orders of magnitude greater than waters in which Np_2O_5 is stable (Figure 2).



NOTE: Calculations were performed for J-13 groundwaters at 25°C with redox potentials of 0.43 V (J-13) (Kaszuba and Runde 1999, p. 4431).

Figure 1. Calculated Neptunium Species Concentrations in J-13 groundwater

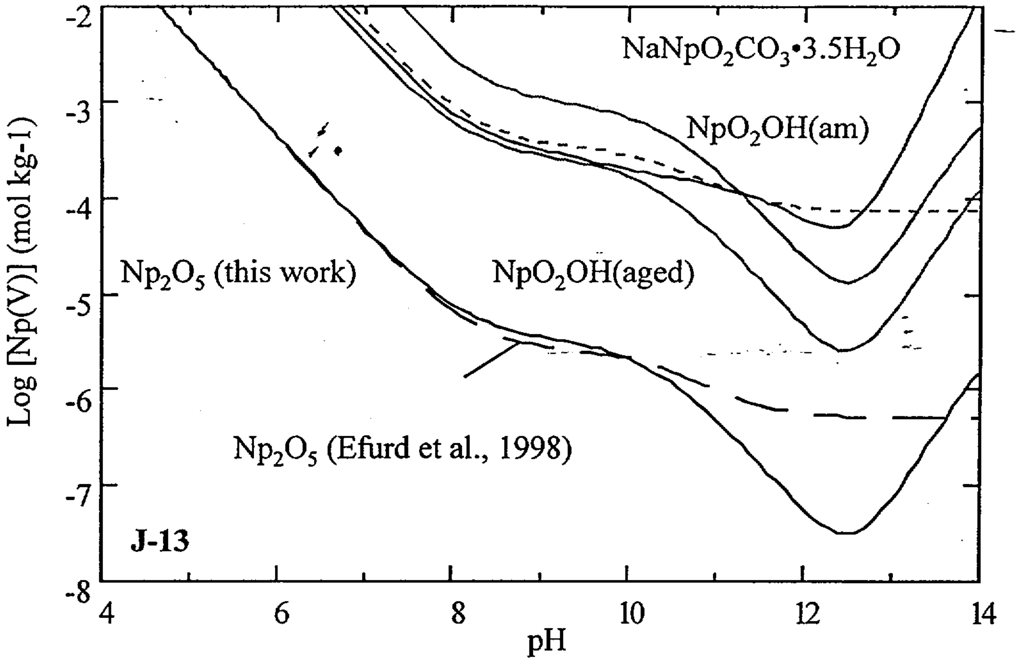
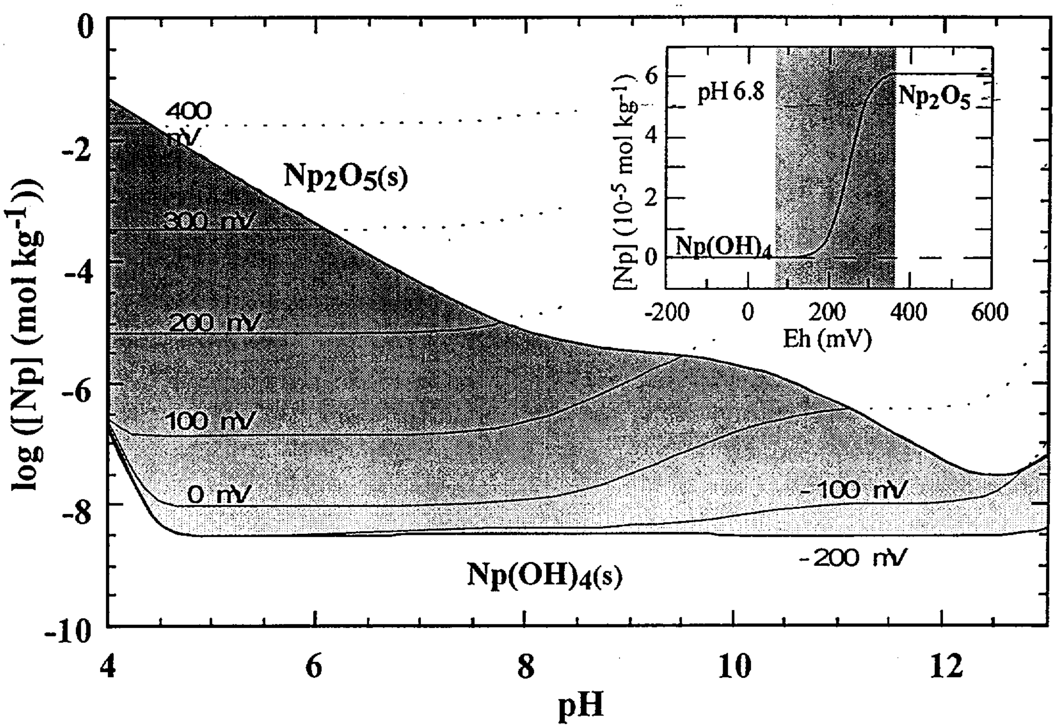


Figure 2. Calculated Solubility Curves for Np_2O_5, $NpO_2(OH)$ (aged), NpO_2OH(am), and $NaNpO_2CO_3{\cdot}3.5H_2O$

6.2.2 Effect of Redox Potential on Neptunium Solubility

Potential release scenarios of radionuclides from high-level nuclear waste (i.e., spent fuel rods) include radionuclide migration to oxidizing aquifers. These aquifers may change the valence state and, thus, the geochemical behavior of redox-sensitive radionuclides such as neptunium. In an aqueous system of neutral pH and low carbonate content, such as water from well J-13, a redox potential of 0.25 V stabilizes Np_2O_5 (Kaszuba and Runde 1999, p. 4432). The solubility product of Np_2O_5 limits soluble neptunium concentrations, even at redox potentials greater than 0.35 V. Under reducing conditions (below 0.12 V), $Np(OH)_4$(am) limits the neptunium concentration to approximately 10^{-8} molar. In the intermediate range of redox potential, between approximately 0.12 and 0.35 V, the soluble neptunium concentration varies between the solubility limits set by $Np(OH)_4$(am) and Np_2O_5 (Kaszuba and Runde 1999, p. 4432). Within this Eh range, the total Np(IV) concentration in solution remains constant at approximately 10^{-8} molar and is controlled by the solubility of $Np(OH)_4$(am). Increasing the redox potential to approximately 0.35 V favors the successive formation and increasing predominance of Np(V) in solution while maintaining Np(IV) in the solid state. A phase transformation to the Np(V)-bearing solid then occurs at 0.35 V. $Np(OH)_4$(am) is substantially less soluble than Np_2O_5 only at pH less than 11 (Kaszuba and Runde 1999, p. 4432). At higher pH, the solubility of neptunium is nearly independent of the redox potential and the neptunium oxidation state. Thus, at the pH (4 to 9) and redox potential (approximately -0.2 to +0.7 V) of most groundwater systems (Langmuir 1997, p. 410), soluble neptunium concentrations would be expected to depend on the redox potential of the aquifer. At lower Eh (<0.30 V), $Np(OH)_4$(am) is predicted to be the stable neptunium solid phase with a total Np(IV) concentration of approximately $10^{-8.5}$ molar as controlled by $Np(OH)_4$(am) solubility (Figure 3). However, Np_2O_5 is stable at 0.43 V, and its solubility product fixes the total soluble neptunium concentration at approximately $10^{-4.5}$ molar. Clearly, evaluation of radionuclide mobility in geochemical environments proximate to nuclear-waste repositories must account for soluble radionuclide concentrations that are controlled by the redox potential of the system as well as the solubility of the solid phases.



NOTE: Np_2O_5 and $Np(OH)_4$(am) were used as solubility limiting solids at 25°C (Kaszuba and Runde 1999, p. 4432). The inset designates regions of solubility control versus redox control (shaded area).

Figure 3. Calculated Neptunium Solubilities in J-13 Groundwater as a Function of Redox Potential

As described above, $Np_2O_5 \cdot xH_2O$ has been identified as the predominant solid phase formed in J-13 groundwater (Efurd et al. 1998, p. 3896). It was also reported to form together with an unidentified carbonate-containing solid phase at pH 5.9 and 7 at 90°C in the earlier study (Nitsche et al. 1993, pp. 42-43). Based on the summarized relevant thermodynamic data in data0.com.V8.R6, taken from (Lemire 1984, pp. 29-31; Lemire and Tremaine 1980, pp. 365 and 368), the more crystalline phase, $Np_2O_5 \cdot xH_2O$, is predicted to be undersaturated with respect to its amorphous hydration product NpO_2OH(am) (Efurd et al. 1998, p. 3898). This contradicts the Gibbs' principle of minimizing free energy with crystallinity and suggests incorrect data in the thermodynamic data file. Use of the solubility product, log $K_s = 5.2 \pm 0.8$, determined in Efurd et al. (1998, p 3898) predicts supersaturation of $Np_2O_5 \cdot xH_2O$ and lower solubility than NpO_2OH(am).

Neptunium(IV) solids also are calculated to be less soluble than NpO_2OH(am) with NpO_2 as the most stable and insoluble in the solid phase. This solid, NpO_2, has the potential to dominate the neptunium solubility under natural conditions (Langmuir 1997, pp. 527-528). However, Np(IV) was not observed to form in these solubility experiments with Np(V) as starting material, probably because of a kinetic barrier for the destruction of the trans–dioxo neptunyl bonds, $(O{=}Np{=}O)^+$, and relatively high redox potentials in laboratory experiments. Thus, the data presented in this study provide upper solubility boundaries for radionuclide-release scenario calculations. The calculated and experimentally determined solubility of neptunium and plutonium differ by several orders of magnitude, mainly due to different oxidation states of the actinide in the solid state. Pu(IV) oxide/hydroxide governs the plutonium solubility, while the higher soluble +V oxidation state determines the solubility of neptunium. Experimental measurements of Pu solubility lie within the broad solubility range calculated (Efurd et al. 1998, p. 3899) by using the solubility products for Pu(IV) hydroxide described in Efurd et al. (1998, p. 3898). In the case of the Pu(IV) system, it is hard to make accurate predictions due to the potential of the formation of the metastable Pu(IV) colloids and amorphous Pu(IV) hydroxide solids. Both compounds span a wide range of structural features, crystallinities, stabilities, and solubilities.

The formation of observed hydrated Pu(IV) solids also has implications for neptunium-solubility calculations in natural environments. While the observed Np(V) solid, $Np_2O_5{\cdot}xH_2O$, is calculated to be metastable with respect to reduction to Np(IV) oxide, the formation of crystalline anhydrous NpO_2 in an aqueous system is rather unlikely. As in the plutonium case where hydrated forms of plutonium oxide/hydroxide were found, hydrated forms of Np(IV) oxide would likely form if the kinetic barrier to reduce Np(V) solids could be overcome. While dissolved plutonium is dominated by $Pu(OH)_4(aq)$ even at Eh = 430 mV, the geochemical behavior of neptunium differs from that of plutonium because solution speciation changes from NpO_2^+ at Eh = 430 mV to predominantly $Np(OH)_4(aq)$ by Eh = 0 mV. The predicted solubility of $Np(OH)_4(s)$ at near neutral pH can range between approximately 10^{-5} M at 430 mV to a minimum of about 10^{-8} M at 0 mV. Note that similarly to $Pu(OH)_4(s)$, the range of K_{sp} for $Np(OH)_4(s)$ in the literature is huge, namely ±4 orders of magnitude. This range translates directly into an uncertainty in the neptunium concentration if Np(IV) solids are formed. The measured neptunium concentration for such solids under reducing conditions is in the 10^{-6} to 10^{-8} M range (Rai and Ryan 1985, p. 250). These values are consistent with dissolution and solubility studies of neptunium-containing fuel rods (Finn et al. 1995, p. 67; Wilson and Bruton 1990, p. 432), where the neptunium-oxidation state in the starting material is +4. Because infiltrating water into the repository is expected to be oxidizing (Langmuir 1997, p. 532; Yang et al. 1996, p. 42), the use of Np(V) as a starting material is the conservative approach to provide defensible upper solubility boundaries.

6.3 SOLUBILITY DISTRIBUTIONS OF RADIONUCLIDES OF SECONDARY PRIORITY

The solubilities of radionuclides of secondary or lower priority was also evaluated (A complex discussion of solid state and solution chemistry, as provided for neptunium, plutonium, and technetium, is not included and was not part of the work scope).

6.3.1 Protactinium

The main oxidation state for protactinium stable in aqueous solutions is the +5 state (Baes and Mesmer 1986, p. 170). Protactinium(IV) is unstable towards oxidation to Pa(V) under normal conditions (Baes and Mesmer 1986, p. 174). Ranges of protactinium solubilities can be obtained from the results of the Swedish Nuclear Power Inspectorate (Andersson 1988, pp. 2-3). The solubility distribution is expected to have a large variance. Berry et al. (1989, p. 341) reported apparent solubilities of protactinium for near-field conditions (pH 9-13) between 5.8×10^{-10} and 9×10^{-12} mol/L and 10^{-8} mol/L at pH 8.4. Protactinium(V) is unstable in solution above pH 1 due to irreversible hydrolytic polymerization and precipitation (Baes and Mesmer 1986, p. 174). Only very few thermodynamic data are available for protactinium compounds. The most relevant oxidation states are Pa(IV) and Pa(V). $PaOOH^{2+}$ and $PaO(OH)_2^+$ have been identified and are believed to be the hydrolysis products of Pa(V) in aqueous solution. Pa(IV) is unstable towards oxidation to Pa(V) except in the presence of strong acid (Baes and Mesmer 1986, p. 174). No quantitative measurements on thermodynamic data have been performed since the 1970s, and only estimated stabilities of the Pa species exist. Pa(V) is the most relevant valence state but is unstable in solution due to hydrolytic polymerization and precipitation. No solubility products of protactinium solids are known.

Potential Solubility-Controlling Compounds in Yucca Mountain Waters–The EQ3/6 data file data0.com.V8.R6 contains thermodynamic data for the following species (DTN: LA9912WR831372.004): Pa^{4+}, $Pa(OH)^{3+}$, $Pa(OH)_2^{2+}$, $Pa(OH)_3^+$, and the solids $PaCl_4$, and PaO_2. No data on the most common Pa oxidation state, Pa(V), exist in the data file.

Potential Solution Species in Yucca Mountain Waters–Pa(IV) hydroxo species and $PaOOH^{2+}$ and $PaO(OH)_2^+$.

Predicted Protactinium Solubility in Yucca Mountain Waters–As a consequence of the lack of thermodynamic data, no recommendations are made for any thermodynamic data for protactinium compounds relevant for YM waters. This conclusion agrees with that of the review by Fuger et al. (1992, pp. 29-31). However, due to the low Pa concentrations found experimentally in solubility and sorption studies and the high sorption coefficient of Pa of at least 10^2 ml/g (Berry et al. 1989, p. 347), a solubility range of 10^{-5} to 10^{-10} mol/L is expected.

6.3.2 Selenium

This element was withdrawn as a radionuclide for investigation from the Work Direction and Planning Document. Selenium is very soluble, and the source term needs to be determined experimentally. At this time a source term of 1 M is a conservative approximation. An overview on selenium species in solution can be found in Baes and Mesmer (1986, pp. 384-388).

6.3.3 Samarium and Curium

Samarium and curium are most stable in the +III oxidation state and are expected to behave like their analogues americium(III) and other trivalent lanthanides. It has been shown that the formation constants of the monocarbonate complexes of Eu(III), Cm(III), and Am(III) are identical (Kim et al. 1994, p. 339). However, Runde et al. (1992, p. 48) investigated the solubility products of $MOHCO_3$ and $M_2(CO_3)_3$,where M = Nd(III), Eu(III), and ^{241}Am(III), and found that the ^{241}Am(III) compound is about one order of magnitude more soluble than the analogous lanthanide compounds. The difference is explained by radiation damage and radiation effects on the crystallinity of the solid Am compounds. Application of the Am(III) data file to model Cm(III) solubilities is technically reasonable based on the present knowledge.

While the Sm(III) solution chemistry can be considered as identical to that of the analogue Am(III), the solubilities of Sm(III) compounds are expected to be lower. Thus, the Am(III) thermodynamic data file is recommended for modeling the Sm(III) complexation in solution. For the solubility products, very conservative values are recommended for Am(III) data. The thermodynamic solubility products for $SmOHCO_3$ and $Sm_2(CO_3)_3$ are expected to resemble those of the corresponding Eu(III) and Nd(III) compounds (Runde et al. 1992, p. 99) following the lanthanide(III) analogy.

Potential Solubility-Controlling Compounds in Yucca Mountain Waters (M=Sm, Cm)–$MOHCO_3$ and $M_2(CO_3)_3$ are favored due to the low ionic strength of the YM waters.

Potential Solution Species in Yucca Mountain Waters (M=Sm, Cm)–MOH^{2+} and $M(CO_3)_n^{3-2n}$ (n= 1-3) are expected to be the main contributors to the speciation in solution. Mixed hydroxo-carbonato complexes may form at neutral pH, but structural or thermodynamic data are lacking.

6.3.4 Molybdenum

Molybdenum exists in aqueous solution in the +3, +4, +5, and +6 oxidation states, but only the +6 oxidation state has a broad stability. The hydrolysis of Mo(VI) has been broadly studied and is reviewed in Baes and Mesmer (1986, pp. 253-257).

Potential Solubility-Controlling Compounds in Yucca Mountain Waters–Molybdate forms insoluble precipitates with most cations (except with the alkali metal cations), and MoO_3 is considered as the stable oxide. Naturally occurring Mo minerals include MoS_2, $PbMoO_4$, and $CaMO_4$ (Cotton and Wilkinson 1988, p. 805).

Potential Solution Species in Yucca Mountain Waters–At pH above 7, Mo(VI) occurs as the molybdate anion, MoO_4^{2-}, which easily polymerizes at Mo concentrations above 10^{-4} mol/L (Baes and Mesmer 1986, p. 253). The data0.com.V8.R6 data file contains thermodynamic data for MoO_4^{2-} as the only solution species and MoS_2 as the only molybdenum-bearing solid (DTN: LA9912WR831372.004).

6.3.5 Niobium

The only oxidation state for niobium that is stable in aqueous solutions is the +5 state (Brookins 1988, pp. 110-111).

Potential Solubility-Controlling Compounds in Yucca Mountain Waters–In pure water, compounds that could control niobium solubility include niobium pentoxide (Nb_2O_5) and polymeric hydrated pentoxides, also known as "niobic acid.. The compound Nb_2O_5 can exist in several crystalline forms including an α-phase and a γ-phase (Fairbrother, 1967, pp. 25-26). "Niobic acid", nominally $Nb(OH)_5(aq)$, is a noncrystalline hydrous oxide of niobium with variable water content. In YM waters, it is likely that niobium solubility would be controlled by a mixed oxide phase. This conclusion is based on the fact that niobium is generally found in nature as a component of mixed oxides (Cotton and Wilkinson 1988, p. 787). For example, one important ore of niobium is columbite $(Fe, Mn)(Nb, Ta)_2O_6$. Others include pyrochlore (Na, Ca,

$Ce)_2(Nb, Ti, Ta)_2(O, OH, F)_7$ and microlite $(Ca, Na)_2(Ta, Nb, Ti)_2(O, OH, F)_7$ (Roberts et al. 1974). Niobium is also found as a minor component in common oxide minerals such as rutile (titanium oxide), ilmenite (iron-titanium oxide) and hematite (ferric oxide).

Potential Solution Species in Yucca Mountain Waters–The aqueous chemistry of niobium is poorly known. This reflects the difficulty in working with insoluble substances that tend to form polymeric species in aqueous solutions (Fairbrother 1967, p. 35). Niobium appears to hydrolyze readily in solution. Babko et al. (1963, p. 960) reported constants for the following hydrolysis reactions (using log K_w = -14):

$$Nb(OH)_5(aq) + H^+ \Leftrightarrow Nb(OH)_4^+ + H_2O \qquad \text{Log } K \cong -0.6$$

$$Nb(OH)_5(aq) + H_2O \Leftrightarrow Nb(OH)_6^- + H^+ \qquad \text{Log } K \cong -7.4$$

The first reaction implies that the activities of $Nb(OH)_4^+$ and $Nb(OH)_5$ (aq) are equal at pH = 0.6 at low ionic strength. Similarly, the second reaction implies that the activities of $Nb(OH)_5$ (aq) and $Nb(OH)_6^-$ are equal at pH = 7.4. Baes and Mesmer (1986, p. 252) considered these reported constants "only very approximate". Data reported for the solubilities of niobium oxides and hydrous oxides show a wide range. Baes and Mesmer (1986, p. 960) reported the following data:

$$1/2Nb_2O_5(act) + 5/2H_2O \Leftrightarrow Nb(OH)_5(aq) \qquad \text{Log } K \cong -4.8$$

This datum implies a solubility for activated Nb_2O_5 on the order of 10^{-5} mol/L in pure water. Starik (1959, p. 80) reported that the logarithmic solubility product for $Nb(OH)_5$ is on the order of -71, which implies a niobium concentration of 10^{-10} mol/L at pH = 2 and 10^{-35} mol/L at pH = 7.

The fact that Babko et al. (1963, p. 958) precipitated active Nb_2O_5 (Baes and Mesmer 1986, p. 252) might explain part of the disparity in solubility estimates. Another possible explanation could lie in the strong tendency of niobium to form polynuclear species in solution. Starik (1959, pp. 80-81) reported that at pH > 2.0, the dissolution of niobic acid produced polymeric species in pure water even at concentrations as low as 10^{-11} mol/L. Further, there are several reports (Fairbrother 1967, p. 35; Jehng and Wachs 1991, p. 88) that point to the existence, in relatively concentrated alkaline aqueous solutions (5×10^{-4} to 0.1 M), of polynuclear species with formulas such as $Nb_6O_{19}(OH)_n^{(8+n)-}$, $Nb_6O_{19}^{8-}$, and $Nb_{12}O_{36}^{12-}$. As these solutions are diluted, hydrous niobium oxides are precipitated. Whether the polynuclear species are also present in dilute aqueous solutions at near-neutral pH has not been determined.

In discussing the results of a set of on the solubility of tantalum in pure water Fairbrother and Taylor (1956, p. 4953-4954) favor the interpretation that niobium exists in dilute solution as polynuclear species as well. Niobium and tantalum have similar aqueous chemistry. Fairbrother and Taylor (1956, p. 4948) precipitated "tantalic acid" by acidifying a solution of irradiated Na-K tantalate. The "tantalic acid" was well washed with de-ionized water and centrifuged. It was subsequently taken up in distilled water and shaken in a thermostat at 25°C for 15 days. Samples of the liquid phase were removed at 4, 7, 8, 9, 10, 11, and 15 days, centrifuged, and dried onto a planchet for counting of ^{182}Ta γ-activity. The results were quite unreproducible varying from 10^{-5} g Ta/100cc to "zero." The greater the centrifugal force and/or the time of centrifugation, the smaller the activity left on the planchet. This result suggested to Fairbrother and Taylor (1956, p. 4948) that those experiments in which ^{182}Ta activity was detected in solution reflected the presence of polymeric or colloidal tantalum. Fairbrother and Taylor (1956, pp. 4949 and 4952) reported that the solutions with polymeric species showed no visible cloudiness or turbidity.

Because Babko et al. (1963, p. 958) simply centrifuged their niobium solutions, it is likely these solutions contained polymeric niobium species. Therefore, their estimate of the solubility of Nb_2O_5(act) likely does not solely reflect monomeric species as required by the equations above. Complexation of niobium by other inorganic ligands in aqueous solutions with compositions such as the groundwaters in YM appears unlikely based on available data. Niobium is known to be solubilized by various organic acids, such as tartaric acid and citric acid, at sufficiently high concentrations but not in presence of malonic, succinic, or adipic acids (Fairbrother 1967, p. 51). Such concentrations are not anticipated in the near-field of the proposed repository in YM.

Equilibrium Modeling of Solubility–Because thermodynamic data are not available for the pertinent aqueous niobium species, modeling of the equilibrium solubility of niobium compounds in Yucca Mountain waters is not possible at this time.

Predicted Niobium Solubility in Yucca Mountain Waters–Based on published information, the solubility of hydrous niobium oxides may be as high as 10^{-5} mol/L (Babko et al. 1963, p. 958) or less than 10^{-11} mol/L (Starik 1959, p. 80) in pure water. The experiments of Fairbrother and Taylor (1956, p. 4947) suggest the "solubility" data reported by Babko et al. (1963, pp. 958-959) for niobium hydroxide reflects polymeric species. Further, the fact that pore waters and ground-waters in YM contain millimolar concentrations of alkali and alkaline earth cations supports the possibility that complex oxides of niobium could control niobium solubility to levels lower than those estimated for pure water solutions. Given these constraints, the solubility of niobium compounds in YM waters is estimated to be within the following range: 10^{-7} to 10^{-15} mol/L. The first value represents the solubility datum of Babko et al (1963, p. 958) with a correction for the fact that these investigators used activated niobium oxide. This value would imply the presence of polymeric or colloidal niobium species. The second value represents the solubility for niobium hydroxide at pH = 9 using the data published by Starik (1959, pp. 80-81) and assuming monomeric niobium species in solution.

6.3.6 Nickel

The only oxidation state for nickel that is stable in aquous solutions is the +2 state (Brookins 1988, p. 68).

Potential Solubility-Controlling Nickel Compounds in Yucca Mountain Waters–Nickel compounds that could precipitate from YM waters include NiO, $Ni(OH)_2$, $NiCO_3$, Ni_2SiO_4, and similar compounds which exist in data0.com.R2 (DTN: MO9911SPATHD62.002). Nickel concentrations in groundwater could also be controlled by other phases in which nickel is a minor component of a solid solution with other components. Such a solid solution could control the concentration of nickel in solution at a level lower than the solubility of pure nickel phases.

Potential Nickel Species in Yucca Mountain Waters–The EQ3/6 data file data0.com.R2 contains thermodynamic data for the following species (DTN: MO9911SPATHD62.002): Ni^{++}, $Ni(CH_3COO)_2(aq)$, $Ni(CH_3OO)_3^-$, $Ni(NH_3)_2^{++}$, $Ni(NH_3)_6^{++}$, $Ni(NO_3)_2(aq)$, $Ni(OH)_2(aq)$, $Ni(OH)_3^-$, Ni_2OH^{+++}, $Ni_4(OH)_4^{++++}$, $NiBr^+$, $NiCH_3COO^+$, $NiHP_2O_7^-$, $NiNO_3^+$, $NiP_2O_7^{--}$, $NiSO_4(aq)$, $NiSeO_4(aq)$.

EQ3/6 Equilibrium Modeling of Nickel Solubility–The EQ3/6 software package was used to calculate the concentrations at which the solid nickel phases in data0.com.R2 would be saturated in representative oxidizing waters from the site (DTN: MO9911SPATHD62.002). The temperature used in these calculations was 35°C to represent the ambient conditions. Bunsenite (NiO) (Roberts et al. 1974) is the most soluble of the pure phases and was used to limit calculated Ni levels. Note though that the pH 6 and 7 calculations required that the charge-balancing feature of EQ3 be cut off. As a result, the numbers are approximate and probably useful in only an order of magnitude sense. The calculations are in DTN: SN0003T0811199.007.

Table 7. Solid Ni Phase Solubility in J-13 groundwater (Moles-Ni/L @ 35°C)

Solid Phase	pH 6.0	pH 7.0	pH 8.0	pH 9.0
Bunsenite (NiO)	3.1	0.016	1.0×10^{-4}	1.4×10^{-6}

Predicted Nickel Solubility in Yucca Mountain Waters–Based on the equilibrium solubility calculations presented above, the solubility-limited nickel concentrations in YM waters are expected to be 3.1 to 1.4×10^{-6} moles-Ni/L.

6.3.7 Radium

The only aqueous species likely to be significant in the environment are Ra^{2+} and $RaSO_4(aq)$ (Langmuir and Riese 1985, p. 1593).

Potential Solubility-Controlling Radium Compounds in Yucca Mountain Waters–The main radium compounds that could control the concentrations of radium in waters such as present at YM include $RaSO_4$ and $RaCO_3$ (Langmuir and Riese 1985, pp. 1598-1599). Thermodynamic data for $RaSO_4$ have been included in the data0.com.V8.R6 data file (DTN: LA9912WR831372.004). Langmuir and Riese (1985, p. 1594) have published an estimate of log $K_{sp} = -8.3$ for $RaCO_3$. This estimate is not included in the data0.com.R2 data file (DTN: MO9911SPATHD62.002). Radium concentrations in groundwater could also be controlled by other phases (e.g., carbonates, sulfates) in which radium is a minor component of a solid solution with other components. Such a solid solution could control the concentration of radium in solution at a level lower than the solubility of pure radium phases (Langmuir and Riese 1985, p. 1599). However, in order for such solid-solution phases to control radium concentrations at levels below those expected for pure radium phases, the solid-solution phases (e.g., anglesite $PbSO_4$ or barite $BaSO_4$ - Roberts et al. 1974) must be present at the percent level.

Potential Radium Species in Yucca Mountain Waters–The EQ3/6 data file data0.com.R2 contains thermodynamic data for the following species (DTN: MO9911SPATHD62.002): Ra^{++}, $Ra(CH_3COO)_2(aq)$, $Ra(CH_3OO)^+$. Langmuir and Riese (1985, p. 1594) have estimated stability constants for the complexes $RaCO_3(aq)$ and $RaSO_4(aq)$. These estimated stability constants are not included in the data0.com.R2 data file (DTN: MO9911SPATHD62.002).

EQ3/6 Equilibrium Modeling of Radium Solubility–The EQ3/6 software package was used to calculate the concentrations at which the solid-radium phases in data0.com.R2 would be saturated in representative oxidizing waters from the site (DTN: MO9911SPATHD62.002). The temperature used was 35°C to represent the ambient conditions. The calculations are in DTN: SN0003T0811199.007.

Table 8. Radium solubility in J-13 groundwater (Moles-Ra/L @ 35°C)

Solubility Controlling Mineral	pH 6.0	pH 7.0	pH 8.0	pH 9.0
$RaSO_4$	1.2×10^{-6}	1.2×10^{-6}	1.1×10^{-6}	2.3×10^{-6}

Predicted Radium Solubility in Yucca Mountain Waters–Based on the equilibrium solubility calculations presented above, the solubility-limited concentrations of radium to be expected in YM waters, assuming control by $RaSO_4$, is expected to be 1.1×10^{-6} to 2.3×10^{-6} moles-Ra/L.

6.3.8 Thorium

The principal oxidation state for thorium is the +4 state (Cotton and Wilkinson 1988, p. 1000).

Potential Solubility-Controlling Thorium Compounds in Yucca Mountain Waters–In pure water, compounds that could control thorium solubility include: ThO_2 (thorianite) (Roberts et al. 1974) and thorium hydroxide, $Th(OH)_4$, or hydrated thorium oxide (Langmuir 1997, p. 532). Because YM waters also contain other metals, it is possible that thorium solubility could be controlled by other phases at concentrations that would be lower than would be the case if solubility were controlled by thorium oxide or thorium hydroxide. The most important of these other phases are the thorium silicates, thorite, and huttonite (Roberts et al. 1974). Thermodynamic data for thorite or huttonite are not included in the data0.com.R2 data file (DTN: MO9911SPATHD62.002). Thorium solubility could also be controlled by other phases in which thorium is a minor component of a solid solution with other components. Thermodynamic data are not available for thorium in these types of phases.

Potential Thorium Solution Species in Yucca Mountain Waters–Within groundwater compositions, thorium forms inorganic complexes with hydroxide and phosphate (Langmuir 1997, pp. 112-115). Thermodynamic data for the following Th(IV) hydrolysis products and complexes with inorganic ligands are in data0.com.R2 (DTN: MO9911SPATHD62.002):

$ThOH^{+++}$, ThF^{+++}, $ThHPO_4^{++}$, $Th(OH)_2^{++}$, ThF_2^{++}, $ThH_2PO_4^{+++}$, $Th(OH)_3^{+}$, ThF_3^{+}, $ThH_3PO_4^{++++}$, $Th(OH)_4(aq)$, $ThF_4(aq)$, $Th(HPO_4)_2(aq)$, $Th_2(OH)_2^{6+}$, $Th(H_2PO_4)_2^{++}$, $ThHPO_4^{++}$, $Th_4(OH)_8^{8+}$, $Th(HPO_4)_3^{--}$, $Th_6(OH)_{15}^{9+}$, $ThSO_4^{++}$, $ThCl^{+++}$, $Th(SO_4)_2(aq)$, $ThCl_2^{++}$, $Th(SO_4)_3^{-2}$, $ThCl_3^{+}$, $Th(SO_4)_4^{-4}$, $ThCl_4(aq)$.

The lack of thermodynamic data for thorium carbonate species in data0.com.R2 prevents a meaningful prediction of thorium solubilities here (DTN: MO9911SPATHD62.002).

6.3.9 Tin

The dominant oxidation state for tin in most groundwaters is the +4 state (Brookins 1988, p. 40). If the redox potential (i.e., Eh) of waters in any part of the flow path between the proposed repository and the accessible environment were sufficiently reducing (e.g., Eh < -200 mv and pH = 7.0), it is possible the +2 oxidation state for tin would be stable. However, such conditions are not currently anticipated in the unsaturated zone or in the shallow saturated zone between the proposed repository and the accessible environment.

Potential Solubility-Controlling Tin Compounds in Yucca Mountain Waters–In pure oxidizing water, compounds that could control tin solubility include: SnO_2 (cassiterite, Roberts et al. 1974) and tin hydroxide, $Sn(OH)_4$. Tin solubility could also be controlled by other phases in which tin is a minor component of a solid solution with other components. Such a solid solution could control the concentration of tin in solution at a level lower than SnO_2 solubility. Thermodynamic data are not available for tin in these types of phases. Therefore, the tin solubility constraints associated with such phases cannot be evaluated at this time.

Potential Tin Species in Yucca Mountain Waters–Data0.com.R2 contains thermodynamic data for the following hydrolysis products and complexes with inorganic ligands (DTN: MO9911SPATHD62.002):

$Sn(OH)_2^{++}$, SnF^+, $Sn(SO_4)_2(aq)$, $Sn(OH)_2(aq)$, $SnF_2(aq)$, SnF_3^-, $SnSO_4^{++}$, $Sn(OH)^{++}$, $Sn(OH)_3^+$, $Sn(OH)_3^-$, $Sn(OH)_4(aq)$, $SnCl^+$, $SnOH^+$, $SnCl_2(aq)$, $SnOH^{+++}$, $SnCl_3^-$.

EQ3/6 Equilibrium Modeling of Tin Solubility–The EQ3/6 software package was used to calculate the concentrations at which the solid tin phases in data0.com.R2 would be saturated in representative oxidizing waters from the site. Thermodynamic data were not available for $Sn(OH)_4$ in data0.com.R2 (DTN: MO9911SPATHD62.002). The temperature used was 35°C to represent the ambient conditions. The calculations are in DTN: SN0003T0811199.007.

Table 9. Tin Solubility in J-13 groundwater (Moles-Sn/L @ 35°C)

Solubility Controlling Mineral	pH 6.0	pH 7.0	pH 8.0	pH 9.0
Cassiterite	4.9×10^{-8}	4.9×10^{-8}	4.9×10^{-8}	4.8×10^{-8}

Predicted Tin Solubility in Yucca Mountain Waters–Based on the equilibrium solubility calculations presented above, the soluble tin concentrations in YM waters when controlled by cassiterite are expected to be 4.8×10^{-8} to 4.9×10^{-8} moles-Sn/L.

6.3.10 Zirconium

The characteristic oxidation state for zirconium is the +4 state (Baes and Mesmer 1986, p. 147).

Potential Zirconium Solubility-Controlling Compounds in Yucca Mountain Waters–In pure water, compounds that could control zirconium solubility include zirconium dioxide (ZrO_2) and hydrated, zirconium oxides (Cotton and Wilkinson 1988, pp. 780-782). The presence of one or the other of these compounds in YM waters would provide an upper bound on zirconium concentrations to be expected in solution. Because YM waters also contain other metals, it is possible zirconium solubility could be controlled by other phases at concentrations that would be lower than would be the case if solubility were controlled by zirconium oxide or hydrous zirconium oxide.

Potential Zirconium Solution Species in Yucca Mountain Waters–Zirconium aqueous solution chemistry is dominated by hydrolysis products and by complexes with the fluoride ion (Baes and Mesmer 1986, pp. 152-156). Complexes with sulfate are less important, and those with halides and nitrate are the least important. Data0.com.R2 contains thermodynamic data for hydrolysis products, fluoride complexes, and sulfate complexes (see below) (DTN: MO9911SPATHD62.002). Computer calculations reported below indicate that the hydrolysis products dominate in all water compositions anticipated in association with the proposed repository at YM. $Zr(OH)_5^-$ is the dominant aqueous zirconium species in dilute solutions at pH>7.0 (Baes and Mesmer 1986, p. 159). However, this species is not included in data0.com.R2 (DTN: MO9911SPATHD62.002). Further, the thermodynamic data for other hydrolysis species included in the data0.com.R2 data file are not in agreement with the data reported by Baes and Mesmer (1986, p. 158). For example, Baes and Mesmer (1986, p. 158) suggest log K = -9.7 for the reaction $Zr^{++++} + 4H_2O \Leftrightarrow Zr(OH)_4\ (aq) + 4\ H^+$ at 25°C. The data0.com.R2 (see below) lists a value of –log K = 1.47 for this reaction (DTN: MO9911SPATHD62.002).

EQ3/6 Equilibrium Modeling of Zirconium Solubility–The EQ3/6 software package was used to calculate the concentrations at which the solid zirconium phases in data0.com.R2 would be saturated in representative waters from the site (DTN: MO9911SPATHD62.002). Calculations were run at 25°C as there exist no data with which to extrapolate to higher temperatures. The calculations are in DTN: SN0003T0811199.007.

Table 10. Solubility in J-13 Groundwater (Moles-Zr/L @ 25°C)

Solubility Controlling Mineral	pH 6.0	pH 7.0	pH 8.0	pH 9.0
ZrO_2	6.8×10^{-10}	6.8×10^{-10}	6.8×10^{-10}	6.8×10^{-10}

The solubility-limited concentrations shown in these tables for J-13 groundwater compositions are quite similar, which suggests they are representative of the concentrations to be expected in YM waters if baddeleyite, ZrO_2, or zircon (Roberts et al. 1974) control Zr concentrations in solution.

Predicted Solubility in Yucca Mountain Waters–Based on the equilibrium solubility calculations presented above, the range of solubility-limited concentrations of zirconium waters, assuming control by zircon or baddeleyite, is expected to be 6.8×10^{-10} to 2.1×10^{-14} mol/L. If a mixed-oxide phase controlled zirconium solubility, then the predicted concentrations would be lower. On the other hand, if the phase that controls zirconium solubility in YM waters were to be a hydrated form of baddeleyite, then the solubility-limited concentrations could be one to two orders of magnitude higher. These equilibrium-solubility calculations are based on the data file included with the EQ3/6 software package. As noted above, some of the data for zirconium complexes included in the data file are suspect.

6.3.11 Lead

The most common oxidation state for lead in aqueous solutions is the +II state (Baes and Mesmer 1986, pp. 358-365). Pb(IV) is a strong oxidant.

Potential Lead Solubility-Controlling Compounds in Yucca Mountain Waters–Pb(II) oxides and sulfates are not readily soluble in water and are the most likely to determine the solubility in YM waters. The solubility of Pb(II) is generally controlled by lanarkite PbO, $Pb(OH)_2$, $PbCO_3$, and $Pb_3(CO_3)_2(OH)_2$ (Marani et al. 1995, p. 1087). Anglesite, $PbSO_4$ (Roberts et al. 1974) is a potential precipitate at higher sulfate concentrations. Because YM waters contain carbonate in the millimolar concentration range, the solid carbonate are most likely to control lead solubility. Baes and Mesmer (1986, p. 364) model the solubility of PbO under absence of carbonate with a minimum concentration of about 10^{-4} mol/L around pH 11 and molar Pb concentrations at neutral pH. Despite the thermodynamic stabilities reported for $Pb(OH)_2$ and $PbSO_4$, these two solids are difficult to form by precipitation at ambient temperature probably due to kinetic limitations (Marani et al. 1995, pp. 1091-1092). Consequently, the solubility constraints for Pb(II) are associated with $PbCO_3$, $Pb_3(CO_3)_2(OH)_2$, and $PbSO_4$.

Potential Lead Solution Species in Yucca Mountain Waters–Lead aqueous solution chemistry is modeled by hydrolysis products and by complexes with the carbonate ion (Marani et al. 1995, p. 1085). Data0.com.V8.R6 contains thermodynamic data for hydrolysis products, chloride complexes, carbonate complexes, and sulfate complexes (DTN: LA9912WR831372.004) (see below). Sulfate complexes are only important at higher chloride and sulfate concentrations, respectively, and carbonate and hydroxide complexes determine the solution speciation of lead. At low Pb(II) concentrations (below 10-5 mol/L), mononuclear Pb species are the dominant species, i.e. $Pb(OH)_n^{2-n}$ (n=1-3) and $Pb(CO_3)_m^{2-2m}$ (m=1,2). At higher Pb concentrations, Pb(II) may form polynuclear solution species, namely $Pb_3(OH)_4^{2+}$, $Pb_4(OH)_4^{4+}$, $Pb_6(OH)_8^{4+}$ (Baes and Mesmer 1986, p. 365). However, due to the low concentrations of lead observed in solubility and sorption studies only the monomeric complexes have been used for geochemical modeling (Carroll et al. 1998, p. 958). In waters with about millimolar carbonate concentrations, the monocarbonate complex, $PbCO_3(aq)$, tends to predominate in the pH range 6-9 (Hem 1976, p. 603) or pH 7-8 (Bilinski and Schindler 1982, p. 925).

Potential Lead Species in Yucca Mountain Waters–Data0.com.V8.R6 contains thermodynamic data for the following hydrolysis products and complexes with inorganic ligands in solution and solid state (DTN: LA9912WR831372.004):

Pb^{++}, $PbCO_3(aq)$, $Pb(CO_3)_2^{--}$, $PbOH^+$, $Pb(OH)_2(aq)$, $Pb(OH)_3^-$, $Pb(SO_4)_2^{--}$, $PbSO_4(aq)$, $PbCl^+$, $PbCl_2(aq)$, $PbCl_3$-, and the solids Pb, Pb_3O_4, $PbCO_3$, PbO, PbS, and $PbSO_4$.

The data file does not include the thermodynamics of the solid phase $Pb_3(CO_3)_2(OH)_2$ that has been identified to be of major importance in carbonate containing waters.

Predicted Lead Solubility in Yucca Mountain Waters–The Pb(II) solubility ranges in carbonate containing waters from about $8x10^{-7}$ to $5x10^{-9}$ mol/L in the pH range 8-11 (Marani et al. 1995, p. 1087). The upper value represents the solubility of $PbCO_3$ as the solubility-controlling solid phase at pH above 7 (Hem 1976, p. 603; Bilinski and Schindler 1982, p. 925).

7. CONCLUSIONS

The valence state of neptunium, one of the most important radionuclides of concern for long-term emplacement of nuclear waste, primarily defines its geochemical reactions and migration behavior. Evaluated were how solid-phase stability and redox potential interact and influence neptunium solubility and aqueous speciation in natural systems. Neptunium thermodynamic data for the most important valence states for natural waters, +IV and +V, were updated to correct data file inconsistencies. The most significant changes are the following (Kaszuba and Runde 1999, p. 4427):

1. $Np_2O_5(cr)$ is two orders of magnitude more stable than reported previously.
2. The importance of $NpO_2OH(aq)$ is reduced.
3. The formerly predominant Np(IV) species $Np(OH)_5^-$ is disregarded.
4. $NpO_2(OH)_2^-$ and mixed hydroxo carbonato species of Np(V) become important at high pH.

As a result, Np_2O_5 and $Np(OH)_4(am)$ are the anticipated solids in aquifers of low ionic strength, the neptunium solubility decreases in the pH range 10 to 12 and increases at pH above 12, and both redox potential and $Np(OH)_4(am)$ solubility product control the soluble neptunium concentrations at neutral pH and Eh between 0 and 350 mV. These relationships are important for effective nuclear-waste package design, such as including cement as an engineered barrier, and evaluating impacts of discharged solutions on natural waters in release scenarios at nuclear-waste storage facilities. Solubilities of neptunium and plutonium were studied in J-13 groundwater from the proposed YM nuclear-waste repository site, Nevada, at three different temperatures (25°C, 60°C, and 90°C) and pH values (6.0, 7.0, and 8.5). Experiments were performed from both over- and under-saturation at defined CO_2 partial pressures. A mean thermodynamic solubility product for $Np_2O_5 \bullet xH_2O$ of log $K°_{sp} = 5.2 \pm 0.8$ for the reaction $Np_2O_5 \bullet xH_2O + 2\ H^+ \rightleftharpoons 2\ NpO_2^+ + x{+}1H_2O$ at 25°C was calculated. Sparingly, soluble Pu(IV) solids, $PuO_2 \bullet xH_2O$, and/or amorphous Pu(IV) hydroxide/colloids control the solubility of plutonium in J-13 groundwater.

The uranium-oxide matrix of spent nuclear fuel contains approximately 0.025 percent neptunium as NpO_2 (Bruton and Shaw 1988, p. 490). In contrast, geochemical models used thermodynamic data for pure compounds to assess the environmental implications of neptunium. A more realistic conceptual model than precipitation of a pure neptunium solid may be the co-precipitation of neptunium and secondary phases within the waste package or the repository host rock. These phases may include ferric-oxide hydrates, phosphates, carbonate minerals, and secondary uranyl minerals (including uranyl-oxide hydrates and uranyl silicates). Both experimental and field evidence suggest that uranium co-precipitates with ferric-oxide hydrates

(Kaszuba and Runde 1999, p. 4432), whereas x-ray absorption spectroscopy suggests that Np(V) does not co-precipitate with goethite (Kaszuba and Runde 1999, p. 4432). Should neptunium co-precipitate with secondary phases, it will be the solubility of these secondary phases, not the solubility of pure neptunium solids, that determines the mobility of neptunium.

The solubilities of radionuclides of secondary importance at YM are estimated to be: Pa - 10^{-5} to 10^{-10} mol/L; Nb - 10^{-7} to 10^{-15} mol/L; Ni - 3.1 to 1.4 x 10^{-6} mol/L; Ra - 1.1 x 10^{-6} to 2.3 x 10^{-6} mol/L; Sn - 4.8 x 10^{-8} to 4.9 x 10^{-8} mol/L; Pb - 10^{-5} and 10^{-10} mol/L.

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DTN SN0003T0811199.007 was developed as output from computer program EQ3NR in this analysis. The input data for EQ3NR remain to be verified.

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