

OCRWM	MODEL COVER SHEET	1. QA: QA Page 1 of 146
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2. Type of Mathematical Model

Process Model
 Abstraction Model
 System Model

Describe Intended Use of Model

The Dissolved Concentration Limits Model is used in TSPA to constrain the maximum release of radioactive elements in the repository after postclosure.

3. Title

Dissolved Concentration Limits of Radioactive Elements

4. DI (including Rev. No. and Change No., if applicable):

ANL-WIS-MD-000010 REV 02

5. Total Attachments	6. Attachment Numbers - No. of Pages in Each
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13. Remarks

This is associated with task F0095.

Checked by Susan LeStrange, Paul Cloke, Jeff Fortner, Karhy Economy, John Frey, Chris Pflum.

Paul Cloke has contributed as an originator to several sections (6.3.1, 6.3.3, 6.4.4, 6.5.6, 6.5.7.1, 6.6.3.4.1, and 6.12). These sections were checked by others on the check team.

TER-02-0066 was resolved by providing adequate model validation in this revision.

2. Title Dissolved Concentration Limits of Radioactive Elements	
3. DI (including Rev. No. and Change No., if applicable): ANL-WIS-MD-000010 REV 02	
4. Revision / Change Number	5. Description of Revision/Change
00	Initial Issue
01	Revised the response surfaces of Np and Pu solubility limits; revised the distribution of Ni solubility. Addressed model validation deficiency (LVM0-00-D-119) found in REV 00. Removed text regarding Cm, Sm, Ni, Sn, Cl, Nb, and Zr solubility. This entire document was revised due to extensive changes.
01/01	Interim Change Notice (ICN) to remove a to be verified (TBV). Pages 14 and 15 are affected. Removed Unresolved Reference Number (URN) from DTN: MO0009THRMODYN.001 on page 64. The changes made are identified by vertical bars in the right margin of the text.
02	Extensive revision. Solubility limits for all the elements have been revised using the newly qualified thermodynamic database data0.ymp.R2.

EXECUTIVE SUMMARY

The purpose of this study is to evaluate dissolved concentration limits (also referred to as solubility limits) of radioactive elements under possible repository conditions, based on geochemical modeling calculations using geochemical modeling tools, thermodynamic databases, and measurements made in laboratory experiments and field work. The scope of this modeling activity is to predict dissolved concentrations or solubility limits for 14 radioactive elements (actinium, americium, carbon, cesium, iodine, lead, neptunium, plutonium, protactinium, radium, strontium, technetium, thorium, and uranium), which are important to calculated dose. Model outputs are mainly in the form of look-up tables plus one or more uncertainty terms. The rest are either in the form of distributions or single values. The results of this analysis are fundamental inputs for total system performance assessment to constrain the release of these elements from waste packages and the engineered barrier system.

Solubilities of plutonium, neptunium, uranium, americium, actinium, thorium, protactinium, lead, and radium have been re-evaluated using the newly updated thermodynamic database (Data0.ymp.R2). For all of the actinides, identical modeling approaches and consistent environmental conditions were used to develop solubility models in this revision. These models cover broad ranges of environmental conditions so that they are applicable to both waste packages and the invert. Uncertainties from thermodynamic data, water chemistry, temperature variation, activity coefficients, and selection of solubility controlling phase have been quantified or otherwise addressed. Moreover, a new blended plutonium solubility model has been developed in this revision, which gives a mean solubility that is three orders of magnitude lower than the plutonium solubility model used for the Total System Performance Assessment for the Site Recommendation. Two alternative neptunium solubility models have also been developed in this revision. The base-case models have been validated to the level of confidence required by their relative importance to the potential performance of the repository system. The plutonium and neptunium solubility models have been validated to a higher level of confidence than the rest.

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ACRONYMS AND ABBREVIATIONS

ANL	Argonne National Laboratory
ATM	approved testing material
BSC	Bechtel SAIC Company, LLC
CSNF	commercial spent nuclear fuel
$\Delta_f G^0$	Standard state Gibbs free energy of formation
$\Delta_f H^0$	Standard state enthalpy of formation
$\Delta_r G^0$	Standard state Gibbs free energy of reaction
$\Delta_r H^0$	Standard state enthalpy of reaction
DOE	U.S. Department of Energy
DTN	Data Tracking Number
F_c	concentrating factor
FEPs	features, events, and processes
LA	License Application
LANL	Los Alamos National Laboratory
NEA	Nuclear Energy Agency
PNNL	Pacific Northwest National Laboratory
QA	quality assurance
TBV	to be verified
TSPA	total system performance assessment
URN	Unresolved Reference Number

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1. PURPOSE

The purpose of this study is to evaluate dissolved concentration limits (also referred to as solubility limits) of radioactive elements under possible repository conditions, based on geochemical modeling calculations using geochemical modeling tools, thermodynamic databases, and measurements made in laboratory experiments and field work. This model report was prepared in accordance with *Technical Work Plan for Waste Form Degradation Modeling, Testing, and Analyses in Support of SR and LA* (BSC 2002a) and the governing procedure AP-SIII.10Q, *Models*.

Several deviations to the technical work plan are noted as follows:

1. Solubility models for uranium, thorium, americium, actinium, protactinium, radium, and lead were re-developed for the same chemical conditions and use the same modeling configurations and thermodynamic database as plutonium and neptunium solubility models, which were developed as planned in the technical work plan.
2. In order to make the solubility models developed in this report applicable to waste packages as planned, but also to the invert, broad ranges of conditions were considered in model development.
3. Solubility models were primarily presented in the form of look-up tables instead of the multivariable functions that were used for Site Recommendation.
4. An additional criterion for model validation will be added at the next modification of that Work Plan. This criterion is denoted as Criterion Eight: Has the model been validated by demonstrating that it is conservative?

The scope of this modeling activity is to predict dissolved concentrations or solubility limits as look-up tables, distributions, or single values for all radioactive elements transported outside breached waste packages identified as important to calculated dose by *Radionuclide Screening* (BSC 2002b). For the time period from 10^2 to 2×10^4 years with a 0.95 screening-product cutoff, 14 radioelements were identified: actinium, americium, carbon, cesium, iodine, lead, neptunium, plutonium, protactinium, radium, strontium, technetium, thorium, and uranium. The results of this analysis are fundamental inputs for total system performance assessment (TSPA).

The initial version, REV 00, of this document (CRWMS M&O 2000a) is the first systematic solubility evaluation based on detailed geochemical modeling. Results from that document were used for *Total System Performance Assessment for the Site Recommendation* (CRWMS M&O 2000b). As stated in REV 00, "revisions to solubility limits are expected as more is learned and understood about the repository conditions and as more data become available." The document was revised at the end of 2000 (CRWMS M&O 2001a) to address quality assurance (QA) issues raised as a result of a U.S. Department of Energy (DOE) QA audit conducted in July 2000, and the revision included consideration of solubility limits for neptunium and plutonium using the then just qualified thermodynamic database data0.ymp.R0. The document was updated again (BSC 2001a) to remove a TBV and a URN. This revision (REV 02) is planned for the TSPA-License Application (LA). The scope of this revision includes an update of this model report to new QA and model validation standards and re-evaluated solubilities of plutonium, neptunium,

uranium, americium, actinium, thorium, protactinium, and radium using the newly updated thermodynamic database Data0.ymp.R2 (MO0302SPATHDYN.000). Lead solubility has also been reevaluated. Alternative dissolved concentration models have also been documented in this revision.

2. QUALITY ASSURANCE

QA Program Applicability: Development of this model report has been determined to be subject to the Yucca Mountain Project's quality assurance program (BSC 2002a, Attachment I) because it will be used to support performance assessments. It does not affect any items on the Q-List.

Electronic Management of Data: The technical work plan contains the Process Control Evaluation used to evaluate the control of electronic management of data (BSC 2002a, Attachment III) during the modeling and documentation activities, and this evaluation determined that the methods in the implementing procedures are adequate. No deviations from these methods were performed.

3. USE OF SOFTWARE

The computer software used to carry out the calculations in this model is summarized in Table 3-1.

Table 3-1. Computer Software Used in this Model

Software Name	Version	Software Tracking Number (Qualification Status)	Description and Components Used	Input and Output Files ^a (Included in Attachment I)
EQ3/6	7.2b	LLNL:UCRL-MA-110662 (LSCR198) (Qualified on Windows 95 and HP-UX 10.20 B)	EQ3NR: a FORTRAN speciation-solubility code	input: *.3i output: *.3o
			EQPT: a data file preprocessor in FORTRAN	input: data0.* output: data1.*
GetEQData	1.0.1	10809-1.0.1-0 (Qualified on Windows NT 4.0 and Windows 2000)	A Microsoft Excel macro. It is used to post-process EQ3/6 output information.	input: *.3o output: *.xls
BuildEQ3.BAS	1.00	10365-1.00-00 (Qualified on Windows NT 4.0)	A QBASIC code used to generate EQ3 input files	input: *.bas output: *.3o
Microsoft Excel	97 SR-2	Commercial off-the-shelf software: Exempt in accordance with AP-SI.1Q, Section 2.1.	Used in this document for graphical representation and arithmetical manipulations	input: *.3o output: *.xls
Sigma Plot	4.0 & 8.0	Commercial off-the-shelf software: Exempt in accordance with AP-SI.1Q, Section 2.1.	Used in this document for graphical representation and arithmetical manipulations	*.jnb

NOTE: ^a Files are explained in more detail in Attachment II.

All applicable products were obtained from Software Configuration Management and have been verified appropriate for the application. The software products were run on standard personal computers and a Unix machine listed in Table 3-2.

Table 3-2. Computers Used

Computer Make	CPU #	Operating System	Software Used
Dell PowerEdge 2200	112378	Windows NT 4.0	BuildEQ.BAS, GetEQData, Microsoft Excel 97 SR-2, Sigma Plot
Dell Optiplex GX400	151295	Windows NT 4.0	BuildEQ.BAS, GetEQData, Microsoft Excel 97 SR-2
Dell Optiplex GX260	152392	Windows 2000	GetEQData, Microsoft Excel 97 SR-2, Sigma Plot
Dell Optiplex GX260	152383	Windows 2000	GetEQData, Microsoft Excel 97 SR-2
Hewlett-Packard workstation	112515	HP-UX 10.20 B	EQ3/6 V7.2b

NOTE: CPU = central processing unit

The EQ3/6 package consists of several components: EQ3NR, EQ6, EQPT, and EQLIB. EQ3NR is designed for analyzing water chemistry and solubility calculation. EQ6 is for reaction path calculation. EQPT is a database pre-processor, and EQLIB is the supporting library. Since no reaction-path calculation was performed in this analysis, EQ6 was not utilized. This software is appropriate for the application and has not been used outside the range of parameters for which it has been verified. Specifically, results for computed ionic strengths greater than 1 molal were rejected. See Section 6.3.3 for rationale.

No previously developed model is used in this analysis.

4. INPUTS

4.1 DATA AND PARAMETERS

4.1.1 Direct Inputs

Direct inputs used in this model report to develop solubility models are summarized in Table 4-1.

One important input for this study is the thermodynamic database used for EQ3NR calculations, as summarized in Table 4-1. This database is valid for temperatures up to 200°C and ionic strength up to 1 molal.

The water composition used as the base case, summarized in Table 4-1 with details given in Table 4-2, was intended to be generically representative of water present in the repository host rock. The composition chosen is J-13 well water, documented in a data qualification report (CRWMS M&O 2000c). Please note that they are not the only conditions for which the solubility models developed in this report are applicable. The composition was merely used as a starting point to develop the solubility models. The applicable ranges for the solubility models developed in this report are much wider than the conditions listed in Table 4-2 (see Section 6.4.4).

Table 4-1. Direct Inputs for Solubility Models

Data Description	Data Source	Data Tracking Number (DTN)	Parameters Used	Used in
Data0.ymp.R2 (thermodynamic database for EQ3NR calculations)	Steinborn et al. 2003	MO0302SPATHDYN.000	All the parameters pertinent to the EQ3NR calculations	Sections 6.5, 6.6.2, 6.6.3, 6.7-6.12 for solubility calculations
Water composition	CRWMS M&O 2000c	MO0006J13WTRCM.000	See Table 4-2	Section 6.4 for solubility model configuration
Dissolution and alteration of spent fuel by ground water	CRWMS M&O 2000d	LL991001251021.090	^{238}U and ^{237}Np concentrations ^a	Section 6.6.4 for the alternative secondary phase neptunium solubility model
Input transmittal for measured solubilities, argonne national laboratory high drip rate tests	CRWMS M&O 2000e	N/A	^{238}U and ^{237}Np concentrations ^a	Section 6.6.4 for the alternative secondary phase neptunium solubility model
Average inventory in CSNF waste packages	BSC 2001b	SN0011T0810599.023	^{234}U , ^{235}U , ^{236}U , ^{238}U , ^{237}Np , and ^{241}Am ^a	Section 6.6.4 for the alternative secondary phase neptunium solubility model
Half-life of isotopes	Lide 1995, Table of the Isotopes	N/A	Half lives of ^{235}Np , ^{236}Np , ^{237}Np , ^{238}Np , ^{239}Np , ^{234}U , ^{235}U , ^{236}U , ^{238}U , ^{241}Am , and ^{241}Pu ^a	Section 6.6.4 for the alternative secondary phase neptunium solubility model
Atomic weight	Lide 1995, Periodic Table, Inner cover page	N/A	All pertinent elements	Throughout this report
Spent fuel characterizations	Guenther et al. 1988a, Table F.2.d, p. F.23; Guenther et al. 1988b, Table F.2.f, p. F.31	N/A	Radioactivities ^{235}Np , ^{236}Np , ^{237}Np , ^{238}Np , ^{239}Np , ^{234}U , ^{235}U , ^{236}U , ^{238}U , ^{241}Am , and ^{241}Pu ^a	Section 6.6.4 to develop the alternative secondary phase neptunium solubility model

NOTE: ^a see Microsoft Excel spreadsheet anl6dripdata.xls in spreadsheet.zip (Attachment I)

The third and fourth rows of Table 4-1 give the input information of radionuclide concentrations measured from spent fuel dissolution and alteration experiments conducted at Argonne National Laboratory (ANL). This data set was used in Section 6.6.4 to develop the alternative secondary phase neptunium solubility model.

The fifth row of Table 4-1 refers to the average inventory of commercial spent nuclear fuel (CSNF) waste packages. The sixth row of Table 4-1 refers to the half-life of isotopes. They were used to develop the alternative secondary phase neptunium solubility model in Section 6.6.4.

Table 4-2. Chemical Composition of Reference Water (J-13 Well Water)

Component	Concentration (mg/L) ^{a,b}	Uncertainty	Source
Na ⁺	45.8	2.29	DTN: MO0006J13WTRCM.000
K ⁺	5.04	0.61	DTN: MO0006J13WTRCM.000
Ca ²⁺	13.0	0.99	DTN: MO0006J13WTRCM.000
Mg ²⁺	2.01	2.01	DTN: MO0006J13WTRCM.000
Si (SiO ₂ (aq))	28.5 (60.97)	1.85	DTN: MO0006J13WTRCM.000
Cl ⁻	7.14	0.61	DTN: MO0006J13WTRCM.000
F ⁻	2.18	0.29	DTN: MO0006J13WTRCM.000
NO ₃ ⁻	8.78	1.03	DTN: MO0006J13WTRCM.000
SO ₄ ²⁻	18.4	1.03	DTN: MO0006J13WTRCM.000

NOTES: ^aDTN: MO0006J13WTRCM.000 contains recommended mean values of major constituents in J-13 well water.

^bIn the TDMS database, the name of abundance was used for this DTN. Concentration was used in this report, because it is more specific for this application.

The seventh row of Table 4-1 refers to the atomic weights of the elements, which were used throughout this model report for solubility calculations and unit conversion.

The last row of Table 4-1 refers to the inventory information for ATM-103 and ATM-106 spent fuels, which were used to calculate the abundance of radionuclides in these fuels for the alternative secondary phase neptunium solubility model in Section 6.6.4.

Uncertainties associated with the inputs included in this section are discussed in Section 4.1.2 and where data are used in Section 6.

4.1.2 Indirect Inputs

Indirect inputs are summarized in Table 4-3 in 18 entries. These indirect inputs were utilized to evaluate uncertainties in the solubility models, or to establish the ranges of environmental conditions for solubility calculations, or to validate solubility models.

Table 4-3. Summary of Indirect Inputs

Entry No.	Input	Source	Used In
1	Uncertainties in Thermodynamic Data	Lemire 2001, Tables 3.1, 3.2, 4.1, and 4.2,	Sections 6.5 and 6.6 for uncertainties in plutonium, Np_2O_5 , and NpO_2 solubility models
2	Uncertainties in Thermodynamic Data	Silva et al. 1995, Table III-2	Section 6.9 for uncertainties in americium solubility model
3	Uncertainties in Thermodynamic Data	Grenthe et al. 1992, Tables III.1, III.2	Sections 6.3.3.1 and 6.7 for uncertainties in uranium solubility model Section 6.6.4 for uncertainties in the alternative secondary phase neptunium solubility model
4	Uncertainties in Thermodynamic Data	Hummel et al. 2002, p. 284, Table 5.21.1	Section 6.5 for uncertainties in plutonium, solubility model Section 6.8 for uncertainties in thorium solubility model
5	pH Ranges in Waste Packages	DTN: SN0009T0811199.008	Section 6.4 for pH ranges used for EQ3NR calculations
6	f_{CO_2} Range	DOE 2002, p. 4-191	Section 6.4 for f_{CO_2} ranges used for EQ3NR calculations
7	Fluoride Concentration Range	DTN: SN0009T0811199.008	Section 6 for uncertainties associated with fluoride concentrations in solubility models
8	Ac(III) and Pa(IV) Radii and Equilibrium constants	Shannon 1976, Table 1	Sections 6.10 and 6.11 for actinium and protactinium solubility analogs
9	log K of actinium and protactinium Species	Baes and Mesmer 1986; Tables 7.2 and 9.1	Sections 6.10 and 6.11 for actinium and protactinium solubility analogs
10	log K of protactinium Species	Yui et al. 1999	Section 6.11 for protactinium solubility analogs
11	Lead Concentrations in Environments	Hem 1985, p. 144	Section 6.13 for lead solubility corroboration
12	Plutonium Solubility	Efurd et al. 1998, Table 4	Section 7.1 to validate the plutonium solubility model
13	Plutonium Solubility	Nitsche et al. 1993a, Table XVI	Section 7.1 to validate the plutonium solubility model
14	Neptunium Concentrations in Spent Fuel Corrosion Experiments	CRWMS M&O 2000d; DTN: LL991001251021.090	Section 7.2 to validate the Np_2O_5 solubility model
15	Neptunium Concentrations in Spent Fuel Corrosion Experiments	CRWMS M&O 2000e	Section 7.2 to validate the Np_2O_5 solubility model
16	Actinide Concentrations in Spent Fuel Corrosion Experiments	Wilson 1990a, Tables A.2-A.5; Wilson 1990b, Tables A.2-A.7	Section 7.1 to validate the plutonium solubility model; Section 7.2 to validate the Np_2O_5 solubility model; Section 6.6.4.5 to corroborate the alternative secondary phase neptunium solubility model
17	Thorium Solubilities	Hummel et al. 2002, Section 5.21	Section 7.4 to validate the thorium solubility model
18	Protactinium Solubility	Berry et al. 1989, p. 339	Section 7.7 to validate the protactinium solubility model

Entries 1-4 are uncertainties in thermodynamic data compiled by the Nuclear Energy Agency (NEA) and Nagra. These uncertainties are propagated to uncertainties in solubility models developed in this model report.

Entries 5-7 are the ranges of environmental conditions for the repository. They were used to determine the ranges of physical-chemical conditions for solubility calculations.

Entries 8-10 are physical and chemical properties of actinium and protactinium species, which were used to determine the analogs for these elements.

Entry 11 is lead solubility data summarized by Hem (1985), which were used to corroborate the lead solubility distribution presented in Section 6.13.

Entries 12-13 are plutonium solubility measurements, which were used to validate the plutonium solubility model. These data were not used, directly or indirectly, in the model development.

Entries 14-15 are measured neptunium concentrations in spent fuel corrosion experiments conducted at ANL. They were used to validate the Np_2O_5 solubility model.

Entry 16 is measured concentrations of radionuclides in spent fuel corrosion experiments conducted at Pacific Northwest National Laboratory (PNNL). They were used to validate the plutonium solubility model and the Np_2O_5 solubility model, and to corroborate the alternative secondary phase neptunium solubility model.

Entry 17 is thorium solubility data summarized by Hummel et al. (2002), which were used to validate the thorium solubility model.

Entry 18 is protactinium solubility data reported by Berry et al. (1989), which were used to validate the protactinium solubility model.

4.2 CRITERIA

Projects Requirements Document (Canori and Leitner 2003) identifies the high-level requirements for the Project. The requirements that pertain to this model report, and their link to 10 CFR 63, are shown in Table 4-4. *Yucca Mountain Review Plan, Draft Report for Comment* (NRC 2002) lists acceptance criteria pertaining to these requirements. Criteria that are applicable to this model report are described below.

Table 4-4. Project Requirements and YMRP Acceptance Criteria Applicable to this Scientific Analysis Report

Requirement Number	Title	10 CFR 63 Link	YMRP Acceptance Criteria
PRD-002/T-014	Performance Objectives for the Geologic Repository After Permanent Closure	10 CFR 63.113	4.2.1.1.3, criteria 1 to 2
PRD-002/T-015	Requirements for Performance Assessment	10 CFR 63.114	4.2.1.3.4.3, criteria 1 to 5
PRD-002/T-016	Requirements for Multiple Barriers	10 CFR 63.115	4.2.1.1.3, criteria 1 to 3

The following requirements were taken from Section 4.2.1.1.3 of *Yucca Mountain Review Plan, Draft Report for Comment* (NRC 2002), and are based on the requirements at 10 CFR 63.113(a) and 63.115(a)–(c):

- Acceptance Criterion 1, Identification of Barriers is Adequate:

Barriers relied on to achieve compliance with 10 CFR 63.113(b), as demonstrated in the total system performance assessment, are adequately identified, and are clearly linked to their capability. The barriers identified include at least one from the engineered system and one from the natural system.

- Acceptance Criterion 2, Description of Barrier Capability to Isolate Waste is Acceptable:

The capability of the identified barriers to prevent or substantially delay the movement of water or radioactive materials is adequately identified and described:

- The information on the time period over which each barrier performs its intended function, including any changes during the compliance period, is provided;
- The uncertainty associated with barrier capabilities is adequately described.

The following requirements were taken from Section 4.2.1.3.4.3 of *Yucca Mountain Review Plan, Draft Report for Comment* (NRC 2002), and are based on the requirements of 10 CFR 63.114(a)–(c) and (e)–(g), relating to the radionuclide release rates and solubility limits mode abstraction:

- Acceptance Criterion 1, System Description and Model Integration are Adequate:

- The abstraction of radionuclide release rates and solubility limits uses assumptions, technical bases, data, and models that are appropriate and consistent with other related U.S. Department of Energy abstractions. The descriptions and technical bases provide transparent and traceable support for the abstraction of radionuclide release rates and solubility limits;
- The U.S. Department of Energy reasonably accounts for the range of environmental conditions expected inside breached waste packages and in the engineered barrier environment surrounding the waste package. For example, the U.S. Department of Energy should provide a description and sufficient technical bases for its abstraction of changes in hydrologic properties in the near field, caused by coupled thermalhydrologic-mechanical-chemical processes;
- Technical bases for inclusion of any thermal-hydrologic-mechanical-chemical couplings and features, events, and processes in the radionuclide release rates and solubility limits model abstraction are adequate. For example, technical bases may include activities, such as independent modeling, laboratory or field data, or sensitivity studies.

- Acceptance Criterion 2, Data are Sufficient for Model Justification:
 - Geological, hydrological, and geochemical values used in the safety case are adequately justified. Adequate description of how the data were used, interpreted, and appropriately synthesized into the parameters is provided;
 - Sufficient data have been collected on the characteristics of the natural system and engineered materials to establish initial and boundary conditions for conceptual models and simulations of thermal-hydrologic-chemical coupled processes. For example, sufficient data should be provided on design features, such as the type, quantity, and reactivity of materials, that may affect radionuclide release for this abstraction;
 - Where the U.S. Department of Energy uses data supplemented by models to support abstraction of solubility limits, the anticipated range of proportions and compositions of phases under the various physicochemical conditions expected are supported by experimental data (U.S. Nuclear Regulatory Commission, 1984);
 - The corrosion and radionuclide release testing program for high-level radioactive waste forms intended for disposal provides consistent, sufficient, and suitable data for the inpackage and in-drift chemistry used in the abstraction of radionuclide release rates and solubility limits. For expected environmental conditions, the U.S. Department of Energy provides sufficient justification for the use of test results, not specifically collected from the Yucca Mountain site, for engineered barrier components, such as high-level radioactive waste forms, drip shield, and backfill.
- Acceptance Criterion 3, Data Uncertainty is Characterized and Propagated Through the Model Abstraction:
 - Models use parameter values, assumed ranges, probability distributions, and/or bounding assumptions that are technically defensible, and reasonably account for uncertainties and variabilities;
 - Parameter values, assumed ranges, probability distributions, and bounding assumptions used in the abstractions of radionuclide release rates and solubility limits in the total system performance assessment are technically defensible and reasonable based on data from the Yucca Mountain region, laboratory tests, and natural analogs. For example, parameter values, assumed ranges, probability distributions, and bounding assumptions adequately reflect the range of environmental conditions expected inside breached waste packages;
 - The U.S. Department of Energy uses reasonable or conservative ranges of parameters or functional relations to determine effects of coupled thermal-hydrologic-chemical processes on radionuclide release. These values are consistent with the initial and boundary conditions and the assumptions for the conceptual models and design concepts for natural and engineered barriers at the Yucca Mountain site. If any correlations between the input values exist, they are adequately established in the

total system performance assessment. For example, estimations are based on a thermal loading and ventilation strategy; engineered barrier system design (including drift liner, backfill, and drip-shield); and natural system masses and fluxes that are consistent with those used in other abstractions;

- Uncertainty is adequately represented in parameter development for conceptual models, process models, and alternative conceptual models considered in developing the abstraction of radionuclide release rates and solubility limits, either through sensitivity analyses or use of bounding analyses;
 - The U.S. Department of Energy uses an appropriate range of time-history of temperature, humidity, and dripping to constrain the probability for microbial effects, such as production of organic by-products that act as complexing ligands for actinides and microbially enhanced dissolution of the high-level radioactive waste glass form;
 - The U.S. Department of Energy adequately considers the uncertainties, in the characteristics of the natural system and engineered materials, such as the type, quantity, and reactivity of material, in establishing initial and boundary conditions for conceptual models and simulations of thermal-hydrologic-chemical coupled processes that affect radionuclide release.
- Acceptance Criterion 4, Model Uncertainty Is Characterized and Propagated Through the Model Abstraction.
 - Alternative modeling approaches of features, events, and processes are considered and are consistent with available data and current scientific understanding, and the results and limitations are appropriately considered in the abstraction;
 - In considering alternative conceptual models for radionuclide release rates and solubility limits, the U.S. Department of Energy uses appropriate models, tests, and analyses that are sensitive to the processes modeled for both natural and engineering systems. Conceptual model uncertainties are adequately defined and documented, and effects on conclusions regarding performance are properly assessed. For example, in modeling flow and radionuclide release from the drifts, the U.S. Department of Energy represents significant discrete features, such as fault zones, separately, or demonstrates that their inclusion in the equivalent continuum model produces a conservative effect on calculated performance.
 - Acceptance Criterion 5, Model Abstraction Output is Supported by Objective Comparisons.
 - The models implemented in this total system performance assessment abstraction provide results consistent with output from detailed process-level models and/or empirical observations (laboratory and field testings and/or natural analogs);
 - The U.S. Department of Energy adopts well-documented procedures that have been accepted by the scientific community to construct and test the numerical models,

used to simulate coupled thermal-hydrologic-chemical effects on radionuclide release. For example, the U.S. Department of Energy demonstrates that the numerical models used for high-level radioactive waste degradation and dissolution, and radionuclide release from the engineered barrier system, are adequate representations; include consideration of uncertainties; and are not likely to underestimate radiological exposures to the reasonably maximally exposed individual and releases of radionuclides into the accessible environment.

4.3 CODES AND STANDARDS

ASTM C 1174-97, *Standard Practice for Prediction of the Long-Term Behavior of Materials, Including Waste Forms, Used in Engineered Barrier Systems (EBS) for Geological Disposal of High-Level Radioactive Waste*, is used to support the model development methodology, categorize the models developed with respect to their usage for long-term TSPA, and relate the information/data used to develop the model to the requirements of the standard.

5. ASSUMPTIONS

5.1 OXIDIZING CONDITIONS

Assumption: It is assumed that the repository is in an oxidizing condition; i.e., oxygen partial pressure equals 0.2 bars (atmospheric value).

Rationale: This assumption is utilized because the existence of reducing conditions has not been proven except for transient and localized conditions.

Confirmation Status: This is a reasonably conservative assumption because radionuclides are either more soluble under such oxygen partial pressure or insensitive to oxygen partial pressure. Thus, it does not need further confirmation.

Use in the Model: This assumption is used throughout Section 6.

5.2 INVENTORY VALUES

Assumption: It is assumed that the abundance of uranium-238 and neptunium-237 in the ATM-103 and ATM-106 samples used in ANL's drip tests can be represented by the inventory values given by Guenther et al. (1998a, 1998b) for fuels out of reactors for 15 years.

Rationale: The abundance of uranium-238 does not change with the out of reactor time, and neptunium-237 abundance changes less than 1.5 percent over a period of 5 years (see Guenther et al. 1998a, Table F.2.d, p. F.23).

Confirmation Status: This assumption is reasonable because the uncertainty introduced by this assumption is small. Therefore, no confirmation is required.

Use in the Model: This assumption is used in Section 6.6.4.1.

6. MODEL DISCUSSION

6.1 MODELING OBJECTIVES

The objective of this modeling effort is to evaluate or abstract dissolved concentration limits of certain radioactive elements in the expected environments. Fourteen elements (actinium, americium, carbon, cesium, iodine, neptunium, protactinium, lead, plutonium, radium, strontium, technetium, thorium, and uranium) are considered, based on *Radionuclide Screening* (BSC 2002b).

Dissolved concentration limits will be mainly presented as look-up tables with one or more uncertainty terms, distributions, or constants. The results of this analysis are inputs for total system performance assessment (TSPA).

The corroborating and supporting data used in this section were summarized in Section 4.1.2.

6.2 FEATURES, EVENTS, AND PROCESSES INCLUDED IN MODEL

The development of a comprehensive list of features, events, and processes (FEPs) potentially relevant to postclosure performance of the repository is an ongoing iterative process based on site-specific information, design, and regulations. The approach for developing an initial list of FEPs, in support *Total System Performance Assessment for the Site Recommendation* (CRWMS M&O 2000b), was documented in *The Development of Information Catalogued in REV00 of the YMP FEP Database* (Freeze et al. 2001). The initial FEP list contained 328 FEPs, of which 176 were included in the Total System Performance Assessment for the Site Recommendation (TSPA-SR) models (CRWMS M&O 2000f, Tables B-9 through B-17). To support the Total System Performance Assessment for the License Application (TSPA-LA), the FEP list was re-evaluated in accordance with *Technical Work Plan for Enhanced FEP Planning and Implementation* (BSC 2002c, Section 3.2). Table 6.2.1 provides a list of FEPs that are included in the TSPA-LA submodels described in this model document. Details of the implementation of these FEPs in the TSPA-LA model are summarized in Section 6.2-1.

For each of the included FEPs listed in Table 6.2-1, the implementation in the TSPA-LA model is described in this model document. Details of the implementations are summarized in the table, including specific references to sections within this document.

Table 6.2-1. Included FEPs for this Model Report and Their Disposition in the TSPA-LA Model

FEP No.	FEP Name	Disposition Section	TSPA-LA Disposition
2.1.09.04.0A	Radionuclide Solubility, Solubility Limits, and Speciation in the Waste Form and EBS	6.3.1 and 6.5 to 6.18.	<p>Abstraction solubility models for 14 elements (plutonium, neptunium, uranium, thorium, americium, actinium, protactinium, radium, lead, technetium, iodine, strontium, carbon, and cesium) included in the TSPA-LA model. They are used to constrain the maximum radionuclide concentrations. In the TSPA model, inventory concentrations are calculated according to the dissolution rate of waste forms, water volume, and radionuclide inventory. Then, the inventory concentrations are compared against their solubility limits. The real concentrations that are available for transport are the lesser between the inventory concentrations and the solubility limits.</p> <p>For plutonium, neptunium, uranium, thorium, americium, actinium, and protactinium, solubilities are in the form of look-up tables as functions of pH and log f_{CO_2} plus 2 or more uncertainty terms accounting for uncertainties associated with thermodynamic data, variations in water chemistry, and identification of solubility controlling solids.</p> <p>For radium and lead, solubilities are given as distributions or segmental constants.</p> <p>Under repository conditions no solubility-controlling solid are expect to form for technetium, carbon, iodine, cesium, and strontium (Sections 6.14 through 6.18), Consequently, they are presumed to be highly soluble, and their releases are considered to be controlled by the dissolution rate of waste forms and the waste inventory.</p>

Source: BSC 2002c

NOTE: EBS = engineered barrier system

Deviations from *Technical Work Plan for Waste Form Degradation Modeling, Testing, and Analyses in Support of SR and LA* (BSC 2002a) are noted in Table 6.2-2.

Table 6.2-2. FEPs Deviation from the Technical Work Plan

FEP No.	FEP Name	Deviation
2.1.09.06.0A	Reduction-oxidation potential in EBS	TSPA-LA disposition will not be given in this report as indicated in the technical work plan. TSPA-LA disposition will be addressed in ANL-EBS-MD-000037 REV 02, <i>In-Package Chemistry Abstraction</i> (BSC 2003a).
2.2.08.12.0A	Chemistry of water flowing into the EBS	TSPA-LA disposition will not be given in this report as indicated in the technical work plan. TSPA-LA disposition will be addressed in ANL-EBS-MD-000037 REV 02, <i>In-Package Chemistry Abstraction</i> (BSC 2003a).
2.1.09.10.0A	Secondary Phase Effects on Dissolved Radionuclide Concentrations	This model report does not provide a direct basis for the inclusion of this FEP in the TSPA-LA base-case analysis. This FEP is considered in an alternative solubility model for neptunium, which is recommended for TSPA-LA in a sensitivity study. Needs more confirmative evidence from experimental tests to include it in the TSPA-LA base-case analysis. TSPA-LA disposition will be addressed in ANL-WIS-MD-000009 REV 01, <i>Miscellaneous Waste-Form FEPs</i> (BSC 2003b).

NOTE: EBS = engineered barrier system

6.3 TECHNICAL ISSUES IN SOLUBILITY EVALUATION

There are two prerequisites to solubility evaluations. First, a thermodynamic database is needed along with a compatible geochemical modeling tool. Second, the environmental conditions for which solubility is to be evaluated must be defined. With these prerequisites, a model is constructed based on environmental information and the chemical properties of RNs using the geochemical modeling tool. Solubility limits are based on the model results.

The first prerequisite is input to this analysis and is discussed in Section 4.1. The second prerequisite is discussed in Section 6.4. The discussion of this section will focus on several technical issues common to solubility evaluation, such as the selection of solubility controlling solids and uncertainty treatment. Specific issues related to certain elements will be discussed in relevant sections.

6.3.1 The Definition of Solubility

From the viewpoint of laboratory chemistry, solubility is defined as the concentration of a substance when the solution is saturated with that substance (Atkins 1994, p. 312). This definition implies that (1) solubility is defined in terms of thermodynamics, and (2) solubility is the maximum concentration (with a certain degree of uncertainty) that the substance can reach in solution at equilibrium. In other words, solubility is the concentration of a substance when the substance is at equilibrium (either stable or metastable) with the solution. For this case, the substance is a radionuclide-bearing solid called solubility-controlling solid.

Performance assessments are more interested in the solubility of specific elements in water than the solubility of a substance. The solubility of an element, the maximum concentration that the element can reach in solution at equilibrium, is called elemental solubility. The phrase “maximum concentration” reflects a key requirement for solubility evaluation (i.e., it shall be bounding).

Solubility limits are a fundamental input for TSPA analyses. They are used to constrain the maximum radionuclide concentrations. In the TSPA model, inventory concentrations are calculated according to the dissolution rate of waste forms, water volume, and radionuclide inventory. Then, the inventory concentrations are compared against the solubility limits. The real concentrations that are available for transport are the lesser between the inventory concentrations and the solubility limits.

Except for colloidal and kinetically transient phenomena such as over-saturation, solubility is the maximum concentration the element can reach under the conditions of interest. From the point of view of performance assessment, it is a bounding property.

By definition, the solubility-controlling solid can be either a pure radionuclide-bearing solid or a solid solution of two (or more) end-members. In practice, pure radionuclide-bearing solids are nearly always used to evaluate solubility. One reason for this is that solubility models based on solid-solution control are more complicated. Moreover, proof of the formation of solid solutions is a more demanding task than demonstration of the formation of pure solids. Use of pure phase control is acceptable to the regulator because it yields higher solubility limits than using a solid solution as the controlling solid phase.

Sorption is another mechanism that controls the concentrations of RNs in solutions. The net effect of sorption is to lower radionuclide concentrations in solutions. This study excludes sorption from current consideration. This is a conservative approach as it overestimates the likely concentrations of radionuclides.

Concentrations in aqueous solutions may be given in several different units. The standard usage for chemical computations is moles of solute per kilogram of solvent, and is known as molality. For dilute solutions this differs only slightly from moles per liter, known as molarity. Conversions between these units must take account of the solution density. Because solution concentrations used herein are limited to an ionic strength of 1 molal, no distinction is made between these units in this model report. Another common specification is mg/L. Strictly speaking, the density must be used in conversions with respect to molality, but again no distinction is made here. A mole of a substance is the number of grams equal to its molecular weight.

6.3.2 Identification of the Controlling Solid

As discussed previously, radioactive element solubility is defined with respect to a solid. To evaluate solubility within a repository, one has to identify the controlling solid or solids. Since solubility depends strongly on the solid phase, the outcome would be quite different (orders of magnitude) if different solids are chosen.

Laboratory experiments and observations of natural systems provide the basis for choosing the controlling phase. For example, experiments with neptunium in J-13 well water show $\text{Np}_2\text{O}_5 \cdot x\text{H}_2\text{O}$ is the controlling solid (Efurud et al. 1998, p. 3896) for the time scale of the experiments. Unfortunately, laboratory evidence and field observations are not available for all the RNs at the environmental conditions of interest. Moreover, the identity of the controlling solid may change with environment conditions.

From the viewpoint of thermodynamics, one would select the most stable solid as the controlling phase because thermodynamically less stable phases would be ultimately replaced by the most stable phase. However, due to kinetic effects, the thermodynamically most stable solid may not appear under the expected repository conditions. This fact makes identification of the controlling solid purely from thermodynamic considerations unreliable.

The Ostwald Step Rule provides a useful guide for such situations. This rule says that unstable or metastable minerals form first, followed by progressively more stable minerals (Langmuir 1997, p. 324). The formation of $\text{Np}_2\text{O}_5 \cdot x\text{H}_2\text{O}$ in neptunium experiments is an example of the Ostwald Step Rule. The thermodynamically more stable phase is $\text{NpO}_2(\text{s})$ (s denotes solid), which is sufficiently more stable than the $\text{Np}_2\text{O}_5(\text{s})$ that it is not oxidized to the $\text{Np}(\text{V})$ state in spite of the presence of atmospheric oxygen (CRWMS M&O 1998a, pp. 19 and 20; Efurud et al. 1998, Figure 5). Precipitation kinetics is the governing factor for the Ostwald Step Rule. In other words, during the process of waste corrosion, more stable minerals may be prevented from precipitating because less stable minerals are kinetically favored. Another good example of the Ostwald Step Rule is the formation of secondary uranyl minerals during spent fuel dissolution. There, less stable schoepite precipitates first, then it is replaced by more stable uranyl silicates (Wronkiewicz et al. 1992, Section 4.2).

The Ostwald Step Rule has significant implications for choosing the controlling phase. To use a more stable phase (rather than the first formed, less stable phase) as the controlling phase for solubility calculations, it is necessary to demonstrate that the less stable mineral will be replaced by the more stable mineral(s) in a shorter period than the characteristic time scale of the problem. Specifically, since the time scale of repository performance for regulatory purpose is 10^4 years, the time scale for more stable mineral(s) to form should be less than 10^2 – 10^3 years. Simply arguing that the more stable phase will ultimately replace less stable minerals is not convincing because under certain conditions it may take infinite time for a more stable phase to replace a less stable phase. For example, the mixture of hydrogen and oxygen gases at room temperature is thermodynamically unstable with respect to water, but water will never form from the mixture unless the mixture is ignited by flame or other means. A good geologic example is the persistence of magnetite, Fe_3O_4 , for millions of years under oxidizing conditions in spite of the tendency to oxidize to hematite or goethite.

For many radioactive elements, the identification of controlling solids for the repository by experiments has yet to be reported (e.g., protactinium and curium) or experimental observations are not conclusive (e.g., plutonium). For situations like this, a conservative approach is, as suggested by Bruno et al. (1997, p. 81), to choose the amorphous solids (oxide or hydroxide) as their controlling solids. The Ostwald Step Rule is the main reason for choosing an amorphous phase. Another reason to do so is that radiation associated with spent nuclear fuel could damage the lattice structure of solids and make it less crystalline (Rai and Ryan 1982, p. 216).

Freshly precipitated solids tend to be fine particles with large specific surface area. The extra surface energy given by the large surface area makes the fresh precipitates more soluble. However, with time the freshly precipitated fine particles will go through a process called aging in which particle size will increase. As a result, an aged product will have a lower solubility than the freshly precipitated solid. Aging could be a long-lasting process. For example, Rai and Ryan (1982) observed $\text{PuO}_2 \cdot x\text{H}_2\text{O}$ (amorphous) continuously aging over a period of 1,266 days.

As solubility experiments usually are carried out within a period of less than a year, it is reasonable to expect that the measured solubility actually is an upper limit. The real solubility of the solid could be lower than the measured one because of aging.

It is well known that radioactive decay, especially α -decay, can damage the crystal structure of plutonium solids. Rai and Ryan (1982) reported that $^{238}\text{PuO}_2(\text{c})$ was found to convert to an amorphous form of PuO_2 , which has higher solubility than $\text{PuO}_2(\text{c})$, in 1,266 days. In waste forms, the fraction of isotope plutonium-238 in the total plutonium inventory is small (BSC 2001c, Table 36), so crystal structure damage is not expected to occur rapidly enough to be significant. However, over the regulatory compliance time period (10,000 years), it is reasonable to expect that $\text{PuO}_2(\text{c})$ would gradually convert to a $\text{PuO}_2(\text{lc})$ (lc = less crystalline) or hydrated amorphous material. Therefore, this phenomenon should be recognized, and the uncertainty it introduces to radionuclide solubility should be addressed.

In fact, aging and decay effects (radiation damage) go in opposite directions. The former could make a radionuclide less soluble if the starting material is an amorphous solid. The latter could make a radionuclide more soluble, provided that the starting material is a crystalline solid. Therefore, it is reasonable to speculate that the real controlling solid may be something between the amorphous phase and the crystalline phase. Indeed, Rai and Ryan (1982, p. 214) found that “the solubility of $^{239}\text{PuO}_2$ and $^{239}\text{PuO}_2 \cdot x\text{H}_2\text{O}$ tend to merge; most, if not all, of the effect is due to decreased solubility of $\text{PuO}_2 \cdot x\text{H}_2\text{O}$ with time.” While there is not enough information to define the thermodynamic properties of this intermediate solid quantitatively and, consequently, to calculate solubility controlled by it, the uncertainty can be enveloped by use of the amorphous phase and the crystalline phase.

For some very soluble elements, solids are not expected to precipitate from water under the repository conditions. The transport of those elements may not be solubility-controlled. An arbitrary large number is assigned to their solubility so that their release will be controlled by the waste inventory and the waste form degradation rate. This is a conservative approach, and no further validation is needed.

It is possible that over the range of conditions considered for any element, there is more than one stable mineral within the range. For situations like this, a multiple controlling-mineral model might be adopted to derive solubility limits. Uranium is the most likely element to be affected by this situation (see Section 6.7). Should the solubility of uranium become of concern to dose calculations, it may be necessary to examine the multiple-controlling phase situation in more detail.

6.3.3 Treatment of Variation and Uncertainty

In general, the solubility of an element in a repository is a variable. As chemical conditions change over time, the solubility will change as well. Knowledge of the solubility is also subject to uncertainty, both because of the chemical conditions and because of the values of the parameters used to calculate it. Although both variation with time and uncertainty have similar effects on solubility limits, distinguishing them from each other is beneficial.

As environmental conditions within a repository vary widely, so does radionuclide solubility. A meaningful solubility evaluation should account for the variation in solubility caused by the changes in environmental conditions. As long as the ranges of environmental conditions are known (as inputs to the analysis), the range of solubility variation can be calculated. It is useful to understand the effects of changes in environmental conditions on solubility limits. For example, one could predict how a repository design feature would affect solubility limits and, ultimately, the repository performance by analyzing the design feature's effects on environmental conditions.

This report has three types of output, each with its own treatments of variation and uncertainty. Solubilities of actinides (i.e., actinium, americium, neptunium, protactinium, plutonium, thorium, and uranium) are tabulated for certain ranges of pH and f_{CO_2} values with several uncertainty terms. For radium and lead, stochastic distributions are given. For those elements for which no solubility controlling solids are expected to form under repository conditions (carbon, cesium, iodine, strontium, and technetium), a constant of 500 molal is assigned to their solubility. This number is not meant to be taken literally. Rather, it is meant to indicate that for these elements and conditions, the TSPA calculation for LA should use concentrations based on waste form dissolution rates and inventory instead of solubility controls. The effects of variations in important environmental conditions (namely, pH and $\log f_{CO_2}$) are accounted for by functional relations (tabulated) between solubilities and those conditions developed in Sections 6.5 through 6.18.

Uncertainty is associated with all of the steps in solubility evaluation. For example, it can be associated with identification of a solubility-controlling solid and with the thermodynamic data used for the calculation. Another source is uncertainty in environmental conditions. Distinguishing uncertainty from temporal variability and understanding the major sources of uncertainty are prerequisites to reducing uncertainty.

The uncertainties discussed in this section apply only to those dissolved concentrations tabulated in this report. This is also true for those elements with constant values because they are merely flags for the TSPA-LA model to use waste form dissolution rates to constrain their releases. The uncertainties in this case should be based on those of the release rates.

Five types of uncertainty are associated with the output of this report. They are uncertainties in the thermodynamic data supporting the EQ3NR calculations, uncertainties due to variations in the chemistry of the water into which dissolution is occurring, uncertainties in the temperature and uncertainties in activity coefficients. For some elements, the uncertainty due to identity of the solubility-controlling phase is also considered as an additional source of uncertainty.

Uncertainties in solubilities due to uncertainties in thermodynamic data, in the chemistry of the water into which dissolution occurs and, for some elements, in the identity of the solubility-controlling phase are included as variability terms in the solubility expressions given for the actinide elements. Temperature and activity coefficient uncertainties are treated as bounding or limiting conditions on the solubilities given.

It is possible that the thermodynamic database (data0.ymp.R2) used for solubility calculations does not cover all the species that may occur for the system of interest; however, the uncertainty

from this source could not be assessed quantitatively until these species are included in the database, which requires extensive review and data compilation efforts and is beyond the scope of this model report. Thus, uncertainty from this source will not be addressed in this study. Nonetheless, since extensive reviews have been conducted by the NEA (Grenthe et al. 1992; Silva et al. 1995; Lemire 2001) and others, the species most commonly observed in laboratory studies of the actinides are included in the database. Therefore, there is no reason to expect other than small uncertainty from this source.

The remainder of this section provides a general discussion of these five types of uncertainty including their sources and the general procedure used for evaluating them. The discussions of each element in Section 6 include element-specific information for evaluating the uncertainty in their concentrations. The element-specific uncertainties themselves are summarized in Table 8-3 and 8-4.

6.3.3.1 Uncertainties in the log K Values of Controlling Solid(s) and Aqueous Species

There are uncertainties in the thermodynamic data used to make the solubility calculations. Because of the complexity of the solubility modeling code EQ3NR (Wolery 1992), uncertainties in the entire suite of supporting thermodynamic data were not propagated rigorously through the solubility calculations. Rather, uncertainties in the solubilities of the elements modeled were found by considering uncertainties in the thermodynamic properties of the solubility-controlling solid and of the aqueous species that dominate the dissolved concentration of each element.

Uncertainties in the thermodynamic properties, specifically $\Delta_f G^0$ values, of the controlling solids and important aqueous species and of the log K values of reactions connecting them are treated explicitly. Uncertainties in these values propagate directly to uncertainties in log(solubilities). The log K values used in the modeling are those in data0.ymp.R2 (DTN: MO0302SPATHDYN.000), which does not include uncertainties. Uncertainties of $\Delta_f G^0$ values for americium, neptunium, plutonium, and uranium are those recommended in the NEA compilations (Grenthe et al. 1992; Silva et al. 1995; Lemire 2001), from which the log K values in data0.ymp.R2 were derived. The uncertainties of log K values for thorium species are based on the review of thorium data made to support the Nagra/PSI data base as documented by Hummel et al. (2002).

The authors of the NEA and Nagra/PSI database compilations (Grenthe et al. 1992; Silva et al. 1995; Lemire 2001; Hummel et al. 2002) characterize the uncertainties they selected to “represent total uncertainties and correspond in principle to the statistically defined 95% confidence interval” (Grenthe et al. 1992, Table III.1, p. 30). The uncertainties are ultimately based on assessment of the uncertainties in the experimental data and calculation path from which they were derived. For use in this report, the “95% confidence interval” is taken to represent two standard deviations (2σ) in a normal distribution.

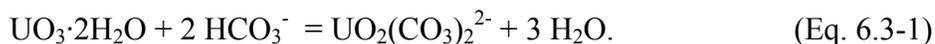
The log K values in data0.ymp.R2 (DTN: MO0302SPATHDYN.000) are related to the standard thermodynamic properties by the expression $\Delta_r G^0 = -RT \ln K$. $\Delta_r G^0$ is derived from the $\Delta_f G^0$ values of reactants and species by the expression $\Delta_r G^0 = \sum \Delta_f G^0_{\text{products}} - \sum \Delta_f G^0_{\text{reactants}}$. Thus, uncertainties in $\Delta_f G^0$ values propagate directly to uncertainties in log K values. These, in turn, propagate directly to uncertainties in log solubilities. The solubility data provided in this report

are given as log solubility values. The uncertainties in them are expressed as normal distributions of the log solubility values because they are derived from uncertainties in the standard thermodynamic properties, which are given as normal distributions.

The solubility of a substance depends not only on the properties of its controlling solid but on the properties of the aqueous species which contribute to its total solution concentration. Thus, the uncertainty of the solubility includes that of the controlling solid and those of the dominant aqueous species. The uncertainty attributable to the controlling solid is constant, but the uncertainty attributable to aqueous species varies because solubilities are reported for a range of chemical conditions and over that range the identity and relative importance of aqueous species differ widely. The uncertainty due to aqueous species is evaluated by examining the solution speciation indicated by the EQ3NR runs at selected chemical conditions. The process by which this uncertainty is evaluated can best be illustrated by a specific example. The uncertainty for uranium is described here to provide this example. The calculations for the other elements to which this process was applied (neptunium, plutonium, and americium) are described in the sections on these elements below.

The outputs of the calculations of uranium solubility (see EQ3NR output files in U.zip of Attachment I) show that the following species constituted more than 5 percent of the dissolved uranium under various of the conditions modeled: $\text{UO}_2(\text{CO}_3)_3^{4-}$, $\text{UO}_2\text{SO}_4(\text{aq})$, $(\text{UO}_2)_2(\text{OH})_2^{2+}$, UO_2F^+ , $\text{UO}_2\text{CO}_3(\text{aq})$, $(\text{UO}_2)_2\text{CO}_3(\text{OH})_3^-$, $\text{UO}_2(\text{CO}_3)_2^{2-}$, $\text{UO}_2\text{F}_2(\text{aq})$, UO_2OH^+ , $\text{UO}_2\text{HPO}_4(\text{aq})$, UO_2PO_4^- , $\text{UO}_2(\text{OH})_3^-$, and HUO_4^- .

Consider the reaction describing the dissolution of the controlling solid, $\text{UO}_3 \cdot 2\text{H}_2\text{O}$, to one of the dominant species, $\text{UO}_2(\text{CO}_3)_2^{2-}$:



This reaction is written in terms of HCO_3^- rather than CO_3^{2-} because under most conditions of interest to this model report the concentration of bicarbonate exceeds that of carbonate.

The standard state Gibbs free energy of the reaction ($\Delta_r G^0$) is the value needed to calculate its log K using $\Delta_r G^0 = -RT \ln K$. This equals:

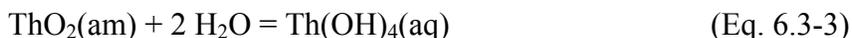
$$\Delta_r G^0(\text{UO}_2(\text{CO}_3)_2^{2-}) = \Delta_f G^0(\text{UO}_2(\text{CO}_3)_2^{2-}) + 3 \cdot \Delta_f G^0(\text{H}_2\text{O}) - \Delta_f G^0(\text{UO}_3 \cdot 2\text{H}_2\text{O}) - 2 \cdot \Delta_f G^0(\text{HCO}_3^-). \quad (\text{Eq. 6.3-2})$$

Because this expression is a simple algebraic sum, the uncertainties of the $\Delta_f G^0$ terms can be combined to give the uncertainty of $\Delta_r G^0(\text{UO}_2(\text{CO}_3)_2^{2-})$ by the usual root-mean-square procedure (Bevington 1969, Section 4-2). This procedure gives ± 2.703 kJ/mol for $2\sigma \Delta_r G^0(\text{UO}_2(\text{CO}_3)_2^{2-})$. Dividing this by $-RT \ln(10)$ ($= -5.708$ kJ/mol at 298.15K) gives $2\sigma \log K = \pm 0.47$ (see Microsoft Excel spreadsheet log K Uncertainties.xls in Attachment I). When this procedure is followed for all 12 dominant aqueous species listed above, it is found that the largest uncertainty at low pH is for the two fluoride complexes, $\text{UO}_2\text{F}_2(\text{aq})$ and UO_2F^+ at $2\sigma \log K \pm 0.5$ and for $\text{UO}_2\text{SO}_4(\text{aq})$ at $2\sigma \log K \pm 0.4$. At high pH the greatest uncertainty is for $(\text{UO}_2)_2\text{CO}_3(\text{OH})_3^-$ at ± 0.99 . This leads to a 1σ standard deviation for the solubility of ± 0.5 , which is applied uniformly to all uranium solubilities.

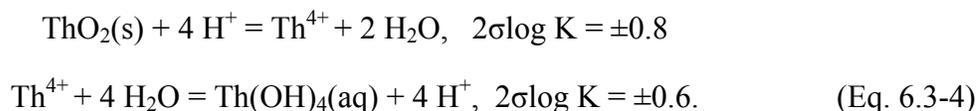
A different approach must be taken to estimate the uncertainty of thorium solubilities because the source of the uncertainty data, Hummel et al. (2002), gives uncertainties for log K values rather than for $\Delta_r G^0$ values. The NEA compilations (Grenthe et al. 1992; Silva et al. 1995; Lemire 2001), from which uncertainty data for uranium, americium, plutonium, and neptunium were taken, also give uncertainty data for some, but not all, necessary log K values. To maintain consistency, uncertainties based on $\Delta_r G^0$ values were used for these elements.

The principal dissolved thorium species accounting for more than 5 percent of the total dissolved thorium were found by examining the EQ3NR output for selected runs representing the range of conditions modeled (see EQ3NR output files in Th.zip of Attachment I). They are: $\text{Th}(\text{SO}_4)_2(\text{aq})$, $\text{Th}(\text{OH})_3\text{CO}_3^-$, $\text{Th}(\text{OH})_4(\text{aq})$, $\text{Th}(\text{CO}_3)_5^{6-}$ and ThF_3^+ .

As an example of the approach taken for thorium consider the reaction for the dissolution of the controlling solid, $\text{ThO}_2(\text{am})$, to one of the dominant species $\text{Th}(\text{OH})_4(\text{aq})$:



The uncertainty of this reaction is not given by Hummel et al. (2002). However, this reaction can be taken as the sum of two other reactions for which Hummel et al. (2002) do give uncertainty data. These are:



These reactions sum to the overall dissolution reaction. Combining their uncertainties using the root-mean-square procedure gives $2\sigma \log K = \pm 1.0$ (see Microsoft Excel spreadsheet Th Uncertainty.xls in Attachment I). When this procedure is followed for all 5 dominant aqueous species listed above, it is found that the largest uncertainty for $2\sigma \log K$ is ± 1.4 for $\text{Th}(\text{CO}_3)_5^{6-}$. This species is dominant at the high end of the pH range. At low pH values the greatest uncertainties are for $\text{Th}(\text{SO}_4)_2(\text{aq})$ and ThF_3^+ with $2\sigma \log K$ values of ± 0.8 and ± 1.3 , respectively. These lead to a 1σ standard deviation for the solubility of ± 0.7 , which is applied uniformly to all thorium solubilities.

$\text{ThO}_2(\text{s})$ appears in the first of the two sub-reactions rather than $\text{ThO}_2(\text{am})$, which is the designation of the controlling phase in data0.ymp.R2 (DTN: MO0302SPATHDYN.000) used for the modeling. The terminology of ThO_2 solids is discussed in Section 5.21.2 of Hummel et al. (2002). The solid they refer to as $\text{ThO}_2(\text{s})$ is also known as $\text{ThO}_2(\text{am})$.

6.3.3.2 Uncertainties in Water Chemistry

The selection of the chemical characteristics of the matrix water used for the solubility calculations is discussed in Section 6.4. The effects of uncertainties on the composition of that water on the modeled solubilities are examined here.

The principal properties of the matrix water to which the solubilities are sensitive are pH, f_{CO_2} , temperature, and fluoride concentration. The effects of varying pH and f_{CO_2} values are

considered explicitly, and the concentrations are presented as look-up tables of solubilities for a range of pH and f_{CO_2} values.

Solubilities of some actinides are also sensitive to the fluoride contents of the matrix water (see Section 6.4). Rather than consider variations in fluoride concentrations explicitly as was done for pH and f_{CO_2} , the effects of different fluoride concentrations are treated as a source of uncertainty in the concentrations. As discussed in Section 6.4, the ranges of fluoride concentrations applicable to CSNF waste differ from those applicable to codisposal waste packages and the invert. To evaluate the fluoride effects on solubilities, calculations were made at the higher fluoride contents possible for each type of waste for a range of pH values at a single f_{CO_2} . The increased solubilities were applied as uncertainties to solubilities calculated for base-case fluoride contents. Two ranges of uncertainty are specified: one for CSNF packages and the other for codisposal packages and the invert. The effects of the highest concentrations on actinide solubilities have been calculated for a range of pH values at a single f_{CO_2} . The uncertainties due to fluoride are treated as a one-sided triangular distribution with the minimum and most probable concentrations those of the base case and the maximum concentration that calculated with the high fluoride concentration.

6.3.3.3 Uncertainties in Temperature

All calculations were made at 25°C, although liquid water can exist at temperatures to 100°C or more. To estimate the effects of changing temperature on solubilities calculations were made at 100°C for a range of pH values at a single f_{CO_2} . These results are summarized in Table 6.3-1.

The differences vary with pH, so the maximum and minimum differences for each element are given. In all cases, the solubilities at 100°C are lower than those at 25°C. The minimum differences in the logs of the solubilities range from -0.27 to -2.06, and the maximum differences from -1.77 to -4.88.

Solubilities given in this report are for 25°C. Because of the lower solubilities at higher temperatures, this is a conservative approach.

Table 6.3-1. Differences in Solubility of Solids Modeled at 25°C and 100°C

	SOLID	PuO ₂	Np ₂ O ₅	NpO ₂	Schoepite (UO ₃ ·2H ₂ O)	AmOHCO ₃
Minimum Difference	$\log[C]_{100C} - \log[C]_{25C}$	-0.79	-1.48	-1.76	-0.27	-2.06
Maximum Difference	$\log[C]_{100C} - \log[C]_{25C}$	-3.74	-4.11	-4.88	-1.77	-3.85

Sources: Microsoft Excel spreadsheets in Spreadsheets.zip in Attachment I: PuO₂ Solubility.xls (cells K63:K64), Np₂O₅ Solubility.xls (cells W29, W32), NpO₂ Solubility.xls (cells Y30:Y31), U Solubility.xls (cells AJ27:AJ28), and Am Solubility.xls (W23:W24)

NOTE: Calculations were made at $\log(f_{CO_2}) = -3.00$ for range of pH values. Maximum and minimum differences occur at different pH values.

6.3.3.4 Uncertainties of Activity Coefficients

Electrolyte solutions differ substantially from ideal solutions. Nevertheless, thermodynamic calculations for electrolytes are based on the equations for ideal solutions with the use of

approximate corrections, known as activity coefficients. Activity coefficients are multiplied by concentrations, specifically molalities, to obtain the activities needed in calculations of solubilities, i.e., $\gamma_i m_i = a_i$, where γ_i is the activity coefficient, m_i , the molality (such as the solubility of a solid), and a_i the activity for the ion, i . The smaller the value of γ for a given activity, calculated, for example, from a solubility product, the larger the molality or solubility. All known activity coefficient models have limitations which introduce uncertainty into the calculations.

Appendix D of *Degraded Mode Criticality Analysis of Immobilized Plutonium Waste Forms in a Geologic Repository* (CRWMS M&O 1997) provides examples comparing activity coefficients derived from experimental measurements with those calculated by EQ3/6 according to the Hückel (called b-dot within the EQ3/6 documentation) equation. For simple salts with low ionic charges, specifically for NaCl, the calculated mean ionic activity coefficient is about 10 percent too small for ionic strength (I) 1.0, and changes to 16 percent too small at I = 2.0. For KCl the deviations are less, about 1 percent too small at I = 1.0 and 2 percent too large at I = 2.0. Deviations become larger with increasing I and in general with increasing ionic charge. For example, for $\text{Al}(\text{NO}_3)_3$ the calculated value is nearly 80 percent too small at I = 1.2, and for LaCl_3 it is about 40 percent too small at I = 6.0.

The “b-dot” equation was used in this report to calculate activity coefficients. One of the main uncertainties within the “b-dot” equation arises from the choice of the \AA parameter, variously called the hard core diameter of the ion or the mean distance of closest approach of ions of opposite charge. Ionic strength was calculated according to $I = 0.5\sum m_i z_i^2$, where m_i represents the concentration of ion, i , and z_i its ionic charge. Thus, the activity coefficient calculated for La^{3+} would be the same for a trace of La in a one molal NaCl solution as in a 1/6 molal solution of LaCl_3 . A 0.1 molal solution of $\text{Pu}(\text{NO}_3)_4$ would also have an ionic strength of 1.0.

The importance of the choice of a value for \AA becomes apparent from the calculations and discussion included in Section 5.1.2 of *In-Drift Accumulation of Fissile Material from Waste Packages Containing Plutonium Disposition Waste Forms* (CRWMS M&O 2000g). This reference includes computations made using the “b-dot” equation:

$$\log_{10} \gamma_i = -\frac{Az_i^2 \sqrt{I}}{1 + \frac{\text{\AA}}{a} B \sqrt{I}} + B^{\circ} I \quad (\text{Eq. 6.3-5})$$

(Wolery 1992, Section 3.3) and compares them with those obtained from the Specific Ion Interaction (SIT) Theory (Grenthe et al. 1992, Appendix B). In the “b-dot” equation, A, B, and B° are temperature dependent parameters and γ_i is the activity coefficient of ion i . For tetravalent ions, such as Th^{4+} and Pu^{4+} , at ionic strength 1.0 and, for the “b-dot” equation, \AA of 4, as given in data0.ymp.R2, the SIT value for γ is about twice the “b-dot” value. A much better fit is obtained for an \AA of 5. This factor of two would translate to a doubling of the solubility as calculated using the “b-dot” equation as compared to using the SIT approach, if the dominant solution species were the Th^{4+} , Pu^{4+} , or some other tetravalent ion, such as $\text{UO}_2(\text{CO}_3)_3^{4-}$. This would occur only at very low pHs for the first two or very high pH for the last.

On the other hand, examination of the outputs of the EQ3NR solubility calculations shows that such high charges for the most important dissolved species seldom occur. Specifically, this is found only for plutonium and neptunium, in the form of the $\text{PuO}_2(\text{CO}_3)_3^{4-}$ and $\text{NpO}_2(\text{CO}_3)_3^{4-}$, respectively, above a pH of about 8. The corresponding species for uranium also is reported in the output for some neutral to high pH calculations, but only as a minor species. Because the use of the “b-dot” equation, as compared to the SIT or similar approaches, results in higher solubilities, it is conservative, and may be used at sufficiently small concentrations without incorporating its uncertainty into the overall solubility uncertainty.

The most important point, however, is that activity coefficients calculated using the “b-dot” equation become increasingly unreliable as ionic strength increases. The valid range of data0.ymp.r2 is up to ionic strengths of 1 molal (Steinborn et al. 2003, p. 60). For this reason results found for calculated ionic strengths greater than 1.0 are considered invalid and are rejected.

6.3.3.5 Uncertainties from Selection of Controlling Phase

For all modeled elements except plutonium solubility control by phases other than that used for the base case are considered as alternative conceptual models. Differences in solubilities of alternative conceptual model phases are not considered uncertainties in the solubilities calculated from the base-case mineral.

For plutonium, the base-case, solubility-controlling phase selected has properties intermediate between those of two known phases. The uncertainties in plutonium solubilities are based on the range of solubilities between the two known solids as discussed in Section 6.5.

6.4 CHEMICAL CONDITIONS FOR SOLUBILITY CALCULATIONS

The solubility of an element depends on the nature of the solubility-controlling phase and the physical and chemical properties of the solution and its environment. In theory, the solubility of a phase can be calculated for a given solution. However, the interactions among solute species are too complicated for their modeling to be included directly in a system performance assessment. Simplifying solubility calculations by focusing on the most important controlling factors allows a feasible, yet realistic model to be included in system assessment. To achieve the most representative simplification, the chemical conditions must be ranked by their importance. The simplification process is broken into three parts: first are the simplifications that can be made based on knowledge of actinide properties and behavior, second are the simplifications that can be made to the site-specific water composition information, and third is how these simplifications can be incorporated into the model.

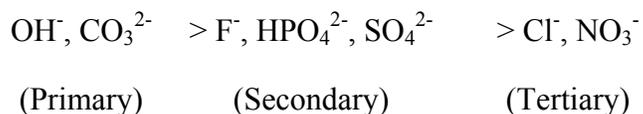
6.4.1 Actinide Properties

The chemical and physical conditions most important to determining the solubilities of actinide elements are oxidation potential, pH, temperature, and concentrations of ligands that form strong solution complexes (including ion pairs) with dissolved actinide species.

Of these, the oxidation potential has the strongest single effect on solubility of all actinides except thorium and americium, which are relatively redox-insensitive. pH affects solubility in

two ways. Typically in acidic solutions hydrogen ion reacts with a solid to release cations to solution, e.g., by combining with oxide in the solid to form water. In basic (high pH) solutions OH^- may act as a ligand that forms complexes with the cations in the solid, thereby increasing the solubility. Temperature changes may raise or lower solubilities depending on the element and the specific conditions being considered.

For the most common ligands in the environment, the trend in strengths of complexation is (Silva and Nitsche 1995):



Primary Ligands: Actinide solubilities increase with decreasing pH values under acid conditions. Because of the strength of OH^- complexes, solubilities also increase with pH values under alkaline conditions. The concentration of CO_3^{2-} increases with f_{CO_2} and pH, which also increases actinide solubility because of the strength of CO_3^{2-} complexes.

Secondary Ligands: The ligands F^- , HPO_4^{2-} , and SO_4^{2-} , if present in high enough concentrations could affect actinide solubilities. The effects of these ligands are considered in Sections 6.4.2.5.1 and 6.4.3.6.

Tertiary Ligands and Cations: Cl^- and NO_3^- are weakly complexing ligands and do not occur in high enough concentrations to be considered in the modeling. Generally speaking, the effect of cation concentrations on actinide solubility is weak because they do not form complexes with actinides. They influence actinide solubility through their effects on ionic strengths and as ligands competing with actinides for complex-forming anions. Because the most common cations in the repository environments (Na^+ , K^+ , Ca^{2+} , and Mg^{2+}) form complexes with carbonate, bicarbonate, or sulfate that account for only a few percent of their total dissolved concentrations, only their ionic strength effects are important (see EQ3NR output files contained in the file U.zip of Attachment I). However, because of the way in which the EQ3NR solubility models are configured, as discussed below, the calculated concentrations of hydroxide and carbonate may be extremely, even unrealistically, high.

Based on the discussion above, f_{O_2} , pH, f_{CO_2} , temperature, and concentration of ligands in water are considered in this report to calculate the actinide solubilities.

The impacts of elements other than those listed in Table 4-2, or considered specifically in sections 6.5 through 6.18, relate either to complexes that these ions may form with radionuclides, their effect on pH, or their effect on ionic strength. Other elements expected to be present in potentially significant amounts within the waste package or the invert are lithium, boron, aluminum, titanium, chromium, manganese, iron, nickel, zirconium, hafnium, and possibly vanadium, cobalt, niobium, molybdenum, and tungsten. None of these is known to form complexes with any of the radionuclides considered in this model report, as shown for the actinides by examination of Table III.1 in *Chemical Thermodynamics of Uranium* (Grenthe et al. 1992), Table III.1 in *Chemical Thermodynamics of Americium* (Silva et al. 1995), and Tables 3.1

and 4.1 in *Chemical Thermodynamics of Neptunium and Plutonium* (Lemire 2001). Therefore, they are not included in model calculations in this report.

The previous discussion considers the relative importance of various chemical conditions to actinide solubility. In order to choose the right variables to be accounted for in solubility evaluation, site-specific information also needs to be considered, such as the levels and ranges of common cations and anions.

6.4.2 Site-Specific Chemical Conditions

The chemical conditions controlling dissolved concentrations may vary widely from place to place and at different periods of repository evolution. Thus, the solubility calculations have been made over a range of conditions that are expected to include the actual conditions. This section discusses how the countless possibilities are simplified, based on site-specific characteristics.

This study considers two types of waste packages, consistent with TSPA models (CRWMS M&O 2000b, Section 3.5.1). One contains CSNF and the other, called codisposal packages, contains defense spent nuclear fuel and high-level waste glass.

6.4.2.1 Oxidation Potential

The design of the repository is such that the waste will be under atmospheric conditions except in isolated, local situations. Thus, oxidizing conditions are assumed (see Assumption 5.1), and all solubilities were calculated with an f_{O_2} of 0.2 bars, the atmospheric value.

6.4.2.2 Temperature

Due to decay heat from the waste, it is expected that the temperature within waste packages will increase from the ambient temperature. Immediately after the emplacement of waste packages, the temperature can go to nearly 200°C (CRWMS M&O 2000b, Figure 3.3-9). The temperature in the repository relevant to this model is between 25 to 100°C since any temperature above boiling is not important for solubility considerations. Only solubilities at 25°C are given. As discussed in Section 6.3.3.3, solubilities decrease with increasing temperature so the use of 25°C solubilities is conservative.

6.4.2.3 pH

According to *In-Package Chemistry for Waste Forms* (BSC 2001d, Table 3, p. 24), the pH range for fluids reacting with CSNF is 3.9 to 8.1, while the range for fluids reacting with codisposal materials is from 3.3 to 10. To cover both types of waste packages and possible extreme conditions, the pH range was set to 3-11.

6.4.2.4 CO₂ Fugacity

The atmospheric value of CO₂ partial pressure is 10^{-3.5} bars. Table 4-17 of *Yucca Mountain Science and Engineering Report* (DOE 2002, p. 4-191) gives the range of log f_{CO_2} from -2.0 to -3.0, except for the boiling period, to which the results of this model report are not applicable. This revision of the document considers a broader range of 10^{-5.0} to 10^{-1.5} bars for the

plutonium, neptunium, uranium, thorium, americium, actinium, and protactinium solubility models to cover its likely range.

6.4.2.5 Water Composition

Table 4-2 gives the composition of the base-case water used in the solubility calculations. A water of this composition has been used as the reference water composition for the Yucca Mountain site for many years. A detailed rationale for using water of this composition as a reference water for the repository has been thoroughly discussed by a project committee (Harrar et al. 1990).

The compositions of ten different pore waters collected from 15 ECRB-SYS-SERIES boreholes of the Yucca Mountain site (USW SD-9 and USW NRG-7/7A) were reported in DTN: GS020408312272.003. For the nine components (Na^+ , K^+ , Ca^{2+} , Mg^{2+} , $\text{SiO}_2(\text{aq})$, Cl^- , F^- , NO_3^- , and SO_4^{2-}) listed in Table 4-2, these pore waters are similar to the composition of the base-case water. The ratios of the average pore water values to the base-case values of those nine components range from 0.43 (for NO_3^-) to 8.98 (for Ca^{2+}), and the ratio of the maximum values of those nine components to the base-case values range from 1.07 to 18.46 (see Microsoft Excel spreadsheet Pore Water.xls in Spreadsheets.zip of Attachment I). As the sensitivity analysis described below covers the range up to 100 times of the base-case values for those nine components, the results and conclusions reached in this section should be also applicable to the pore waters that might become infiltrating waters.

6.4.2.5.1 Sensitivity Analysis

To assess the effects of varying ligand concentrations on solubility, a series of sensitivity analyses was conducted over a range of pH values at a fixed f_{CO_2} ($10^{-3.0}$ bars). The sensitivity analysis mainly studied the solubility of plutonium, an actinide important to dose at $t < 10,000$ years.

A first set of test cases was run with the base-case water composition given in Table 4-2. Additional sets were run with concentrations of all constituents increased up to 1000 times their original values ($1\times$ [base case], $10\times$, $100\times$, and $1000\times$), with the results shown in Figure 6.4-1. Then, separate sets of runs were conducted that varied selected solutes individually at $10\times$ and $100\times$. These files are located in Attachment I in the Sensitivities directory. The results of these calculations are shown in Figure 6.4-2 through Figure 6.4-11.

The purpose of the sensitivity studies is to analyze the effects of a single factor on solubility. Often, it is not possible to isolate the effects of one factor, because when that factor is changed, it causes something else to change. For example, to change the value of pH in the EQ3NR code, anions or cations are added to the solution for charge balance. The effect of adding these ions was minimized by selecting the most innocuous ions to get the desired pH (using the charge balance feature in EQ3NR). More acidic solutions were balanced by adding Cl^- , while more basic solutions by adding Na^+ . These reactants were chosen because actinide chloride and sodium species are some of the least likely to form. For the specific Na^+ and Cl^- sensitivities (Figures 6.4-4 and 6.4-8, respectively) the cation and anions that were used were K^+ and NO_3^- , so as not to interfere with the actual subject of the sensitivity.

All of the plutonium solubility plots have similar shapes. Solubilities are highest at the lowest pH values and decrease to minima at pH values in the range of 7 to 8. Solubilities increase slightly with increasing pH values above 8 or 9.

The sensitivity analyses show that increases in both F^- and SO_4^{2-} concentrations lead to higher solubilities under neutral and moderately acid conditions (Figures 6.4-2 and 6.4-3). The concentrations of the four cations (Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Figures 6.4-4, 6.4-5, 6.4-6, and 6.4-7) affect plutonium solubility very little at low to circum-neutral pH values. The concentrations of Cl^- , NO_3^- and $SiO_2(aq)$ show little effect as well, as seen in Figures 6.4-8 through 6.4-10.

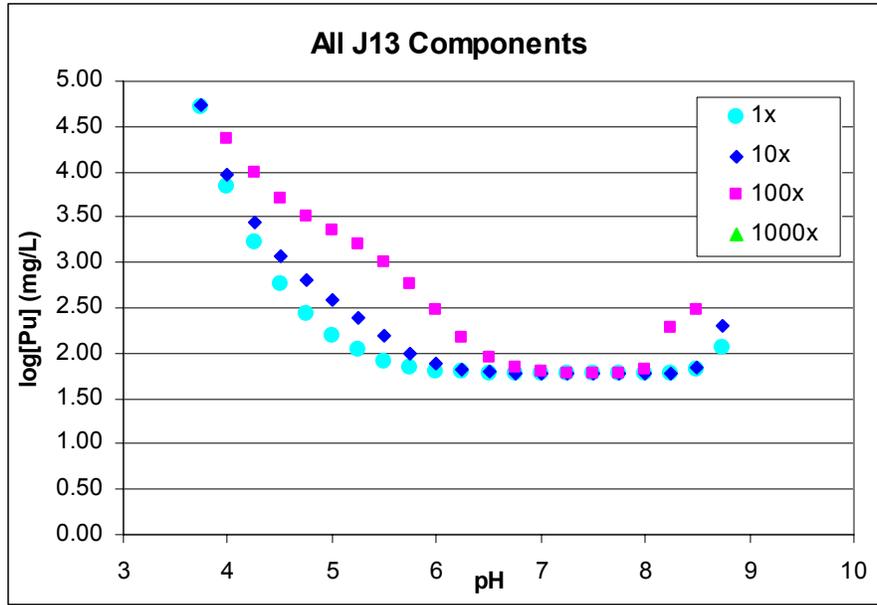
The effects of changing phosphate concentrations were examined using a different procedure. Because there are relatively few data available for plutonium–phosphate solid and aqueous species, the sensitivity analysis was done using uranium for which there are many more data. The uranium solubilities reported in this report are based on schoepite ($UO_3 \cdot 2H_2O$). A number of sparingly-soluble uranyl phosphate solids are given in data0.ymp.R2 including $(UO_2)_3(PO_4)_2$, $(UO_2)_3(PO_4)_2 \cdot 4H_2O$ and $(UO_2)_3(PO_4)_2 \cdot 6H_2O$. In examining the effects of changing phosphate concentrations on schoepite solubility, the influence of these solids was also considered.

An additional set of solubility cases were run for a range of pH values at a fixed f_{CO_2} of $10^{-3.5}$ bars. The uranium concentration was fixed by schoepite saturation and the total phosphate concentration by saturation with $(UO_2)_3(PO_4)_2 \cdot 4H_2O$. The results are shown in Figure 6.4-11.

As the figure shows, the phosphate contents are about 10^{-3} mg/L at low pH values, but begin to rise at pH values above about 6. For reasons discussed in Section 6.4.4, the model does not converge for pH values above 8.25. Thus no modeled phosphate concentrations are available above this pH.

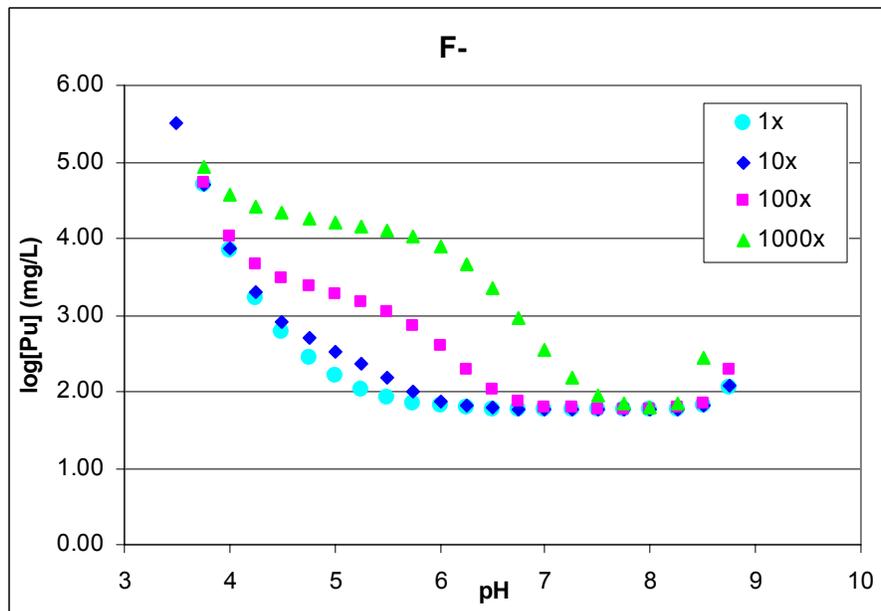
Phosphate analyses of the water chosen as the reference water (Table 4-2) vary from less than 0.01 mg/L to more than 0.1 mg/L (Harrar et al. 1990). As discussed in Section 6.4.3.6, the phosphate concentration of the base-case water is chosen as 0.1 mg/L. This value is also shown for reference on Figure 6.4-11. Dissolved phosphate concentrations at saturation with both schoepite and $(UO_2)_3(PO_4)_2 \cdot 4H_2O$ are below the reference water concentration at pH values below about 7.5 and above it at higher pH values.

The point of this sensitivity exercise is to examine whether phosphate concentrations above the reference water value will increase the dissolved uranium concentration. As the figure shows, the uranium concentrations are virtually identical whether modeled using the reference water phosphate concentration or with phosphate concentrations controlled by $(UO_2)_3(PO_4)_2 \cdot 4H_2O$ saturation. This also means that should phosphate be added to the system from the degradation of waste glass, for example, the dissolved phosphate concentration of the solution will not rise because it will be fixed by the precipitation of a $(UO_2)_3(PO_4)_2$ solid.



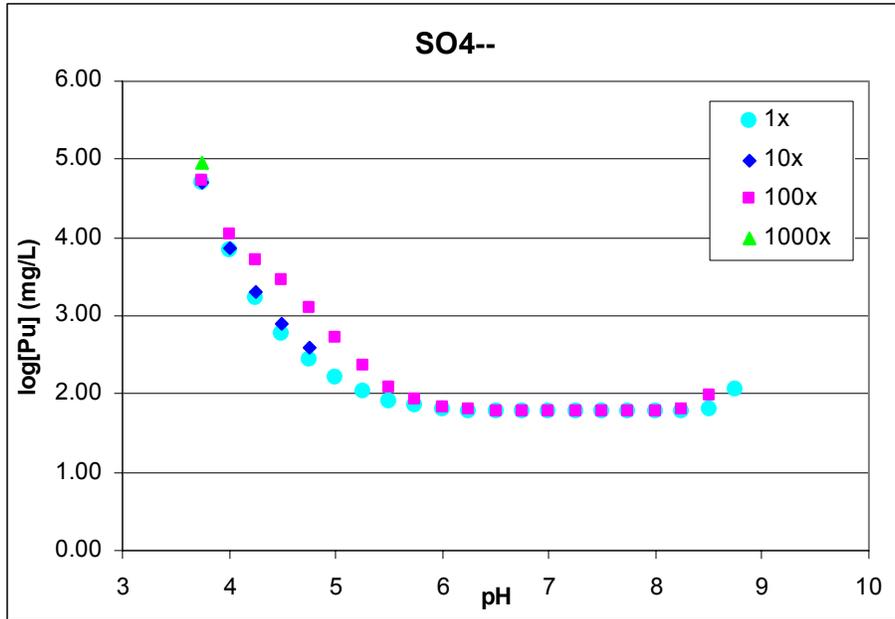
Source: Microsoft Excel spreadsheet Sensitivies.xls in Spreadsheets.zip (Attachment I)

Figure 6.4-1. Sensitivity to Variation in the Total Concentration of the Base-Case Water



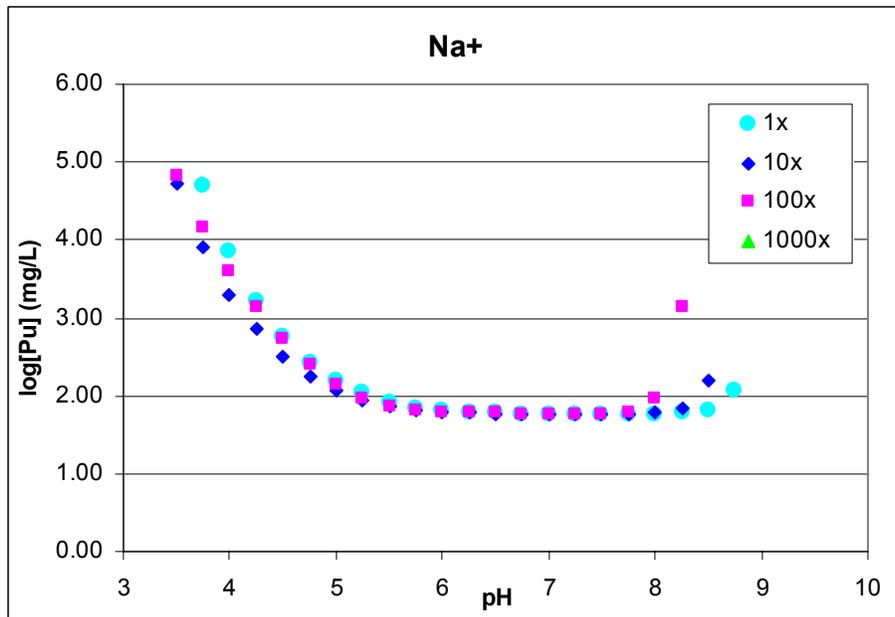
Source: Microsoft Excel spreadsheet Sensitivies.xls in Spreadsheets.zip (Attachment I)

Figure 6.4-2. F⁻ Sensitivity



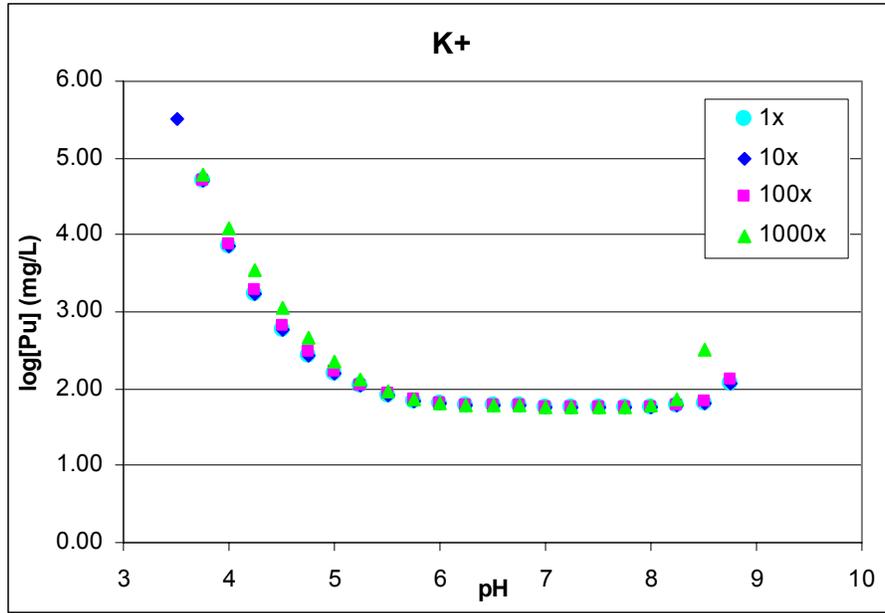
Source: Microsoft Excel spreadsheet Sensitivies.xls in Spreadsheets.zip (Attachment I)

Figure 6.4-3. SO₄²⁻ Sensitivity



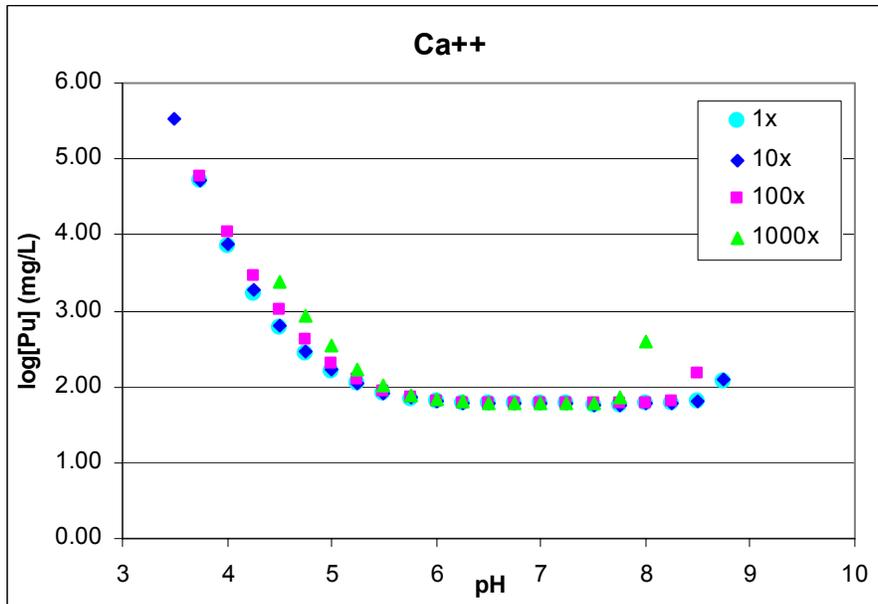
Source: Microsoft Excel spreadsheet Sensitivies.xls in Spreadsheets.zip (Attachment I)

Figure 6.4-4. Na⁺ Sensitivity



Source: Microsoft Excel spreadsheet Sensivities.xls in Spreadsheets.zip (Attachment I)

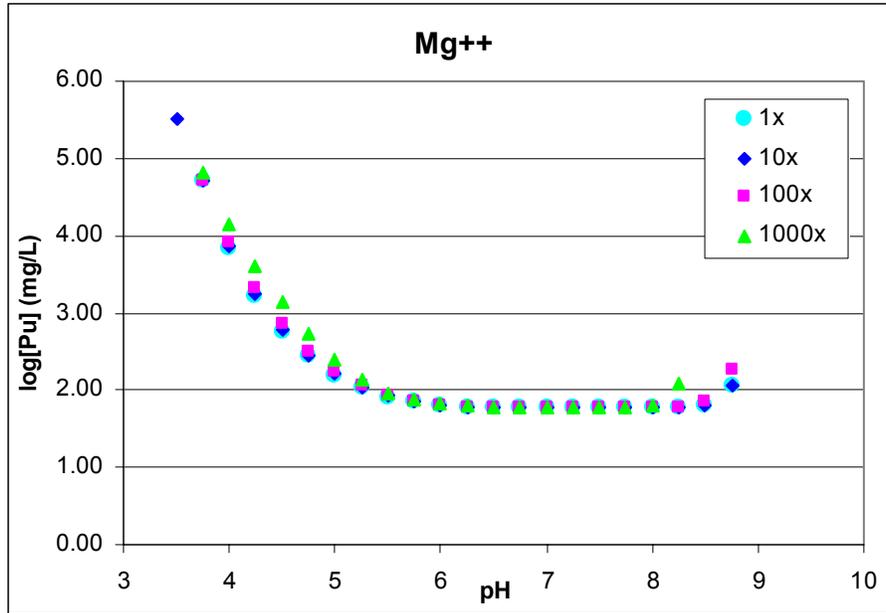
Figure 6.4-5. K⁺ Sensitivity



Source: Microsoft Excel spreadsheet Sensivities.xls in Spreadsheets.zip (Attachment I)

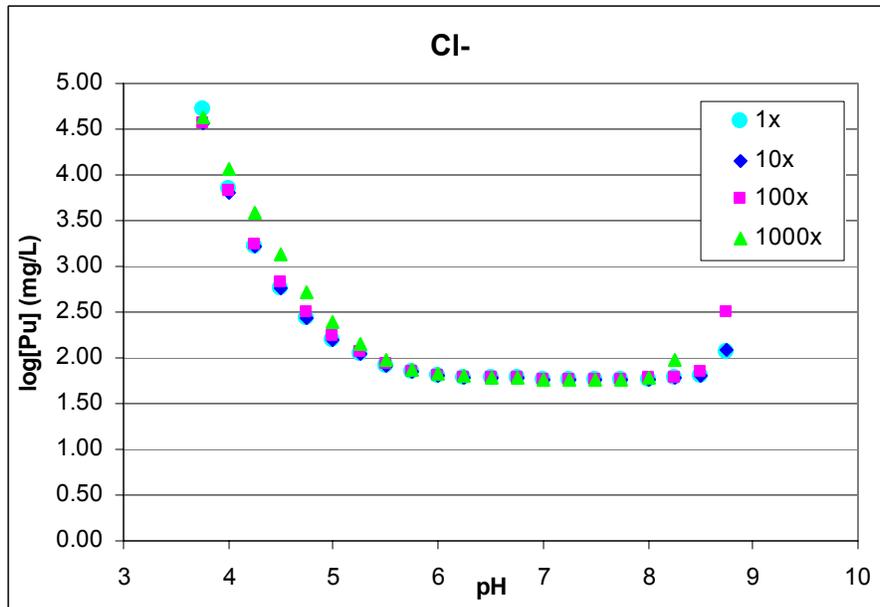
Figure 6.4-6. Ca²⁺ Sensitivity

Dissolved Concentration Limits of Radioactive Elements



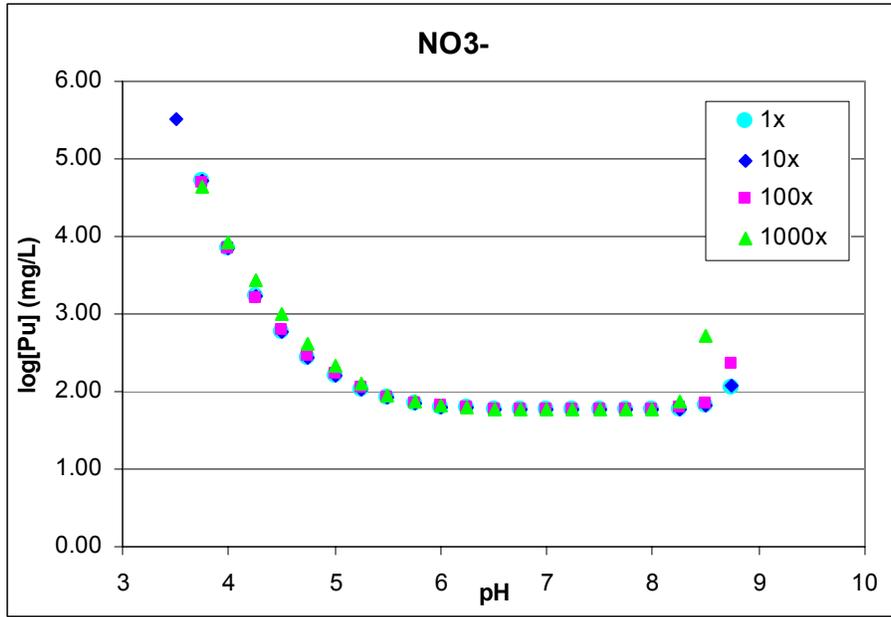
Source: Microsoft Excel spreadsheet Sensivities.xls in Spreadsheets.zip (Attachment I)

Figure 6.4-7. Mg²⁺ Sensitivity



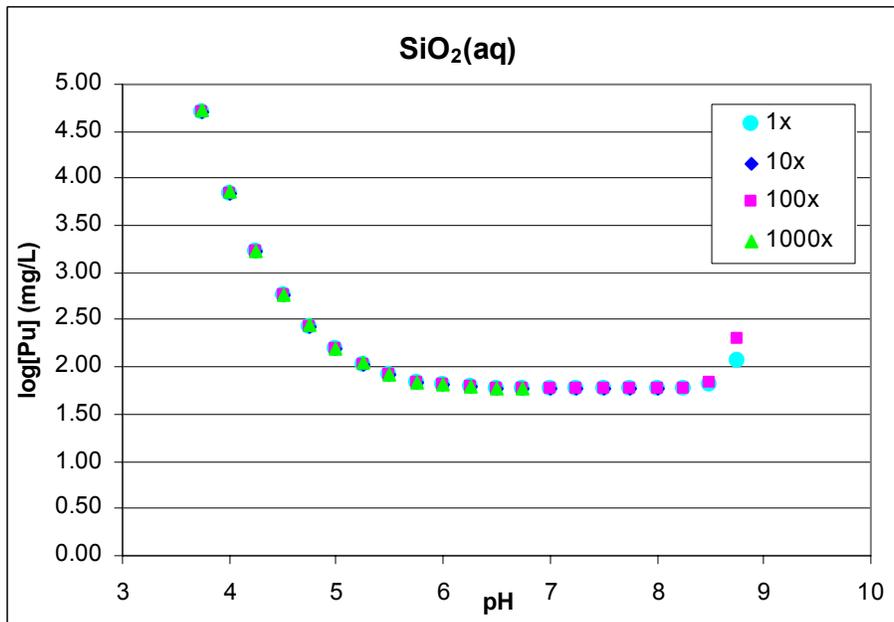
Source: Microsoft Excel spreadsheet Sensivities.xls in Spreadsheets.zip (Attachment I)

Figure 6.4-8. Cl⁻ Sensitivity



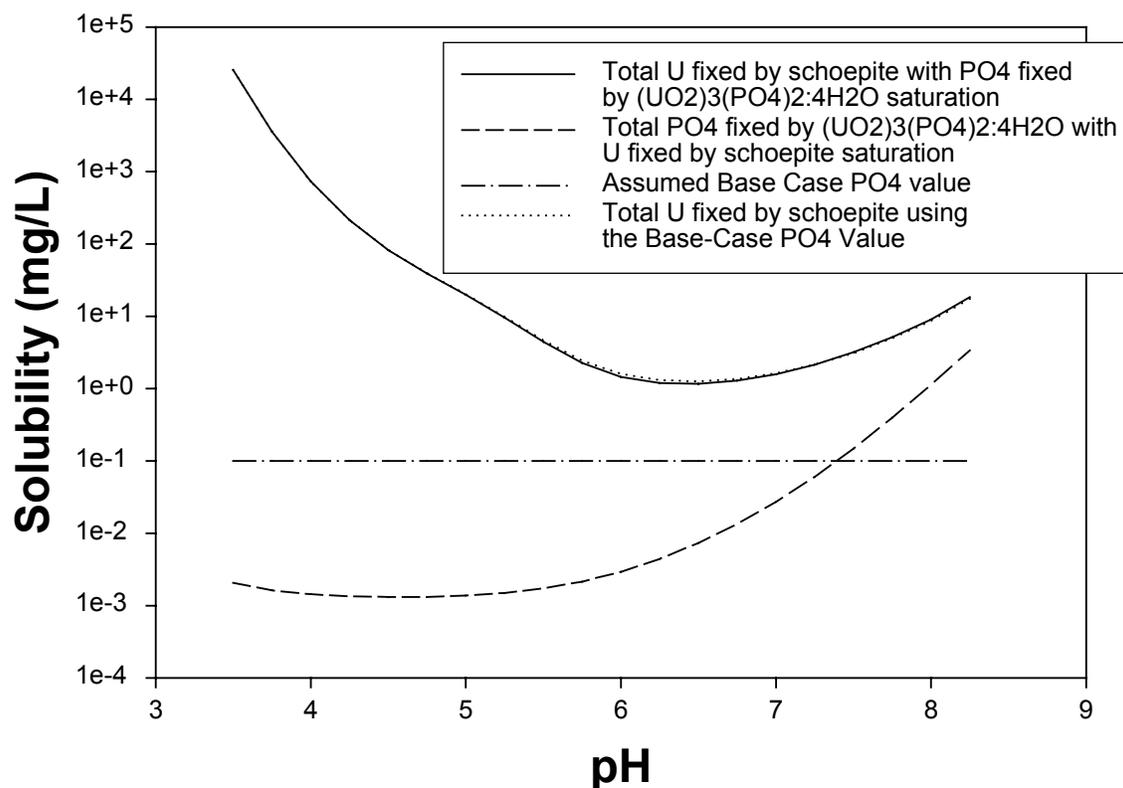
Source: Microsoft Excel spreadsheet Sensivities.xls in Spreadsheets.zip (Attachment I)

Figure 6.4-9. NO₃⁻ Sensitivity



Source: Microsoft Excel spreadsheet Sensivities.xls in Spreadsheets.zip (Attachment I)

Figure 6.4-10. SiO₂(aq) Sensitivity



Source: PO4solb2.jnb in SigmaPlots.zip and Microsoft Excel spreadsheet PO4sensitivity.xls in Spreadsheets.zip (Attachment I)

Figure 6.4-11. Effect of $(\text{UO}_2)_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ Saturation on Uranium Solubility

From the sensitivity analyses, it is concluded that the important chemical conditions, in addition to f_{O_2} , pH and f_{CO_2} are the concentrations of F^- and SO_4^{2-} .

6.4.3 Model Configuration

In the previous discussion, it is concluded that the important physical and chemical conditions for solubility evaluation are oxidation potential, pH, f_{CO_2} , concentrations of SO_4^{2-} and F^- , and temperature. This section explains how each parameter is accounted for in geochemical model calculations, whether they will be treated as an independent variable or as an uncertainty term, and how each parameter is varied.

6.4.3.1 Oxidation Potential

The oxidation state is assumed to be controlled by the atmosphere (see Assumption 5.1). To achieve this, the value of f_{O_2} is set to 0.2 bars.

6.4.3.2 Temperature

Solubility is calculated at 25°C. As shown in Section 6.3.3.3, the solubility of plutonium, neptunium, uranium, and americium decreases with temperature. By analogy, thorium should behave similarly to other actinide elements. Thus, it is reasonable to expect that thorium should have retrograde solubility as well. Therefore, using actinide solubilities at 25°C would be conservative for temperatures higher than 25°C.

6.4.3.3 pH

Because of its strong effect on actinide solubility pH is selected as an independent variable in solubility calculations. In other words, solubility calculations are carried out for different pH values. According to *In-Package Chemistry for Waste Forms* (BSC 2001d, Table 3, p. 24), the pH range for CSNF is 3.9 to 8.1, while the range for codisposal waste packages is from 3.3 to 10. To cover both types of waste packages and possible extreme conditions, a pH range from 3.0 to 11.0 was chosen. The pH was varied in increments of 0.25 pH units.

6.4.3.4 CO₂ Fugacity

As discussed above, f_{CO_2} is another important independent variable in actinide solubility models because of the strong tendency for actinides to form complexes with CO_3^{2-} . The atmospheric value of CO_2 partial pressure is $10^{-3.5}$ bars. Table 4-17 of *Yucca Mountain Science and Engineering Report* (DOE 2002, p. 4-191) gives the range of $\log f_{\text{CO}_2}$ from -2.0 to -2.8 bars, except for the boiling period, to which the results of this model report are not applicable. This is also the value used in *In-Package Chemistry for Waste Forms* (BSC 2001d, Section 5). The f_{CO_2} range used for actinide solubility calculations in this report is from 10^{-5} to $10^{-1.5}$ bars. It is varied in increments of 0.5 log units.

6.4.3.5 Charge Balance Species: SO_4^{2-} and Na^+

In the EQ3NR modeling done to calculate solubilities, assigning a pH value different from that of the initial base-case water leads to solutions that are not electrically neutral (charge balanced). To maintain charge balance in the solution modeled, a charge-balancing cation or anion can be added during the modeling. The in-package chemistry study indicates that the major driving force for lowering pH is the oxidation of A516 carbon steel (which contains sulfur), while the major driving force for pH increase is the release of alkali and alkaline earth metals from waste glass dissolution (BSC 2001d, p. 23). In accordance with these studies, SO_4^{2-} is specified as the anion added to balance low pH solutions and Na^+ as the cation to balance high pH solutions. This is achieved by specifying one of them, in EQ3NR calculations as the species to be adjusted for charge balance. For runs near neutral, the choice of whether to balance on SO_4^{2-} or Na^+ is made by checking to see if the code is balancing by adding or subtracting the charge-balancing ion. If the balancing ion is being subtracted, the resulting solution will have a lower concentration of the balancing ion than the input water composition. Only runs balanced by adding the charge-balancing ion were used. Because SO_4^{2-} is one of the balancing ions, the effects of changing concentration on solubility are also accounted for.

6.4.3.6 Concentration of Secondary Ligands (F^- , HPO_4^- , and SO_4^{2-})

TSPA models two types of waste packages. The CSNF waste packages comprise more than 90 percent of the waste inventory with codisposal waste package making up the remainder (CRWMS M&O 2000b, Section 3.5.1). The concentration range of fluorides in CSNF waste packages was given in *In-Package Chemistry for Waste Forms* (BSC 2001d; DTN: SN0009T0811199.008). The maximum value is $7.71E-4$ mol/kg (14.6 mg/L), which is about 6.7 times that of the base-case value. The minimum value is $1.22E-6$ mol/kg (0.0232 mg/L), which is less than the base-case value. A range from the base-case value (2.18 mg/L) to 10 times the base-case value (21.8 mg/L) is assigned to fluoride concentration in the CSNF waste packages.

In-Package Chemistry Abstraction (BSC 2001e) also gives fluoride concentrations for 11 codisposal waste packages (DTN: SN0009T0811199.008). The highest fluorine concentration is $2.27E-2$ mol/kg, which is 198 times higher than the base-case value. The lowest concentration is $1.05E-17$ mol/kg, which is 13 orders of magnitude lower than the base-case value, but a lower fluorine concentration yields a lower solubility, so it is conservative to set the minimum fluorine concentration to the base-case value. For the codisposal waste packages, the maximum fluorine concentration is set at 200 times the base-case value (436 mg/L). There are no known sources of fluorine in the invert other than that coming from the high level waste glass contained in the codisposal waste packages; therefore, the maximum fluorine concentration should not be greater than that in the solution in the codisposal waste packages. Thus, the same range of fluorine concentration (from the base-case value to 200 times the base-case value) is assigned to the invert.

Because of the existence of large quantities of uranium in the repository and the low solubility of uranium-phosphate minerals, Section 6.4.2.5 concludes that the influence of phosphate concentration on actinide solubility is negligible. Nonetheless, phosphate as a component is included in the model calculation and a base-case value is elected based on Table 4.2 of *Report of the Committee to Review the Use of J-13 Well Water in Nevada Nuclear Waste Storage Investigations* (Harrar et al. 1990), which gives 9 measurements of PO_4^{3-} for the reference water. Four of them are listed as less than 10 $\mu\text{g/L}$, two of them as less than 100 $\mu\text{g/L}$, and the remaining three are 120, 100, and 2800 $\mu\text{g/L}$ respectively. However, the latter two are marked as “probably erroneous” and, thus, are excluded from consideration. Because the majority of the remaining 7 measurements are less than 100 $\mu\text{g/L}$, this model report assigns the value of 0.1 mg/L to HPO_4^{2-} .

SO_4^{2-} concentrations also have an influence on actinide solubilities. As discussed in Section 6.4.3.5, this ligand is associated with the acidity of waste package solutions and is treated as the charge-balancing species in the EQ3NR solubility calculations. As there is no known source of SO_4^{2-} other than steels in waste packages, the effect of SO_4^{2-} concentration on actinide solubilities is accounted for by linking its variation with pH changes.

6.4.3.7 Concentration of Tertiary Ligands (Cl^- and NO_3^-) and Cations

Based on the discussion in Section 6.4.1 and Section 6.4.2.5.1, the effects of the tertiary ligands (Cl^- and NO_3^-) and the four common cations (K^+ , Na^+ , Ca^{2+} , and Mg^{2+}) are very minor. Thus,

using their base-case values is justified. In addition, Na^+ is used to balance charge in the solution (see Section 6.4.3.5), which accounts for the potential variation in common cation concentrations.

Depending on the fugacity of CO_2 , when pH increases sufficiently, some cations would be expected to precipitate. This is because the solution is set to be in equilibrium with f_{CO_2} , which could result in the formation of carbonate solids. For example, the EQ3NR runs show that the solution becomes supersaturated in calcite at pH between 8.0 and 8.25 when $\log f_{\text{CO}_2} = -3.0$. Similarly, the EQ3NR outputs commonly show fluorapatite $[\text{Ca}_5\text{F}(\text{PO}_4)_3]$ supersaturation at high pH owing to the conversion of protonated phosphate anions, such as HPO_4^{2-} , to PO_4^{3-} . If precipitation does not occur, the ionic strength will remain relatively high, thereby maintaining a somewhat higher solubility of radionuclides as a consequence of the salting in effect (i.e., activity coefficients will stay relatively low). However, the main effect of the supersaturation in carbonate and fluoride will be to leave these ions in solution and thereby increase the concentrations of carbonate and fluoride complexes with actinides. Thus, the actinide solubilities calculated by EQ3NR without precipitation will be conservatively high.

The above discussion on model configuration is summarized in Table 6.4-1.

Table 6.4-1. Summary of EQ3NR Model Configuration

Variable	Treatment in Model	Value or Range
pH	Independent variable	3.0 to 11.0
$\log f_{\text{CO}_2}$	Independent variable	-5.0 to -1.5
Temperature	Conservatively using 25°C value	25 to 100°C
$\log f_{\text{O}_2}$	Constant	-0.7
F ⁻ concentration	Uncertainty term	1 to 10 times the base-case value for CSNF waste packages; 1 to 200 times the base-case value for codisposal waste packages; and 1 to 200 times the base-case value for the invert
SO_4^{2-} concentration	Charge balance species	Concentration automatically determined by the code
Na^+ concentration	Charge balance species	Concentration automatically determined by the code
PO_4^{3-} , NO_3^- , and Cl^-	Constant	The base-case value
K^+ , Ca^{2+} , and Mg^{2+}	Constant	The base-case value

6.4.4 Valid Ranges of Solubility Models

As discussed in the previous section, the solubility models developed in this model report are valid for broad ranges of water composition as listed in Table 6.4-1. However, three exceptions should be noted.

The first exception arises from the limitations in activity coefficient corrections. Thermodynamic properties of electrolyte solutions differ significantly from ideal solutions owing to the charges on the ions. The greater the ionic charges and the more concentrated the solutions, the greater are the deviations. For sufficiently dilute solutions the Debye-Hückel equation provides an accurate calculation for these deviations. However, this equation fails for more

concentrated solutions. The Hückel equation, called the B-dot equation in the computer code package, EQ3/6, provides a good approximate extension of the equation for solutions of somewhat higher concentration. For solutions consisting only of univalent ions, such as in NaCl solutions, this approximation gives good results up to ionic strengths of 3 molal or higher. However, corrections from ideality, known as activity coefficients, for polyvalent ions that may be present in these simple solutions are generally very inaccurate because of the higher charges on these ions and are unsuitable for use in the present models. A reasonable limitation on the use of the B-dot equation in these models is an ionic strength of 1 molal. Whereas this still is likely to incur some inaccuracies, the errors will be markedly less than those arising from other uncertainties. As a result, the solubility models developed in this model report should not be used for solutions with an ionic strength higher than 1.0 molal. On the other hand, any calculation results with ionic strength higher than 1.0 molal should be deemed invalid. Calculation results are examined and those invalid results have been removed from consideration in this report. This limitation imposes further restrictions in applicability for specific cases than those given in Table 6.4-1. These cases are discussed in the element-specific sections in Section 6.

The second exception is a result of mechanical difficulties in the modeling process. Under some ranges of pH and f_{CO_2} values, the EQ3NR model did not converge and so no solubilities can be specified for those conditions. When convergence difficulties were observed they occurred under conditions of low pH or of high pH and high f_{CO_2} .

The model's inability to converge can be attributed to several factors. If it occurs at low pH values it is due largely to the rapid increases in total actinide and SO_4^{2-} concentrations. These are due to the strength of actinide- SO_4^{2-} solution complexes such as AmSO_4^+ and $\text{Th}(\text{SO}_4)_2(\text{aq})$ and the addition of SO_4^{2-} as the charge-balancing anion as discussed in Section 6.4.3.4. Instability from this cause occurs in calculations for thorium and has a particularly strong effect on the calculations of americium solubilities (Section 6.9.4).

In the high f_{CO_2} and pH region, increasing CO_3^{2-} concentrations favor the formation of actinide carbonate complexes such as $\text{Am}(\text{CO}_3)_3^{3-}$, $\text{Th}(\text{CO}_3)_5^{6-}$ and $\text{Th}(\text{OH})_3\text{CO}_3^-$. f_{CO_2} is fixed in the modeling, so CO_3^{2-} concentrations are sensitive to pH changes. This will produce rapid changes in total actinide concentrations with pH changes and leads to the non-convergence noted for all actinides under these modeling conditions.

In the low pH and high pH-high f_{CO_2} regions, calculation results may be invalid even if the EQ3NR modeling does converge because the total solute concentrations in these regions may exceed 1 molal ionic strength. As discussed previously in this section, EQ3NR solubility models should not be used above this ionic strength.

When the first and second exceptions were observed, no solubility values were reported in the tables of calculated results. For the abstracted log solubility look-up tables, they are flagged by a given number of "500." For TSPA modeling for LA, when values of 500 are encountered they should be considered flags that concentrations should be established not from a solubility control but by its release rate.

The third exception arises from the assigned fluoride concentration ranges in waste packages and in the invert (Section 6.4.3.6). These ranges are based on modeling results of in-package chemistry for certain scenarios and may be revised at a later date if needed when new information becomes available for other scenarios and for the invert. This new information would come from a future revision of *In-Package Chemistry Abstraction* (BSC 2001e) and from a future revision of *Engineered Barrier System: Physical and Chemical Environment Model* (CRWMS M&O 2000h). If new information shows any of these ranges were not broad enough, the relevant uncertainty terms may be modified to cover the broader ranges.

6.4.4.1 EQ3 Input Files

The EQ3 input file names follow this convention:

Pu010203.3I

- The first two characters are the element name.
- The next two numbers are the f_{O_2} step (since f_{O_2} was not varied, this value is always 01).
- The next two numbers give the f_{CO_2} step
01 to 08: varying the f_{CO_2} from $10^{-1.5}$ to $10^{-5.0}$ in $10^{-0.5}$ increments.
- The last two numbers give the pH step
01 to 37: varying the pH from 3.0 to 12.0 in 0.25 pH increments.

The input files are located in Attachment I, with the directory structure given in Attachment II. The runs balanced on different elements (see Section 6.4.3.5) are stored in directories named for the balancing element. For example, all of the runs for the Am solubility that were balanced on Na^+ are in the “na” directory under Am. In some cases, a different naming convention was used, where the “Filebd +” directory means the runs were balanced on the cation (usually Na^+), and the “Filebd -” directory means the runs were balanced on the anion (usually SO_4^{2-}), but the meaning is the same as the “na” and “so4” directories.

6.5 PLUTONIUM SOLUBILITY

6.5.1 Introduction

Data0.ymp.R2 (DTN: MO0302SPATHDYN.000) incorporates newly published plutonium data compiled by Lemire (2001). This database was used for plutonium solubility calculations. The database contains data for PuO_2 , corresponding to the NEA phase $PuO_2(cr)$ and $PuO_2(hyd, aged)$, corresponding to the NEA phase of the same name.

6.5.2 Selection of Solubility-Controlling Solids

Despite numerous studies regarding plutonium solubility, understanding of the stability fields of plutonium solids remains largely uncertain. The most studied plutonium solids are PuO_2 and

$\text{PuO}_2 \cdot 2\text{H}_2\text{O}(\text{am})$, where am stands for amorphous. The latter is written as $\text{Pu}(\text{OH})_4(\text{am})$ or $\text{PuO}_2 \cdot x\text{H}_2\text{O}$. The newly published neptunium/plutonium thermodynamic data by the NEA (Lemire 2001) use both $\text{PuO}_2(\text{hyd, aged})$ and $\text{Pu}(\text{OH})_4(\text{hyd, aged})$ to denote the same Pu(IV) hydrated oxide/hydroxide “aged for several months near room temperature.”

Solids precipitated from Los Alamos National Laboratory (LANL)'s over-saturation experiments (CRWMS M&O 2001b, Section 6.1) have a dark green color, which is characteristic of Pu(IV) solid phases. X-ray diffraction data match the data reported for PuO_2 . However, the diffuse and broad X-ray diffraction peaks suggest poor crystalline structures. Precipitates at a higher temperature (90°C) have a sharper X-ray pattern than solids precipitated at a lower temperature.

Similar results were obtained in another plutonium solubility experiment for Yucca Mountain waters (Nitsche et al. 1993a, p. 63). In that study, at least two solid phases have been observed for experiments at 90°C. One is a yellow-green powdery phase, probably non-crystalline. The other consists of darker green clumps. Nitsche et al. (1993a, p. 63) believe that “such a combination of crystalline and amorphous materials in this solid can explain the observed powder pattern, which is composed of both very sharp and diffuse lines.”

The observed co-existence of both crystalline and amorphous materials in plutonium solubility experiments can be explained by the aging of precipitates. Freshly precipitated solids tend to be fine particles with a large specific surface area. The extra surface energy given by the large surface area makes the fresh precipitates more soluble. However, with time the freshly precipitated fine particles will go through a process called aging in which the smallest particles dissolve and reprecipitate on larger ones, thereby increasing the average particle size, or as a different less soluble solid. As a result, an aged product will have a lower solubility than the freshly precipitated solid. Aging could be a long-lasting process. For example, Rai and Ryan (1982) observed $\text{PuO}_2 \cdot x\text{H}_2\text{O}$ (amorphous) continuously aging over a period of 1,266 days. As solubility experiments usually are carried out within a period of less than a year, it is reasonable to expect that the solubility measured in laboratory experiments actually is an upper limit.

Therefore, it appears that the solubility-controlling solids in those laboratory experiments are “plutonium hydroxides and/or plutonium colloids,” which “age towards $\text{PuO}_2 \cdot x\text{H}_2\text{O}$ ” (CRWMS M&O 2001b, Section 6.1). The value of X should vary from 2 to 0. For $X = 2$, it is $\text{Pu}(\text{OH})_4$, the amorphous end member. For $X = 0$, it is PuO_2 , the crystal end member. Since the crystalline phase has been formed within laboratory time scale, it is reasonable to expect that over geological time, plutonium hydroxides will convert to $\text{PuO}_2(\text{c})$, and it should be used as the solubility-controlling mineral for plutonium for the repository.

However, another process makes the selection of the controlling mineral for plutonium solubility calculation less straightforward. This process is the damage of the crystal structure of plutonium solids caused by α -decay of plutonium isotopes. Rai and Ryan (1982) reported that $^{238}\text{PuO}_2(\text{c})$ was found to convert to an amorphous form of PuO_2 in 1,266 days, which has higher solubility than $\text{PuO}_2(\text{c})$. In waste forms, the fraction of isotope plutonium-238 in the total plutonium inventory is small, so it is not expected that crystal structure damage will occur rapidly enough to be significant to plutonium solubility. Over the regulatory compliance period (10,000 years), it is reasonable to expect that $\text{PuO}_2(\text{c})$ would gradually convert to a less crystalline (denoted as lc) PuO_2 or hydrated amorphous material.

Aging and decay effects go in opposite directions. Aging effects could make a radionuclide less soluble if the starting material is an amorphous solid. Decay effects could make a radionuclide more soluble, provided that the starting material is a crystalline solid. Indeed, Rai and Ryan (1982, p. 214) found that “the solubility of $^{239}\text{PuO}_2$ and $^{239}\text{PuO}_2 \cdot x\text{H}_2\text{O}$ tend to merge; most, if not all, of the effect is due to decreased solubility of $\text{PuO}_2 \cdot x\text{H}_2\text{O}$ with time.” This suggests that both $\text{PuO}_2(\text{c})$ and $\text{PuO}_2 \cdot x\text{H}_2\text{O}(\text{am})$ would be converted to $\text{PuO}_2(\text{lc})$ over time, and they should have similar solubility. In other words, regardless of which starting materials ($\text{PuO}_2(\text{c})$ or $\text{PuO}_2 \cdot x\text{H}_2\text{O}(\text{am})$) to use to measure plutonium solubility, the aging process and radiation process will convert the starting material into an intermediate solid: $\text{PuO}_2(\text{lc})$.

There is not enough information to quantitatively define the thermodynamic properties of $\text{PuO}_2(\text{lc})$, and it is not possible to calculate plutonium solubility directly using $\text{PuO}_2(\text{lc})$ as the solubility controlling solid. Because the properties of $\text{PuO}_2(\text{lc})$ lie between those of $\text{PuO}_2(\text{c})$ and those of $\text{Pu}(\text{OH})_4(\text{am})$ (or $\text{PuO}_2(\text{hyd, aged})$ as denoted by the NEA), the plutonium solubility controlled by $\text{PuO}_2(\text{lc})$ must lie between that controlled by $\text{PuO}_2(\text{c})$ and that controlled by $\text{PuO}_2(\text{hyd, aged})$. A working model can be built for plutonium solubility controlled by $\text{PuO}_2(\text{lc})$ based on $\text{PuO}_2(\text{c})$ and $\text{PuO}_2(\text{hyd, aged})$ solubility models. Specifically, the plutonium solubility model covers the range spanned by $\text{PuO}_2(\text{c})$ and $\text{PuO}_2(\text{hyd, aged})$ solubility models. In other words, the plutonium solubility model is a blended, one that uses $\text{PuO}_2(\text{c})$ and $\text{PuO}_2(\text{hyd, aged})$ as the two end members.

The following sections develop plutonium solubility models controlled by $\text{PuO}_2(\text{c})$ and $\text{PuO}_2(\text{hyd, aged})$ separately, followed by the blended plutonium solubility model using them as the lower and upper bounds.

6.5.3 Chemical Conditions

See Table 6.4-1 for the chemical conditions used for the plutonium calculations.

6.5.4 $\text{PuO}_2(\text{hyd,aged})$ Solubility Model

Table 6.5-1 gives the calculated plutonium solubility using $\text{PuO}_2(\text{hyd,aged})$ as the controlling solid. This solubility is denoted as $[\text{Pu}]_1$ hereafter. Among the 296 calculations, 108 do not converge. Of those converged calculations, some of them have ionic strength values larger than 1.0 molar. Those results are excluded from consideration because they are outside the valid range of the database (see Section 6.4.3). The pH range within which the calculations are valid varies with f_{CO_2} . The higher the f_{CO_2} , the narrower the converging pH range. The lower ends of valid calculations are at pH of 3.75 while the upper ends are from 7.25 to 10.25. Of those valid calculations, the maximum solubility is $1.69\text{E}+5$ mg/L, which appears at pH of 3.75. The minimum solubility is $6.09\text{E}-01$ mg/L, which appears at pH of 8.75 and $\log f_{\text{CO}_2} = -5.0$ (bars).

Table 6.5-1. Calculated Plutonium Solubility Controlled by PuO₂(hyd, aged) ([Pu]₁ mg/L)

pH	log f _{CO2}							
	-1.50	-2.00	-2.50	-3.00	-3.50	-4.00	-4.50	-5.00
3.75	1.69E+05	1.67E+05						
4.00	3.58E+04	3.45E+04	3.41E+04	3.40E+04	3.39E+04	3.39E+04	3.39E+04	3.39E+04
4.25	8.14E+03	6.88E+03	6.48E+03	6.35E+03	6.31E+03	6.30E+03	6.30E+03	6.29E+03
4.50	3.17E+03	1.91E+03	1.51E+03	1.38E+03	1.34E+03	1.33E+03	1.33E+03	1.33E+03
4.75	2.23E+03	9.65E+02	5.66E+02	4.40E+02	4.00E+02	3.88E+02	3.84E+02	3.82E+02
5.00	1.99E+03	7.27E+02	3.27E+02	2.01E+02	1.61E+02	1.49E+02	1.45E+02	1.43E+02
5.25	1.91E+03	6.46E+02	2.47E+02	1.20E+02	8.03E+01	6.77E+01	6.37E+01	6.24E+01
5.50	1.87E+03	6.12E+02	2.13E+02	8.63E+01	4.63E+01	3.37E+01	2.97E+01	2.85E+01
5.75	1.86E+03	5.97E+02	1.97E+02	7.11E+01	3.12E+01	1.85E+01	1.46E+01	1.33E+01
6.00	1.85E+03	5.90E+02	1.91E+02	6.44E+01	2.45E+01	1.19E+01	7.88E+00	6.61E+00
6.25	1.85E+03	5.87E+02	1.88E+02	6.14E+01	2.15E+01	8.86E+00	4.86E+00	3.60E+00
6.50	1.85E+03	5.86E+02	1.86E+02	6.00E+01	2.01E+01	7.42E+00	3.43E+00	2.16E+00
6.75	1.85E+03	5.85E+02	1.86E+02	5.93E+01	1.93E+01	6.70E+00	2.70E+00	1.44E+00
7.00	1.85E+03	5.85E+02	1.85E+02	5.89E+01	1.89E+01	6.32E+00	2.32E+00	1.06E+00
7.25	1.88E+03	5.86E+02	1.85E+02	5.87E+01	1.87E+01	6.11E+00	2.12E+00	8.53E-01
7.50		5.89E+02	1.85E+02	5.86E+01	1.86E+01	6.00E+00	2.00E+00	7.40E-01
7.75		6.14E+02	1.86E+02	5.87E+01	1.86E+01	5.94E+00	1.94E+00	6.78E-01
8.00			1.90E+02	5.89E+01	1.86E+01	5.91E+00	1.91E+00	6.43E-01
8.25			2.20E+02	6.00E+01	1.87E+01	5.90E+00	1.89E+00	6.24E-01
8.50				6.48E+01	1.90E+01	5.92E+00	1.88E+00	6.14E-01
8.75				1.14E+02	2.03E+01	6.03E+00	1.89E+00	6.09E-01
9.00					2.86E+01	6.41E+00	1.92E+00	6.10E-01
9.25					1.78E+02	8.60E+00	2.05E+00	6.21E-01
9.50						3.15E+01	2.68E+00	6.63E-01
9.75							8.51E+00	8.54E-01
10.00							1.38E+02	2.51E+00
10.25								3.17E+01

Source: Microsoft Excel spreadsheet PuO₂_hyd_aged Solubility.xls in Spreadsheets.zip (Attachment I)

NOTES: Some cells have no data because the EQ3NR calculations do not converge.

Runs with ionic strengths > 1.0 are outside the range of validation, and are not reported in this table.

Figure 6.5-1 shows the calculated solubility using PuO₂(hyd,aged) as the controlling solid. It clearly shows that plutonium solubility is a function of pH and fugacity of CO₂. Under the same f_{CO2}, plutonium solubility increases with pH under alkaline conditions; while under acid conditions it increases with decrease in pH. This U shape (or V shape) curve is typical for actinides.

Pu Solubility - PuO₂(hyd,aged)

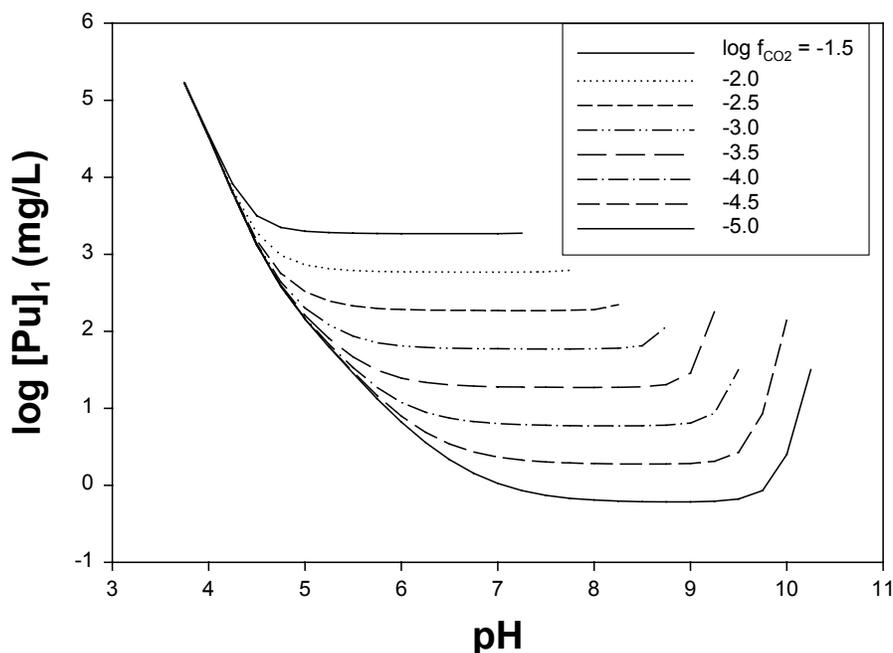


Figure 6.5-1. PuO₂(hyd, aged) Solubility Modeled as a Function of pH and log f_{CO2}

6.5.5 PuO₂ Solubility Model

Table 6.5-2 gives the calculated plutonium solubility using PuO₂ as the controlling solid. This solubility is denoted as [Pu]₂ hereafter. Among the 296 calculations, 63 do not converge (see Section 6.4). Of those converged calculations, some of them have ionic strength values larger than 1.0 molar. Those results are excluded from consideration because they are outside the valid range of the database (see Section 6.4.3). The pH range within which the calculations are valid varies with f_{CO2}. The higher the f_{CO2}, the narrower the converging pH range. The lower ends are pH 3.0 while the upper ends change from 8.75 to 10.75. The valid range of PuO₂ solubility calculations are broader than that of PuO₂(hyd,aged). Of those valid calculations, the maximum solubility is 6.07E+2 mg/L, which appears at pH of 9.25 and log f_{CO2} = -2.00. The minimum solubility is 5.59E-07 mg/L, which appears at pH of 8.75 and log f_{CO2} = -5.0 bars.

6.5.6 Abstraction: The Blended Plutonium Solubility Model

Comparing Tables 6.5-1 and 6.5-2 reveals that under the same pH and f_{CO2} conditions, the difference between the logarithm solubility given by the PuO₂(hyd, aged) model (log[Pu]₁) and that given by the PuO₂ model (log[Pu]₂) varies from 5.86 to 6.60, depending on pH and log f_{CO2}. For the majority data points, it is about 6.04.

Table 6.5-2. Calculated Plutonium Solubility Controlled by PuO₂ ([Pu]₂ mg/L)

pH	log f _{CO2}							
	-1.50	-2.00	-2.50	-3.00	-3.50	-4.00	-4.50	-5.00
3.00	1.09E+00	1.09E+00	1.09E+00	1.09E+00	1.09E+00	1.09E+00	1.09E+00	1.09E+00
3.25	3.68E-01	3.67E-01						
3.50	1.26E-01	1.25E-01						
3.75	4.37E-02	4.26E-02	4.22E-02	4.21E-02	4.20E-02	4.20E-02	4.20E-02	4.20E-02
4.00	1.57E-02	1.46E-02	1.42E-02	1.41E-02	1.40E-02	1.40E-02	1.40E-02	1.40E-02
4.25	6.34E-03	5.19E-03	4.82E-03	4.71E-03	4.67E-03	4.66E-03	4.65E-03	4.65E-03
4.50	3.24E-03	2.09E-03	1.72E-03	1.60E-03	1.57E-03	1.56E-03	1.55E-03	1.55E-03
4.75	2.22E-03	1.06E-03	6.96E-04	5.80E-04	5.43E-04	5.32E-04	5.28E-04	5.27E-04
5.00	1.88E-03	7.21E-04	3.55E-04	2.39E-04	2.02E-04	1.91E-04	1.87E-04	1.86E-04
5.25	1.76E-03	6.05E-04	2.38E-04	1.22E-04	8.57E-05	7.41E-05	7.04E-05	6.93E-05
5.50	1.72E-03	5.64E-04	1.97E-04	8.11E-05	4.44E-05	3.28E-05	2.91E-05	2.80E-05
5.75	1.71E-03	5.48E-04	1.81E-04	6.55E-05	2.88E-05	1.72E-05	1.36E-05	1.24E-05
6.00	1.70E-03	5.42E-04	1.75E-04	5.92E-05	2.25E-05	1.09E-05	7.24E-06	6.08E-06
6.25	1.70E-03	5.39E-04	1.72E-04	5.64E-05	1.97E-05	8.13E-06	4.46E-06	3.30E-06
6.50	1.70E-03	5.38E-04	1.71E-04	5.51E-05	1.84E-05	6.81E-06	3.14E-06	1.98E-06
6.75	1.70E-03	5.37E-04	1.70E-04	5.44E-05	1.77E-05	6.15E-06	2.48E-06	1.32E-06
7.00	1.70E-03	5.37E-04	1.70E-04	5.41E-05	1.74E-05	5.80E-06	2.13E-06	9.72E-07
7.25	1.71E-03	5.38E-04	1.70E-04	5.39E-05	1.72E-05	5.61E-06	1.94E-06	7.83E-07
7.50	1.76E-03	5.41E-04	1.70E-04	5.38E-05	1.71E-05	5.51E-06	1.84E-06	6.80E-07
7.75	2.04E-03	5.53E-04	1.71E-04	5.39E-05	1.71E-05	5.45E-06	1.78E-06	6.22E-07
8.00	5.68E-03	6.17E-04	1.74E-04	5.41E-05	1.71E-05	5.42E-06	1.75E-06	5.90E-07
8.25	8.32E-02	1.25E-03	1.90E-04	5.51E-05	1.71E-05	5.42E-06	1.74E-06	5.73E-07
8.50	2.24E+00	1.25E-02	3.17E-04	5.93E-05	1.74E-05	5.44E-06	1.73E-06	5.63E-07
8.75	7.78E+01	3.01E-01	2.19E-03	8.81E-05	1.86E-05	5.53E-06	1.73E-06	5.59E-07
9.00		1.06E+01	4.58E-02	4.48E-04	2.59E-05	5.89E-06	1.77E-06	5.60E-07
9.25		6.07E+02	1.61E+00	8.03E-03	1.05E-04	7.88E-06	1.88E-06	5.70E-07
9.50			1.02E+02	2.80E-01	1.63E-03	2.74E-05	2.46E-06	6.09E-07
9.75				2.04E+01	5.64E-02	3.77E-04	7.71E-06	7.84E-07
10.00					4.64E+00	1.30E-02	9.71E-05	2.30E-06
10.25						1.18E+00	3.34E-03	2.71E-05
10.50							3.26E-01	9.31E-04
10.75								9.51E-02

Source: Microsoft Excel spreadsheet PuO2 Solubility.xls in Spreadsheets.zip (Attachment I)

NOTES: Some cells have no data because the EQ3NR calculations do not converge.

Runs with ionic strengths > 1.0 are outside the range of validation, and are not reported in this table.

As discussed in Section 6.5.2, the plutonium solubility model should be bounded by [Pu]₁ and [Pu]₂. Although the aging experiments carried out by Rai and Ryan (1982) show that the final plutonium solubility is close to the solubility of the PuO₂(cr) end member, no quantitative information is available. Derivations based on the second law of thermodynamics show that the stability of a chemical compound, hence its solubility, is related directly to its free energy of formation. The difference in free energy between products and reactants of a chemical reaction is equal to $-2.303RT \log K$, where R is the ideal gas constant, T the temperature in Kelvin, and

K the equilibrium constant, and log the decadic logarithm. It is appropriate in determining the mean of solubilities for this abstraction to average the free energies, or logs of the solubilities. Therefore, the mean of the logarithm of the recommended plutonium solubility was set equal to the average of $\log[\text{Pu}]_1$ and $\log[\text{Pu}]_2$. The uncertainty associated with this solubility is represented by a stochastic variable, ε_1 . Since the two end member solids (PuO_2 and $\text{PuO}_2(\text{hyd,aged})$) would be converted to $\text{PuO}_2(\text{lc})$ rapidly, low probabilities should be assigned to them. Thus, ε_1 is assigned a triangular distribution with its peak (b) equal to 0 and its two vertices equal to the distances between the mean value of $\log[\text{Pu}]$ and $\log[\text{Pu}]_1$ and between that and $\log[\text{Pu}]_2$, as shown in Figure 6.5-2.

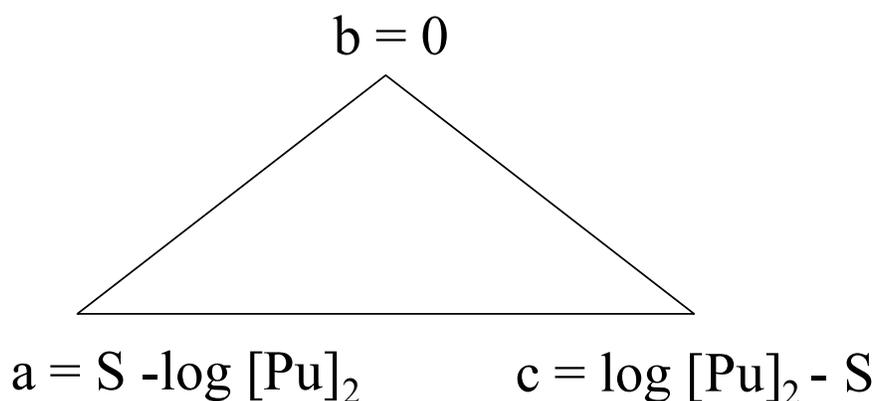


Figure 6.5-2. Illustration of a Triangular Distribution

Mathematically, this abstracted solubility model is:

$$\log[\text{Pu}] = S(\text{pH}, \log f_{\text{CO}_2}) + \varepsilon_1 \quad (\text{Eq. 6.5-1})$$

where S, the mean value of $\log[\text{Pu}]$, is given by Table 6.5-3 as a function of pH and $\log f_{\text{CO}_2}$; and ε_1 is a stochastic variable with a triangular distribution.

The maximum difference between calculated $\log[\text{Pu}]_1$ and $\log[\text{Pu}]_2$ is 6.60 (see Microsoft Excel spreadsheet Pu Composite Results.xls in Spreadsheets.zip of Attachment I), which yields $a = -3.30$ and $c = 3.30$ for ε_1 .

The model applies for pH from 3.75 to 10.25 and for $\log f_{\text{CO}_2}$ from -5.0 to -1.5 (bars).

Table 6.5-3. The Mean Value of log[Pu] (mg/L)

pH	log f_{CO_2}							
	-1.5	-2.0	-2.5	-3.0	-3.5	-4.0	-4.5	-5.0
3.75	1.93E+00	1.93E+00	1.92E+00	1.92E+00	1.92E+00	1.92E+00	1.92E+00	1.92E+00
4.00	1.37E+00	1.35E+00	1.34E+00	1.34E+00	1.34E+00	1.34E+00	1.34E+00	1.34E+00
4.25	8.56E-01	7.76E-01	7.47E-01	7.38E-01	7.35E-01	7.34E-01	7.33E-01	7.33E-01
4.50	5.06E-01	3.00E-01	2.07E-01	1.73E-01	1.62E-01	1.58E-01	1.57E-01	1.57E-01
4.75	3.47E-01	5.54E-03	-2.02E-01	-2.96E-01	-3.31E-01	-3.43E-01	-3.47E-01	-3.48E-01
5.00	2.86E-01	-1.40E-01	-4.68E-01	-6.59E-01	-7.43E-01	-7.74E-01	-7.84E-01	-7.87E-01
5.25	2.64E-01	-2.04E-01	-6.15E-01	-9.16E-01	-1.08E+00	-1.15E+00	-1.17E+00	-1.18E+00
5.50	2.55E-01	-2.31E-01	-6.89E-01	-1.08E+00	-1.34E+00	-1.48E+00	-1.53E+00	-1.55E+00
5.75	2.51E-01	-2.43E-01	-7.23E-01	-1.17E+00	-1.52E+00	-1.75E+00	-1.85E+00	-1.89E+00
6.00	2.49E-01	-2.48E-01	-7.38E-01	-1.21E+00	-1.63E+00	-1.94E+00	-2.12E+00	-2.20E+00
6.25	2.49E-01	-2.50E-01	-7.45E-01	-1.23E+00	-1.69E+00	-2.07E+00	-2.33E+00	-2.46E+00
6.50	2.48E-01	-2.51E-01	-7.48E-01	-1.24E+00	-1.72E+00	-2.15E+00	-2.48E+00	-2.68E+00
6.75	2.49E-01	-2.51E-01	-7.50E-01	-1.25E+00	-1.73E+00	-2.19E+00	-2.59E+00	-2.86E+00
7.00	2.49E-01	-2.51E-01	-7.51E-01	-1.25E+00	-1.74E+00	-2.22E+00	-2.65E+00	-2.99E+00
7.25	2.53E-01	-2.51E-01	-7.51E-01	-1.25E+00	-1.75E+00	-2.23E+00	-2.69E+00	-3.09E+00
7.50	500	-2.48E-01	-7.51E-01	-1.25E+00	-1.75E+00	-2.24E+00	-2.72E+00	-3.15E+00
7.75	500	-2.35E-01	-7.48E-01	-1.25E+00	-1.75E+00	-2.24E+00	-2.73E+00	-3.19E+00
8.00	500	500	-7.40E-01	-1.25E+00	-1.75E+00	-2.25E+00	-2.74E+00	-3.21E+00
8.25	500	500	-6.89E-01	-1.24E+00	-1.75E+00	-2.25E+00	-2.74E+00	-3.22E+00
8.50	500	500	500	-1.21E+00	-1.74E+00	-2.25E+00	-2.74E+00	-3.23E+00
8.75	500	500	500	-9.98E-01	-1.71E+00	-2.24E+00	-2.74E+00	-3.23E+00
9.00	500	500	500	500	-1.57E+00	-2.21E+00	-2.73E+00	-3.23E+00
9.25	500	500	500	500	-8.64E-01	-2.08E+00	-2.71E+00	-3.23E+00
9.50	500	500	500	500	500	-1.53E+00	-2.59E+00	-3.20E+00
9.75	500	500	500	500	500	500	-2.09E+00	-3.09E+00
10.00	500	500	500	500	500	500	-9.36E-01	-2.62E+00
10.25	500	500	500	500	500	500	500	-1.53E+00

Source: Microsoft Excel spreadsheet Pu Composite Results.xls in Spreadsheets.zip (Attachment I)

NOTES: Some cells have no valid data because the EQ3NR calculations do not converge, and those results are reported as 500 in this table.

Runs with ionic strengths > 1.0 are outside the range of validation, and are reported as 500 in this table.

The user of the look-up table needs to ensure that when the flag (500) is encountered, the inventory concentrations calculated according to the dissolution rate of waste forms, water volume, and radionuclide inventory should be used instead of the flag itself. For any conditions that fall between a valid solubility and a flag of 500, the flag should be used. In addition, for any conditions outside of the 3.0-11.0 pH range, the -1.5 to -5.0 f_{CO_2} range, or with an ionic strength greater than 1.0 molal, the inventory concentrations calculated according to the dissolution rate of waste forms, water volume, and radionuclide inventory should be used.

6.5.7 Other Uncertainties

In addition to the uncertainty inherent in the blended model itself which is discussed above, there are several other sources of uncertainty requiring discussion with effects that need to be propagated to the plutonium solubility model.

6.5.7.1 Uncertainty in log K of the Solubility-Controlling Solids and Aqueous Species

The uncertainty in solubility involves uncertainties in the thermodynamic properties of both the controlling solid and significant dissolved species. The rationale behind the evaluation and combination of these uncertainties are discussed in some detail in Section 6.3.3.1.

The principal dissolved plutonium species accounting for more than 5 percent of the dissolved plutonium were found by examining the EQ3NR output for selected runs representing the range of conditions modeled. They are $\text{PuO}_2\text{SO}_4(\text{aq})$, PuO_2F^+ , PuO_2^{2+} , $\text{PuO}_2\text{CO}_3(\text{aq})$, PuO_2^+ , $\text{PuO}_2(\text{OH})_2(\text{aq})$, and $\text{PuO}_2(\text{CO}_3)_3^{4-}$. The 95 percent uncertainties in log K given for these species by the NEA (Lemire 2001, Table 4.2) range, with one exception, from ± 0.1 to ± 0.5 . The exception is $\text{PuO}_2\text{CO}_3(\text{aq})$ to which Lemire (2001, Table 4.2) assign an uncertainty of ± 3.0 . Hummel et al. (2002, p. 284) disagree with the assignment of such a large error. They derive their log K value from reaction data, some of which were not considered by Lemire (2001) and assign it an uncertainty of ± 0.5 . A procedure essentially the same as that described in Section 6.3.3.1 was used to calculate the uncertainty in the free energy of formation of $\text{PuO}_2\text{CO}_3(\text{aq})$ using auxiliary data for PuO_2^{2+} and CO_3^{2-} to obtain 4.03 kJ/mol (see Microsoft Excel spreadsheet Log K uncertainties.xls, included in Attachment I). The difference consists only in transposing the term for $\Delta_f G^0(\text{PuO}_2\text{CO}_3(\text{aq}))$ to the left side of the uncertainty equation and the term for $\Delta_f G^0(\text{PuO}_2\text{CO}_3(\text{aq}))$ to the right side (but, in keeping with the root-mean square procedure, always adding rather than subtracting the uncertainties.).

The extensive review of Lemire (2001) recommends Gibbs free energies of formation for both end members of the blended solid. They are -963.654 ± 6.324 kJ/mol for $\text{PuO}_2(\text{hyd,aged})$ and -998.113 ± 1.031 kJ/mol for PuO_2 . Dissolution reactions for these solids to each of the seven dissolved plutonium species identified above were evaluated in Microsoft Excel spreadsheet log K uncertainties.xls, included in Attachment I. The two greatest uncertainties were for the reactions to $\text{PuO}_2(\text{OH})_2(\text{aq})$ and $\text{PuO}_2(\text{CO}_3)_3^{4-}$. These are significant only at high pH. For $\text{PuO}_2(\text{OH})_2(\text{aq})$ the 2σ uncertainties in log K for $\text{PuO}_2(\text{hyd,aged})$ and PuO_2 are ± 1.929 and ± 1.590 , respectively. Corresponding uncertainties for $\text{PuO}_2(\text{CO}_3)_3^{4-}$ are ± 1.530 and ± 1.071 , respectively. Uncertainties for other dissolved species range from ± 0.526 to ± 1.315 .

The properties of PuO_2 are based on calorimetric studies (Lemire 2001, Section 17.2.1.2) while those of $\text{PuO}_2(\text{hyd,aged})$ are based on solubility studies (Lemire 2001, Section 17.2.2.1). Thus, the data for the two solids can be considered independent and the root-mean-square method is appropriate to combine them. The resulting 2σ log K combined by the root-mean-square method for $\text{PuO}_2(\text{OH})_2(\text{aq})$ is ± 2.5 and for $\text{PuO}_2(\text{CO}_3)_3^{4-}$ is 1.9. As these represent 2σ values, the 1σ uncertainties assigned to log[Pu] values to account for maximally high uncertainties in the thermodynamic data is ± 1.3 .

6.5.7.2 Uncertainty from Fluoride Concentration

Table 6.5-4 lists the calculated plutonium solubilities at the base-case value and higher concentrations (10 times and 200 times of the base-case value) of fluoride, along with their differences on a log scale. The fugacity of CO₂ is set to 10^{-3.00}. Only PuO₂ is considered in these calculations because the differences caused by variations in fluoride concentration should be the same for PuO₂(hyd,aged). The differences vary with pH. The maximum difference of log[Pu] between the base-case results and the 10 times fluoride results is 0.885. This is the uncertainty term of log[Pu] for CSNF waste packages (ε_3^{CSNF}), which obeys a triangular distribution, with a = b = 0.00, and c = 0.885. For codisposal waste packages and the invert, the uncertainty term ε_3^{CO-IN} associated with fluoride concentration also obeys a triangular distribution but with a c value equal to 2.94.

6.5.8 Summary

The plutonium solubility model can be summarized by the following equation:

$$\log[Pu] = S(pH, \log f_{CO_2}) + \varepsilon_1 + \varepsilon_2 + \varepsilon_3^i \quad (\text{Eq. 6.5-4})$$

where

$S(pH, \log f_{CO_2})$ is given by Table 6.5-3

ε_1 is the uncertainty term associated with the selection of controlling phases

ε_2 is the uncertainty term associated with uncertainty in log Ks

ε_3^i is the uncertainty term associated with variations in fluoride concentration

i corresponds to either CSNF or codisposal waste package and the invert

The distribution properties of these uncertainty terms are listed in Table 6.5-5.

6.5.9 What Does PuO_{2+x} mean to Plutonium Solubility?

Haschke et al. (2000), Haschke and Oversby (2002), and Haschke and Allen (2002) describe a solid with the general formula PuO_{2+x} that forms from PuO₂ in the presence of water vapor at temperatures from 25 to 350°C. At 300K, free energies of formation of this solid range from -1,033 kJ/mol at x=0.1 to -1,146 kJ/mol at x=0.5 (Haschke and Allen 2002). At 298.15K the free energy of formation of PuO₂ is -998 kJ/mol and that of PuO₂(hyd, aged) is -964 kJ/mol (Lemire 2001, Table 4.1). The latter phases were used to bound the plutonium solubility recommended above. The logs of the recommended mean values for plutonium concentrations are the means of the logs of the concentrations calculated for PuO₂ and PuO₂(hyd, aged) as discussed in Section 6.5.6. The free energy of formation corresponding to this solubility is the mean of the free energies of formation of PuO₂ and PuO₂(hyd, aged), which is -981 kJ/mol.

PuO_{2+x} contains both Pu(IV) and Pu(V) in the proportion (1-x):x. Haschke et al. (2000) attributed the increase in the average oxidation state in PuO_{2+x} to the presence of Pu(VI), and concluded that this would make plutonium more soluble than PuO₂ because Pu(VI) ions are more soluble than Pu(IV) ions. Haschke et al. (2000) also concludes that because PuO_{2+x} forms from

PuO₂ in the presence of O₂, it is more stable. This is borne out by the free energy data of Haschke and Allen (2002) showing that as x increases, the free energy becomes more negative. However, Haschke and Allen (2002) also conclude from EXAFS fine structure spectra that PuO_{2+x} contains Pu(V) rather than Pu(VI).

Table 6.5-4. The Effects of Variations in Fluoride Concentration on Plutonium Solubility

pH	Base Case (1× F)	CSNF (10× F)	Codisposal (200× F)	CSNF Difference	Codisposal Difference
	[Pu mg/L]			$\log[\text{Pu}_{\text{CSNF}}] - \log[\text{Pu}_{\text{Base Case}}]$	$\log[\text{Pu}_{\text{Codisp}}] - \log[\text{Pu}_{\text{Base Case}}]$
3.00	1.09E+00	4.67E+00	1.76E+02	6.30E-01	2.21E+00
3.25	3.67E-01	1.99E+00	9.88E+01	7.35E-01	2.43E+00
3.50	1.25E-01	8.00E-01	4.93E+01	8.07E-01	2.60E+00
3.75	4.21E-02	3.00E-01	2.28E+01	8.53E-01	2.73E+00
4.00	1.41E-02	1.06E-01	1.01E+01	8.78E-01	2.85E+00
4.25	4.71E-03	3.61E-02	3.99E+00	8.85E-01	2.93E+00
4.50	1.60E-03	1.20E-02	1.39E+00	8.73E-01	2.94E+00
4.75	5.80E-04	3.94E-03	4.58E-01	8.32E-01	2.90E+00
5.00	2.39E-04	1.32E-03	1.48E-01	7.42E-01	2.79E+00
5.25	1.22E-04	4.67E-04	4.72E-02	5.81E-01	2.59E+00
5.50	8.11E-05	1.90E-04	1.51E-02	3.71E-01	2.27E+00
5.75	6.55E-05	1.00E-04	4.82E-03	1.84E-01	1.87E+00
6.00	5.92E-05	7.02E-05	1.57E-03	7.38E-02	1.42E+00
6.25	5.64E-05	5.99E-05	5.33E-04	2.59E-02	9.76E-01
6.50	5.51E-05	5.62E-05	2.06E-04	8.55E-03	5.73E-01
6.75	5.44E-05	5.48E-05	1.02E-04	2.74E-03	2.74E-01
7.00	5.41E-05	5.42E-05	6.92E-05	8.74E-04	1.07E-01
7.25	5.39E-05	5.39E-05	5.87E-05	2.66E-04	3.70E-02
7.50	5.38E-05	5.38E-05	5.54E-05	8.07E-05	1.22E-02
7.75	5.39E-05	5.39E-05	5.44E-05	8.06E-06	4.28E-03
8.00	5.41E-05	5.41E-05	5.45E-05	6.42E-05	2.76E-03
8.25	5.51E-05	5.51E-05	5.59E-05	3.94E-04	6.70E-03
8.50	5.93E-05	5.95E-05	6.40E-05	1.64E-03	3.27E-02
8.75	8.81E-05	8.97E-05	1.27E-04	7.87E-03	1.57E-01
9.00	4.48E-04	4.65E-04	8.61E-04	1.59E-02	2.83E-01
9.25	8.03E-03	8.26E-03	1.35E-02	1.21E-02	2.27E-01
9.50	2.80E-01	2.84E-01	3.79E-01	6.51E-03	1.31E-01
9.75	2.04E+01	2.05E+01	2.30E+01	2.49E-03	5.27E-02
			Maximum:	8.85E-01	2.94E+00
			Minimum:	8.06E-06	2.76E-03
			Average:	3.05E-01	1.26E+00

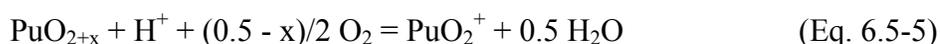
Source: Microsoft Excel spreadsheet PuO₂ Solubility.xls in Spreadsheets.zip (Attachment I)

NOTE: $\log f_{\text{CO}_2} = -3.0$

Table 6.5-5. Uncertainty Terms of log[Pu]

Uncertainty Term	Associated With	Distribution Type	Distribution Parameter	Applicable To
ε_1	Selection of solubility controlling solids	Triangular	a = -3.33, b = 0, c = 3.33	
ε_2	Uncertainties in log K	Normal	$\mu = 0, \sigma = 1.3$	
ε_3^{CSNF}	Fluoride concentration in CSNF waste packages	Triangular	a = b = 0, c = 0.885	CSNF waste packages
ε_3^{CO-IN}	Fluoride concentration in codisposal waste packages	Triangular	a = b = 0, c = 2.94	Codisposal waste packages and the invert

The dissolution reaction for PuO_{2+x} under the oxidizing conditions used for the calculations described in Section 6.5.4 can be written:



The results of such calculations are given in Table 6.5-7 and show that at equilibrium the solubilities of PuO_{2+x} decrease by 25 powers of ten as x ranges from 0.0 to 0.5. These calculations were made without considering activity coefficients or the formation of aqueous complexes. To illustrate the magnitude of the errors that might have been introduced by these simplifications, the last two columns of Table 6.5-7 give the total plutonium contents calculated by EQ3NR at $\text{pCO}_2 = 10^{-5}$ bars for $\text{PuO}_2(\text{hyd, aged})$ and PuO_2 from Tables 6.5-1 and 6.5-2, respectively. The solubilities from the simple calculations are lower by factors of less than two, considerably less than the solubility differences due to increasing values of x.

Thus, it can be concluded that, in contradiction of the assertion of Haschke et al. (2000), the equilibrium solubility of PuO_{2+x} is considerably lower than that of PuO_2 and that the solubility decreases with x.

Haschke and Bassett (2002) review whether modeling with solids designated as $\text{PuO}_2(\text{s})$ or $\text{Pu}(\text{OH})_4(\text{am})$ better describe plutonium concentrations reported in a number of laboratory investigations. These phases correspond to the phases designated $\text{PuO}_2(\text{cr})$ and $\text{PuO}_2(\text{hyd, aged})$ by Lemire (2001, Sections 17.2.1.2 and 17.2.2.3). Haschke and Bassett (2002) conclude that $\text{Pu}(\text{OH})_4(\text{am})$ is a better predictor of laboratory results than the $\text{PuO}_2(\text{s})$. This is understandable because the properties of the amorphous or poorly-crystalline hydrated actinide dioxide solids, of which $\text{Pu}(\text{OH})_4(\text{am}) (= \text{PuO}_2(\text{hyd, aged}) + 2 \text{H}_2\text{O})$ are one example, are derived from laboratory solubility experiments as illustrated by Lemire (2001, Section 17.2.2.3) for plutonium, and Hummel et al., (2002, Section 5.21.2) for thorium and Section 5.23.3.1.3 for uranium.

Table 6.5-7. Data of PuO_{2+x} Stability

PuO _{2+x}	ΔGf kJ/mol	ΔGr kJ/mol	log(PuO ₂₊)	mg Pu /L	mg Pu /L at f _{CO2} = 10 ⁻⁵	
					[Pu] ₁	[Pu] ₂
					Table 6.5-1	Table 6.5-2
x						
0.00	-998.113	26.943	-10.90	3.06E-06		6.08E-06
0.10	-1032.611	61.441	-16.90	2.99E-12		
0.20	-1060.958	89.788	-21.84	3.51E-17		
0.30	-1089.304	118.134	-26.77	4.11E-22		
0.40	-1117.651	146.481	-31.70	4.82E-27		
0.50	-1145.998	174.828	-36.63	5.65E-32		
PuO ₂ (hyd,aged)						
0.00	-963.654	-7.516	-4.86	3.33E+00	6.60E+00	

Source: Microsoft Excel spreadsheet PUO(2+x)_Calc.xls in Spreadsheets.zip (Attachment I)

NOTES: Free energies of formation, free energy of reaction for Eq. 6.5-5, and PuO₂⁺ concentrations calculated at fO₂ = 0.2 and pH = 6 for PuO_{2+x} with x ranging from 0.0 to 0.5, and for PuO₂(hyd, aged). The last two columns give the total plutonium contents calculated at pCO₂ = 10⁻⁵ bars for PuO₂(hyd, aged) and PuO₂ from Tables 6.5-1 and 6.5-2, respectively.

Haschke and Bassett's (2002) conclusions are not directly relevant to the solubility calculations in this report for two reasons. First, their calculations were made at lower oxidation potentials than used in this report. Their Eh values range from 0.92 V at pH = 3 to 0.26 V at pH = 8 (Haschke and Bassett 2002). Table 3 corresponds to pO₂ values from 10⁻¹⁰ to 10⁻³⁵ bars (Langmuir 1997, Figure 11.2), while the calculations for this report were made with pO₂ = 0.2 bars. Second, Haschke and Bassett (2002) used thermodynamic data for their calculations that predate and have been superseded by *Chemical Thermodynamics of Neptunium and Plutonium* (Lemire 2001). The latter data are included in Data0.ymp.R2, the thermodynamic database used for this report. In addition, it is curious that Haschke and Bassett (2002) do not include PuO_{2+x} in their review of plutonium-controlling phases, considering the importance attributed to it by Haschke et al. (2000) and Haschke and Oversby (2002).

Haschke and Oversby (2002, p. 193) review selected experimental data on plutonium concentrations in laboratory experiments and conclude “. . . that a dissolution model based solely on equilibrium thermodynamics and solubility of PuO₂ and Pu(OH)₄(am) is not consistent with the experimental data.” Instead, they propose “. . . a kinetically controlled chemical process involving release of Pu(V) from PuO_{2+x} formed by spontaneous reaction of dioxide or hydroxide with water.” They propose a sequence of equilibrium and kinetic processes (summarized in their Table 2) that lead to steady-state solution plutonium concentrations that are similar to the experimental data they review (Haschke and Oversby 2002, Table 3). The initiating reaction they propose is the formation of PuO_{2+x} by reaction with water according to:



Haschke and Oversby (2002) also note that because this reaction produces hydrogen gas, which leaves the system, their plutonium cycle is not an equilibrium process. There is considerable

uncertainty in the steady-state concentrations they calculate because of uncertainties in the rate constants required to evaluate the kinetic expressions in their model. In addition, uncertainties exist because of the lack of experimental data to evaluate one of the key factors in their model: the conversion factor between rates expressed in terms of areas and those expressed in terms of volumes (Haschke and Oversby 2002, p. 196).

The results of Haschke and Oversby's (2002) model are given in their Table 3. For conditions most like those modeled in this report (controlling phase $\text{Pu}(\text{OH})_4(\text{am})$, pH 6 to 7, low ionic strength) their modeled concentrations are from -0.1 to -0.9 $\log[\text{Pu}]$ (in mg/L), and the range of observed concentrations they cite is -0.1 to -2.0 $\log[\text{Pu}]$. For comparison, the concentrations calculated above using $\text{PuO}_2(\text{hyd, aged})$ as the controlling solid at an f_{CO_2} of -5.0 (to minimize the effects of carbonate solution complexes on solubility) are 0.8 at pH 6 and 0.0 at pH = 7 (Table 6.5-1). These are similar to, but slightly higher than, the steady-state values of Haschke and Oversby (2002), suggesting that for this solid the equilibrium model leads to a higher concentration and so is conservative relative to the steady-state model.

The data of Haschke et al. (2000) and the model developed to account for them by Haschke and Oversby (2002) are of considerable interest and possible importance to the understanding of plutonium chemistry. However, because the steady-state model is only in its first stages of development and in any case leads to concentrations lower than those calculated under the same conditions in this report, the theoretically more robust thermodynamic equilibrium model is retained here.

6.6 NEPTUNIUM SOLUBILITY

6.6.1 Conceptual Models

Lengthy discussions have been held concerning neptunium-bearing phase(s) that could form under the repository conditions (CRWMS M&O 1998a). Two types of solubility controlling phases have been examined. One is pure neptunium phases, consisting primarily of neptunium oxides and hydroxides. The other is neptunium bearing uranium phases, wherein neptunium constitutes a trace element component in solid solutions.

6.6.1.1 Pure Neptunium Phase Models

Several pure neptunium phases have been identified in neptunium solubility experiments, including Np_2O_5 , $\text{NaNpO}_2\text{CO}_3 \cdot x\text{H}_2\text{O}$, NpO_2 (Efurd et al. 1998; Nitsche et al. 1993; Roberts et al. 2003). At the conditions relevant to the repository (oxidizing conditions and temperature from 25 to 90°C), the precipitates in solubility experiments are $\text{Np}_2\text{O}_5 \cdot x\text{H}_2\text{O}$ and $\text{NaNpO}_2\text{CO}_3 \cdot x\text{H}_2\text{O}$ (Efurd et al. 1998; Nitsche et al. 1993a, p. 37). Based on the discussion below and in Section 6.6.5, the base-case model uses Np_2O_5 as the neptunium solubility-controlling phase. NpO_2 is used as an alternative neptunium solubility model (denoted hereafter as Alternative Neptunium Solubility Model I).

6.6.1.1.1 Base-Case Conceptual Model: Np_2O_5

Efurd et al. (1998) conducted neptunium solubility experiments using J-13 well water at pH values of 6.0, 7.0, and 8.5 at 25, 60, and 90°C from both oversaturation and undersaturation.

They identified the neptunium-controlling solid using x-ray diffraction as $\text{Np}_2\text{O}_5 \cdot x\text{H}_2\text{O}$ and noted that the crystallinity of the solid, as shown by the sharpness of the diffraction patterns, increased with increasing temperature. As discussed in Section 6.6.2, the thermodynamic properties derived by Efurud et al. (1998, p. 3893) from their experimental data indicate that their solid is more soluble than the solid whose properties are given by Lemire (2001, Table 3.1). This is attributed to the hydrated nature of Efurud's solid.

$\text{NaNpO}_2\text{CO}_3 \cdot x\text{H}_2\text{O}$ was observed in neptunium solubility experiments also using J-13 well water (Nitsche et al. 1993a, p. 37). However, a detailed analysis by Runde in *Pure Phase Solubility Limits—LANL* (CRWMS M&O 2001b) found that $\text{NaNpO}_2\text{CO}_3 \cdot 3.5\text{H}_2\text{O}$ is stable only when $[\text{Na}^+]$ is greater than 0.05 molar at neutral pH. Based on the x-ray diffraction data and by further analyzing the stability field for Np(V) solid phases (Np_2O_5 , $\text{NpO}_2(\text{OH})$, and $\text{NaNpO}_2\text{CO}_3 \cdot 3.5\text{H}_2\text{O}$), the report concludes that Np_2O_5 is the solubility controlling phase in J-13 well water under oxidizing conditions (CRWMS M&O 2001b, p. 21).

6.6.1.1.2 Alternative Conceptual Model I: NpO_2

Lemire (2001, Table 3.1, p. 41) gives the free energy of formation ($\Delta_f G^0$) of NpO_2 as -1021.731 kJ/mol, while $\Delta_f G^0$ of Np_2O_5 is -2031.574 kJ/mol. If the data are correct, then, NpO_2 is more stable than Np_2O_5 at 298.15 K, because of for the following reaction:



$\Delta_r G^0 = 2 \times \Delta_f G_{\text{NpO}_2}^0 - \Delta_f G_{\text{Np}_2\text{O}_5}^0 = 2 \times (-1021.731) - (-2031.574) = -11.888$ (kJ). If kinetic barriers do not prevent NpO_2 from precipitating, it should control neptunium equilibrium solubility under most conditions, even those with atmospheric f_{O_2} .

In laboratory solubility experiments, NpO_2 has been found precipitating at 200°C (Roberts et al. 2003). In a neptunium-doped U_3O_8 corrosion experiment (Adkins 2003), it was also observed at 150°C. At 90°C, it co-exists with Np_2O_5 (Adkins 2003). It is not clear yet whether this is a transient phenomenon in which NpO_2 was transforming to Np_2O_5 or vice versa.

At temperature conditions relevant to the repository (25 to 90°C), in contrast to what is predicted by thermodynamics, $\text{Np}_2\text{O}_5 \cdot x\text{H}_2\text{O}$ has been identified experimentally as controlling neptunium solubility (Efurud et al. 1998). As discussed in Section 6.3.2, the Ostwald Step Rule can be used to explain the contrast between the thermodynamic prediction and laboratory observations.

In selection of solubility controlling solids, laboratory observations override thermodynamic prediction (Section 6.3.2). Nonetheless, neptunium solubility controlled by NpO_2 is considered an alternative conceptual model.

6.6.1.2 Alternative Conceptual Model II: Neptunium Incorporation into Uranyl Secondary Phases

Although by definition the solubility-controlling solid can be either a pure solid or a solid solution, in practice, pure solids are generally used to evaluate radionuclide solubility. Using pure-phase control is acceptable for TSPA calculations in support of regulatory compliance because it is conservative. However, it is well recognized that the concentration of most radionuclides released during the corrosion of spent nuclear fuel is likely to be very low (except for uranium and thorium) and that the radionuclides may not form their own pure phases (Grenthe 1991, pp. 429 and 430; Langmuir 1997, p. 531). Rather, they may be incorporated into secondary uranium minerals as solid solutions because of the large availability of uranium in the repository.

Neptunium concentrations in solution have been measured in a number of spent fuel degradation experiments (Finn et al. 1994; Finn et al. 1997; CRWMS M&O 2000d; Wilson 1990a; Wilson 1990b). Neptunium concentrations based on Np_2O_5 and NpO_2 solubilities are several orders of magnitude higher than the neptunium concentrations measured in the degradation experiments as will be discussed in Section 7.2. This suggests that neptunium concentrations resulting from fuel degradation in a repository may be lower than the concentrations predicted by pure phase solubility models. It is also notable that no pure neptunium phases have ever been reported in any spent fuel corrosion experiments.

This discrepancy between the experimental and calculated actinide solubility, which is usually several orders of magnitude, has also been noted by others (e.g., Werme and Spahiu 1998; Quinones et al. 1996, p. 42). Simple mass balance calculations (Werme and Spahiu 1998) on the results of these degradation experiments revealed that the amount of neptunium in the aqueous solution was just a small portion of what should have been released from the dissolved spent fuel. An explanation for this observation is that released neptunium is included in uranyl solids that form during the degradation process. There is both theoretical and experimental support for the inclusion of neptunium in uranyl solids.

Based on an analysis of the crystal-chemical properties of the U-O bond, Np-O bond, and Pu-O bond, Burns et al. (1997, p. 8) predicted that “the substitutions Pu^{6+} for U^{6+} and (Np^{5+} , Pu^{5+}) for U^{6+} are likely to occur in most U^{6+} structures.”

The previous theoretical prediction has been confirmed by direct observations of neptunium in uranyl minerals. Buck et al. (1998) examined corrosion products of spent fuel drip tests by electron energy loss spectroscopy (EELS) analyses in a transmission electron microscope. In their study, neptunium was reported to be incorporated into dehydrated schoepite ($\text{UO}_3 \cdot 0.8\text{H}_2\text{O}$) or metaschoepite ($\text{UO}_3 \cdot 2\text{H}_2\text{O}$). Finch et al. (2002) also reported experimental results on neptunium incorporation into dehydrated schoepite and estimated that the amount of neptunium incorporated in dehydrated schoepite can be as high as 2 percent of the host solid based on EELS measurement. However, Finch has since questioned the reliability of the EELS measurement (Adkins 2003).

More significant progress in this direction is the successful synthesis of neptunium-bearing uranium minerals. Burns et al. reported the synthesis of uranophane ($\text{Ca}(\text{UO}_2\text{SiO}_3\text{OH})_2 \cdot 5\text{H}_2\text{O}$)

and Na-compreignacite ($\text{Na}_2[(\text{UO}_2)_3\text{O}_2(\text{OH})_3]_2(\text{H}_2\text{O})_5$) containing neptunium ranging up to 497 ppm (Howard 2003). Furthermore, they found that “there is a linear relationship between the neptunium content of α -uranophane and Na-compreignacite and the Np^{5+} concentration in the initial solution,” and “Np is incorporated into crystals of alpha-uranophane and Np-compreignacite in approximately the same concentrations as presented in the mother solutions.” Buck (2003) and Friese (2003) also reported the successful synthesis of neptunium-bearing studtite ($\text{UO}_4 \cdot 4\text{H}_2\text{O}$). In the neptunium incorporation experiments conducted by Burns et al. (Howard 2003), it is found that schoepite, the major secondary uranyl mineral that forms in the process of spent fuel degradation and is believed to be critical for neptunium immobilization, contains only a small amount of neptunium (a few parts per million). Burns et al. attribute this to the lack of suitable low-valence cations in their experiments (Howard 2003). This may have prevented a charge-balance mechanism from happening, which is a prerequisite for neptunium incorporation into uranyl minerals. Burns et al. planned to conduct experiments using various counter ions (potassium, cesium, and calcium, etc.) to examine their effects on neptunium incorporation into schoepite (Howard 2003).

Finally, as discussed in Section 6.6.4, Chen (2001) and Chen et al. (2002) analyzed the relative release rates of neptunium and uranium in the fuel degradation experiments referred to above and found a close correlation between neptunium and uranium concentrations in the leachates. In other words, the ratio of neptunium to uranium in the leachate is equal to the ratio in the spent fuel used in the experiments. Bruno et al. (1998) have also observed a coherent relation between neptunium and uranium in spent fuel dissolution experiments in the Spanish Nuclear Waste Program. These results are corroborated by the linear relationship between neptunium contents in uranophane and Na-compreignacite and the mother solution that was found by Burns et al. (Howard 2003).

There are several conceivable explanations for this coherent relation between neptunium and uranium. A simple one is that it is the result of congruent dissolution of fuel matrix with few effects of secondary phases. Another explanation is that neptunium and uranium behave coherently, not only in the dissolution process but also in the process of secondary phase precipitation. The third one is that uranium and neptunium form their own solid phases, and the uranium and neptunium solubility controlled by them respectively would have a ratio equal to the ratio of uranium to neptunium in the fuel. Because in spent fuel corrosion experiments a large portion of reacted uranium was precipitated as secondary uranium minerals, they are incongruent reactions. Thus, the first explanation does not hold. The third hypothesis relies on coincidence, and as stated earlier, no neptunium pure phases have been reported in fuel dissolution experiments; thus, it is unsubstantiated. Therefore, the second explanation is the most reasonable explanation. In other words, the coherent relation between neptunium and uranium is the result of formation of solid solutions between neptunium and uranium.

6.6.2 Base-Case Neptunium Solubility Model: Np_2O_5 Model

6.6.2.1 Chemical Conditions

See Table 6.4-1 for the chemical conditions used for the Np_2O_5 solubility calculations.

6.6.2.2 EQ3NR Results

Table 6.6-1 gives the calculated neptunium solubility (in units of mg/L) using Np_2O_5 as the controlling solid. Among the 298 calculations, 37 do not converge. None of the converged results are outside the valid ionic strength range (1.0 molal). The pH range within which the calculation converges varies under different f_{CO_2} conditions. The higher the f_{CO_2} , the narrower the converging pH range. The lower ends are pH 3.0, while the upper ends change from 8.0 to 10.5. Of those converged calculations, the maximum solubility is $3.07\text{E}+4$ mg/L, which appears at pH 3.0. The minimum solubility is $3.01\text{E}-02$ mg/L, which appears at pH of 9.0 and $\log f_{\text{CO}_2} = -5.0$.

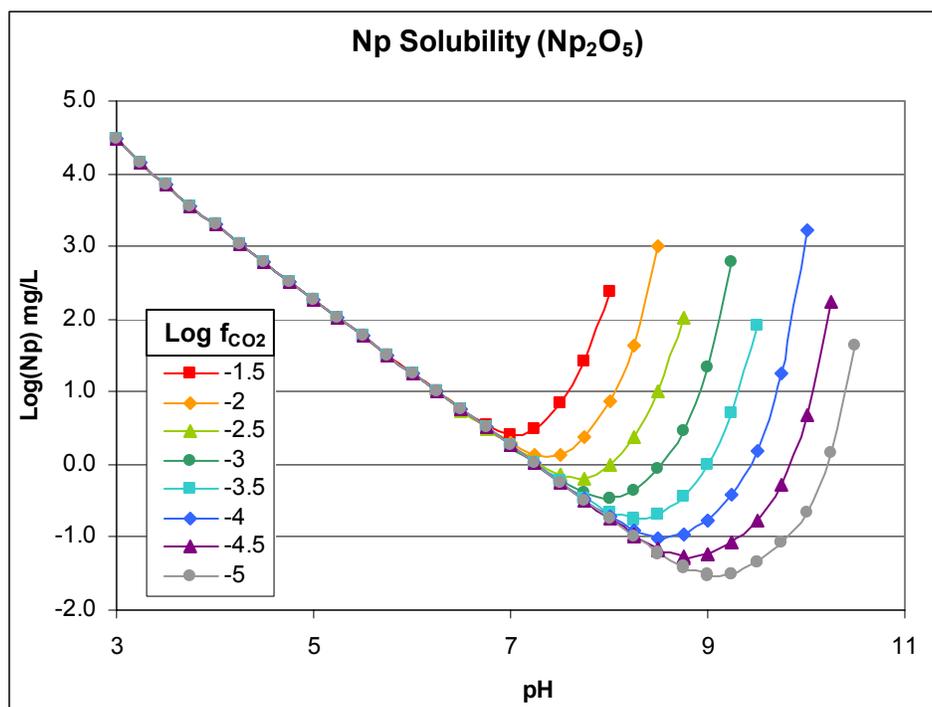
Table 6.6-1. Calculated Np_2O_5 Solubility (mg/L)

pH	log f_{CO_2}							
	-1.50	-2.00	-2.50	-3.00	-3.50	-4.00	-4.50	-5.00
3.00	3.07E+04	3.07E+04	3.07E+04	3.07E+04	3.07E+04	3.07E+04	3.07E+04	3.07E+04
3.25	1.40E+04	1.40E+04	1.40E+04	1.40E+04	1.40E+04	1.40E+04	1.40E+04	1.40E+04
3.50	6.95E+03	6.95E+03	6.95E+03	6.95E+03	6.95E+03	6.95E+03	6.95E+03	6.95E+03
3.75	3.64E+03	3.64E+03	3.64E+03	3.64E+03	3.64E+03	3.64E+03	3.64E+03	3.64E+03
4.00	1.96E+03	1.96E+03	1.96E+03	1.96E+03	1.96E+03	1.96E+03	1.96E+03	1.96E+03
4.25	1.07E+03	1.07E+03	1.07E+03	1.07E+03	1.07E+03	1.07E+03	1.07E+03	1.07E+03
4.50	5.91E+02	5.91E+02	5.91E+02	5.91E+02	5.91E+02	5.91E+02	5.91E+02	5.91E+02
4.75	3.29E+02	3.29E+02	3.29E+02	3.29E+02	3.29E+02	3.29E+02	3.29E+02	3.29E+02
5.00	1.84E+02	1.84E+02	1.84E+02	1.84E+02	1.84E+02	1.84E+02	1.84E+02	1.84E+02
5.25	1.03E+02	1.03E+02	1.03E+02	1.03E+02	1.03E+02	1.03E+02	1.03E+02	1.03E+02
5.50	5.77E+01	5.77E+01	5.77E+01	5.77E+01	5.77E+01	5.77E+01	5.77E+01	5.77E+01
5.75	3.24E+01	3.24E+01	3.24E+01	3.24E+01	3.24E+01	3.24E+01	3.24E+01	3.24E+01
6.00	1.82E+01	1.82E+01	1.82E+01	1.82E+01	1.82E+01	1.82E+01	1.82E+01	1.82E+01
6.25	1.03E+01	1.02E+01						
6.50	5.83E+00	5.78E+00	5.76E+00	5.76E+00	5.76E+00	5.75E+00	5.75E+00	5.75E+00
6.75	3.56E+00	3.30E+00	3.25E+00	3.24E+00	3.24E+00	3.24E+00	3.24E+00	3.24E+00
7.00	2.61E+00	1.95E+00	1.86E+00	1.83E+00	1.82E+00	1.82E+00	1.82E+00	1.82E+00
7.25	3.09E+00	1.34E+00	1.10E+00	1.04E+00	1.03E+00	1.03E+00	1.02E+00	1.02E+00
7.50	6.92E+00	1.35E+00	7.18E-01	6.14E-01	5.87E-01	5.79E-01	5.77E-01	5.76E-01
7.75	2.66E+01	2.42E+00	6.45E-01	3.99E-01	3.45E-01	3.30E-01	3.26E-01	3.24E-01
8.00	2.33E+02	7.35E+00	9.61E-01	3.29E-01	2.22E-01	1.94E-01	1.86E-01	1.83E-01
8.25		4.26E+01	2.37E+00	4.28E-01	1.78E-01	1.24E-01	1.09E-01	1.04E-01
8.50		1.04E+03	1.01E+01	8.77E-01	2.08E-01	9.75E-02	6.95E-02	6.13E-02
8.75			1.07E+02	2.90E+00	3.69E-01	1.09E-01	5.40E-02	3.90E-02
9.00				2.10E+01	9.84E-01	1.72E-01	5.83E-02	3.01E-02
9.25				6.00E+02	5.21E+00	3.88E-01	8.66E-02	3.19E-02
9.50					8.00E+01	1.55E+00	1.73E-01	4.56E-02
9.75						1.77E+01	5.41E-01	8.40E-02
10.00						1.68E+03	4.76E+00	2.18E-01
10.25							1.70E+02	1.46E+00
10.50								4.23E+01

Source: Microsoft Excel spreadsheet Np2O5 solubility.xls in Spreadsheets.zip (Attachment I)

NOTES: Some cells have no data because the EQ3NR calculations do not converge.
Runs with ionic strengths > 1.0 are outside the range of validation, and are not reported in this table.

Figure 6.6-1 shows the calculated solubility using Np_2O_5 as the controlling solid. It is a function of pH and fugacity of CO_2 . Under the same f_{CO_2} , neptunium solubility increases with pH under alkaline conditions; while under acid conditions it increases with decrease in pH. This V shape curve is characteristic for actinides. Note the insensitivity to f_{CO_2} on the acid leg, but extreme sensitivity on the basic leg.



Source: Microsoft Excel spreadsheet Np2O5 Solubility.xls in Spreadsheets.zip (Attachment I)

Figure 6.6-1. Np_2O_5 Solubility Modeled as a Function of pH and $\text{log } f_{\text{CO}_2}$

6.6.2.3 Abstraction

As the independent variables (pH and $\text{log } f_{\text{CO}_2}$) are both in log scale, solubility entries in the look-up table for TSPA use should also be in log scale. Table 6.6-2 gives $\text{log}[\text{Np}]$ in units of mg/L. For those calculations that do not converge or are not valid, a large number (500) is entered to flag that under such pH and f_{CO_2} conditions, solubility of neptunium is not defined or the calculation results are outside the valid range of the computing tool. The user of the look-up table needs to ensure that when the flag (500) is encountered, the inventory concentrations calculated according to the dissolution rate of waste forms, water volume, and radionuclide inventory should be used instead of the flag itself. For any conditions that fall between a valid solubility and a flag of 500, the flag should be used. In addition, for any conditions outside of the 3.0-11.0 pH range, the -1.5 to -5.0 f_{CO_2} range, or with an ionic strength greater than 1.0 molal, the inventory concentrations calculated according to the dissolution rate of waste forms, water volume, and radionuclide inventory should be used.

Table 6.6-2. Np_2O_5 Solubility Look-up Table ($\log[\text{Np}]$, mg/L)

pH	$\log f_{\text{CO}_2}$							
	-1.50	-2.00	-2.50	-3.00	-3.50	-4.00	-4.50	-5.00
3.00	4.49E+00	4.49E+00	4.49E+00	4.49E+00	4.49E+00	4.49E+00	4.49E+00	4.49E+00
3.25	4.15E+00	4.15E+00	4.15E+00	4.15E+00	4.15E+00	4.15E+00	4.15E+00	4.15E+00
3.50	3.84E+00	3.84E+00	3.84E+00	3.84E+00	3.84E+00	3.84E+00	3.84E+00	3.84E+00
3.75	3.56E+00	3.56E+00	3.56E+00	3.56E+00	3.56E+00	3.56E+00	3.56E+00	3.56E+00
4.00	3.29E+00	3.29E+00	3.29E+00	3.29E+00	3.29E+00	3.29E+00	3.29E+00	3.29E+00
4.25	3.03E+00	3.03E+00	3.03E+00	3.03E+00	3.03E+00	3.03E+00	3.03E+00	3.03E+00
4.50	2.77E+00	2.77E+00	2.77E+00	2.77E+00	2.77E+00	2.77E+00	2.77E+00	2.77E+00
4.75	2.52E+00	2.52E+00	2.52E+00	2.52E+00	2.52E+00	2.52E+00	2.52E+00	2.52E+00
5.00	2.26E+00	2.26E+00	2.26E+00	2.26E+00	2.26E+00	2.26E+00	2.26E+00	2.26E+00
5.25	2.01E+00	2.01E+00	2.01E+00	2.01E+00	2.01E+00	2.01E+00	2.01E+00	2.01E+00
5.50	1.76E+00	1.76E+00	1.76E+00	1.76E+00	1.76E+00	1.76E+00	1.76E+00	1.76E+00
5.75	1.51E+00	1.51E+00	1.51E+00	1.51E+00	1.51E+00	1.51E+00	1.51E+00	1.51E+00
6.00	1.26E+00	1.26E+00	1.26E+00	1.26E+00	1.26E+00	1.26E+00	1.26E+00	1.26E+00
6.25	1.01E+00	1.01E+00	1.01E+00	1.01E+00	1.01E+00	1.01E+00	1.01E+00	1.01E+00
6.50	7.66E-01	7.62E-01	7.61E-01	7.60E-01	7.60E-01	7.60E-01	7.60E-01	7.60E-01
6.75	5.51E-01	5.19E-01	5.12E-01	5.11E-01	5.10E-01	5.10E-01	5.10E-01	5.10E-01
7.00	4.17E-01	2.89E-01	2.69E-01	2.63E-01	2.61E-01	2.60E-01	2.60E-01	2.60E-01
7.25	4.90E-01	1.28E-01	3.98E-02	1.87E-02	1.27E-02	1.09E-02	1.03E-02	1.01E-02
7.50	8.40E-01	1.30E-01	-1.44E-01	-2.11E-01	-2.31E-01	-2.37E-01	-2.39E-01	-2.40E-01
7.75	1.42E+00	3.83E-01	-1.90E-01	-3.99E-01	-4.62E-01	-4.81E-01	-4.87E-01	-4.89E-01
8.00	2.37E+00	8.66E-01	-1.73E-02	-4.82E-01	-6.54E-01	-7.13E-01	-7.31E-01	-7.37E-01
8.25	500	1.63E+00	3.74E-01	-3.69E-01	-7.49E-01	-9.07E-01	-9.63E-01	-9.81E-01
8.50	500	3.01E+00	1.00E+00	-5.70E-02	-6.83E-01	-1.01E+00	-1.16E+00	-1.21E+00
8.75	500	500	2.03E+00	4.62E-01	-4.32E-01	-9.64E-01	-1.27E+00	-1.41E+00
9.00	500	500	500	1.32E+00	-7.19E-03	-7.63E-01	-1.23E+00	-1.52E+00
9.25	500	500	500	2.78E+00	7.17E-01	-4.12E-01	-1.06E+00	-1.50E+00
9.50	500	500	500	500	1.90E+00	1.90E-01	-7.63E-01	-1.34E+00
9.75	500	500	500	500	500	1.25E+00	-2.67E-01	-1.08E+00
10.00	500	500	500	500	500	3.22E+00	6.78E-01	-6.62E-01
10.25	500	500	500	500	500	500	2.23E+00	1.64E-01
10.50	500	500	500	500	500	500	500	1.63E+00

Source: Microsoft Excel spreadsheet Np2O5 solubility.xls in Spreadsheets.zip (Attachment I)

NOTES: Some cells have no valid solubility values because the EQ3NR calculations do not converge, and those calculations results are reported as 500 in this table.

Runs with ionic strengths > 1.0 are outside the range of validation, and are reported as 500 in this table.

6.6.2.4 Uncertainty

6.6.2.4.1 Uncertainties in $\log K$ Values of Controlling Solid and Aqueous Species

The uncertainty in solubility involves uncertainties in the thermodynamic properties of both the controlling solid and significant dissolved species. The rationale behind the evaluation and combination of these uncertainties are discussed in some detail in Section 6.3.3.1.

The dissolved species accounting for more than 5 percent of the dissolved neptunium were found by examining the EQ3NR output for selected runs representing the range of conditions modeled. They are NpO_2^+ , $\text{NpO}_2\text{SO}_4(\text{aq})$, $\text{NpO}_2(\text{SO}_4)_2^{2-}$, $\text{NpO}_2(\text{CO}_3)_2^{2-}$, $\text{NpO}_2\text{CO}_3^-$, and $\text{NpO}_2(\text{CO}_3)_3^{4-}$. The uncertainties for species except $\text{NpO}_2(\text{CO}_3)_2^{2-}$ are ± 0.1 or less. For $\text{NpO}_2(\text{CO}_3)_2^{2-}$ the uncertainty is high, ± 0.7 , because it is based on only one, very sparse, experimental data set (Lemire 2001, Section 12.1.2.1.2.b).

After an extensive review, Lemire (2001) recommended -2031.6 ± 11.2 kJ/mol for the Gibbs free energy of formation of Np_2O_5 , based on calorimetric studies. The procedure outlined in Section 6.3.3.1 leads to $\log K$ of 3.7 with a 2σ uncertainty of ± 2.8 (at 25°C) for the reaction:



This $\log K$ value is adopted in data0.ymp.R2. Efurd et al. (1998) report a $\log K$ value of 5.2 for the above reaction based on solubility experiments using J-13 well water. This higher $\log K$ value is attributed to the hydrated nature of the precipitate, which is expected to become a crystalline solid with time due to the aging process. The difference between the $\log K$ value adopted in data0.ymp.R2 and the value obtained by Efurd et al. (1998) is 1.5. This is within the calculated 2σ range based on the NEA data (± 2.8 , above).

The evaluation of reactions from Np_2O_5 to each of the six dissolved species noted above leads to a maximum uncertainty in $\log K$ for reaction to $\text{NpO}_2(\text{CO}_3)_2^{2-}$, ± 3.16 . This applies at pH above about 7. For lower pHs NpO_2^+ prevails with a $\log K$ uncertainty of ± 2.785 . Conservatively the higher of these is chosen to represent all neptunium solubilities.

The selected Np_2O_5 dissolution reaction discussed in the previous paragraph, which has a 2σ uncertainty in $\log K$ of ± 3.2 , produces 2 moles of neptunium in solution per Np_2O_5 formula unit. The uncertainty of the $\log K$ of this reaction per mol neptunium is half this value, or ± 1.6 . This is a 2σ uncertainty so the 1σ uncertainty to be applied to $\log[\text{Np}]$ is ± 0.8 .

6.6.2.4.2 Uncertainty from Fluoride Concentration

Table 6.6-3 lists the calculated Np_2O_5 solubilities at the base-case value and higher concentrations (10 times and 200 times of the base-case value) of fluoride, along with their differences in log scale. The fugacity of CO_2 is set to $10^{-3.0}$. The differences between the base-case results and the uncertainty case results vary with pH. The maximum difference between the base-case results and the 10 times fluoride results is $1.59\text{E-}02$. This is the uncertainty term of $\log[\text{Np}]$ for CSNF waste packages ($\varepsilon_2^{\text{CSNF}}$), which obeys a triangular distribution, with $a = b = 0.00$, and $c = 1.59\text{E-}02$. For codisposal waste packages and the invert, the uncertainty term $\varepsilon_2^{\text{CO-IN}}$ associated with fluoride concentration also obeys a triangular distribution but with a c value equal to $4.74\text{E-}01$. Unlike plutonium, neptunium solubility is not very sensitive to fluoride concentration.

Table 6.6-3. The Effects of Variations in Fluoride Concentration on Np₂O₅ Solubility

pH	Base Case (1× F)	CSNF (10× F)	Codisposal (200× F)	CSNF Difference	Codisposal Difference
	[Np mg/L]			$\log[\text{Np}]_{\text{CSNF}} - \log[\text{Np}]_{\text{Base Case}}$	$\log[\text{Np}]_{\text{Codisp}} - \log[\text{Np}]_{\text{Base Case}}$
3.00	3.07E+04	3.10E+04	3.62E+04	4.28E-03	7.11E-02
3.25	1.40E+04	1.43E+04	1.81E+04	7.22E-03	1.10E-01
3.50	6.95E+03	7.13E+03	1.02E+04	1.06E-02	1.64E-01
3.75	3.64E+03	3.76E+03	6.29E+03	1.37E-02	2.38E-01
4.00	1.96E+03	2.03E+03	4.15E+03	1.53E-02	3.26E-01
4.25	1.07E+03	1.11E+03	2.78E+03	1.45E-02	4.15E-01
4.50	5.91E+02	6.08E+02	1.76E+03	1.20E-02	4.74E-01
4.75	3.29E+02	3.36E+02	9.74E+02	9.28E-03	4.72E-01
5.00	1.84E+02	1.87E+02	4.76E+02	7.27E-03	4.13E-01
5.25	1.03E+02	1.04E+02	2.22E+02	5.96E-03	3.34E-01
5.50	5.77E+01	5.84E+01	1.06E+02	5.21E-03	2.65E-01
5.75	3.24E+01	3.28E+01	5.33E+01	4.76E-03	2.16E-01
6.00	1.82E+01	1.84E+01	2.78E+01	4.48E-03	1.84E-01
6.25	1.02E+01	1.03E+01	1.50E+01	4.35E-03	1.65E-01
6.50	5.76E+00	5.81E+00	8.20E+00	4.26E-03	1.53E-01
6.75	3.24E+00	3.27E+00	4.55E+00	4.21E-03	1.47E-01
7.00	1.83E+00	1.85E+00	2.54E+00	4.16E-03	1.43E-01
7.25	1.04E+00	1.05E+00	1.44E+00	4.06E-03	1.40E-01
7.50	6.14E-01	6.20E-01	8.39E-01	3.76E-03	1.35E-01
7.75	3.99E-01	4.01E-01	5.33E-01	2.25E-03	1.26E-01
8.00	3.29E-01	3.36E-01	4.28E-01	8.40E-03	1.14E-01
8.25	4.28E-01	4.35E-01	5.43E-01	7.55E-03	1.03E-01
8.50	8.77E-01	8.94E-01	1.19E+00	8.51E-03	1.33E-01
8.75	2.90E+00	2.98E+00	4.77E+00	1.23E-02	2.17E-01
9.00	2.10E+01	2.18E+01	3.97E+01	1.55E-02	2.76E-01
9.25	6.00E+02	6.22E+02	1.28E+03	1.59E-02	3.31E-01
			Maximum:	1.59E-02	4.74E-01
			Minimum:	2.25E-03	7.11E-02
			Average:	8.06E-03	2.26E-01

Source: Microsoft Excel spreadsheet Np2O5 solubility.xls in Spreadsheets.zip (Attachment I)

6.6.2.5 Summary of Np_2O_5 Solubility Model

The Np_2O_5 solubility model can be summarized by Eq. 6.6-3.

$$\log[\text{Np}] = S(\text{pH}, \log f_{\text{CO}_2}) + \varepsilon_1 + \varepsilon_2^i \quad (\text{Eq. 6.6-3})$$

where

$S(\text{pH}, \log f_{\text{CO}_2})$ is the calculated log solubility values given by Table 6.6-2

ε_1 is the uncertainty term associated with uncertainty in log Ks

ε_2^i is the uncertainty term associated with variations in fluoride concentration

i corresponds to either CSNF or codisposal waste package and the invert

The distribution properties of these uncertainty terms are listed in Table 6.6-4.

Table 6.6-4. Uncertainty Terms of $\log[\text{Np}]$ of Np_2O_5 Model

Uncertainty Term	Associated With	Distribution Type	Distribution Parameter	Applicable to
ε_1	Uncertainties in log K	Normal	$\mu = 0, \sigma = 0.8$	
$\varepsilon_2^{\text{CSNF}}$	Fluoride concentration in CSNF waste packages	Triangular	$a = b = 0, c = 1.59\text{E-}2$	CSNF waste packages
$\varepsilon_2^{\text{CO-IN}}$	Fluoride concentration in codisposal waste packages	Triangular	$a = b = 0, c = 0.474$	Codisposal waste packages and the invert

6.6.3 Alternative Solubility Model I: NpO_2 Model

6.6.3.1 Water Composition Used for the Calculation

See Table 6.4-1 for the chemical conditions for the NpO_2 solubility calculations.

6.6.3.2 EQ3NR Results

The results of the NpO_2 solubility are presented in Table 6.6-5. Among the 296 calculations, 38 do not converge and are not listed in the table. None of the converged results are outside the valid ionic strength range (1.0 molal). The pH range within which the calculation converges varies under different f_{CO_2} conditions. The higher the f_{CO_2} , the narrower the converging pH range. The lower ends are pH 3.0, while the upper ends change from 8.25 to 10.75. Of those converged calculations, the maximum solubility is 1.44 mg/L, which appears at the high pH end (under both $\log f_{\text{CO}_2} = -2.00$ and -3.00) before the calculation diverges. The minimum solubility is $1.83\text{E-}3$ mg/L, which appears at pH of 9.0 and $\log f_{\text{CO}_2} = -5.0$.

Figure 6.6-2 shows the calculated solubility using NpO_2 as the controlling solid. It is a function of pH and fugacity of CO_2 . Under the same f_{CO_2} , just like Np_2O_5 solubility, NpO_2 solubility increases with pH under alkaline conditions; while under acid conditions it increases with decrease in pH.

Comparing Tables 6.6-1 and 6.6-5 (see Microsoft Excel spreadsheet diff of Np2O5 and NpO2.xls in Spreadsheets.zip of Attachment I) reveals that the average difference between calculated Np₂O₅ solubility and NpO₂ solubility at 25°C is 1.24 log units, which is less than the uncertainty from log Ks of Np₂O₅ (1.6 log units; see Section 6.6.2.4.1).

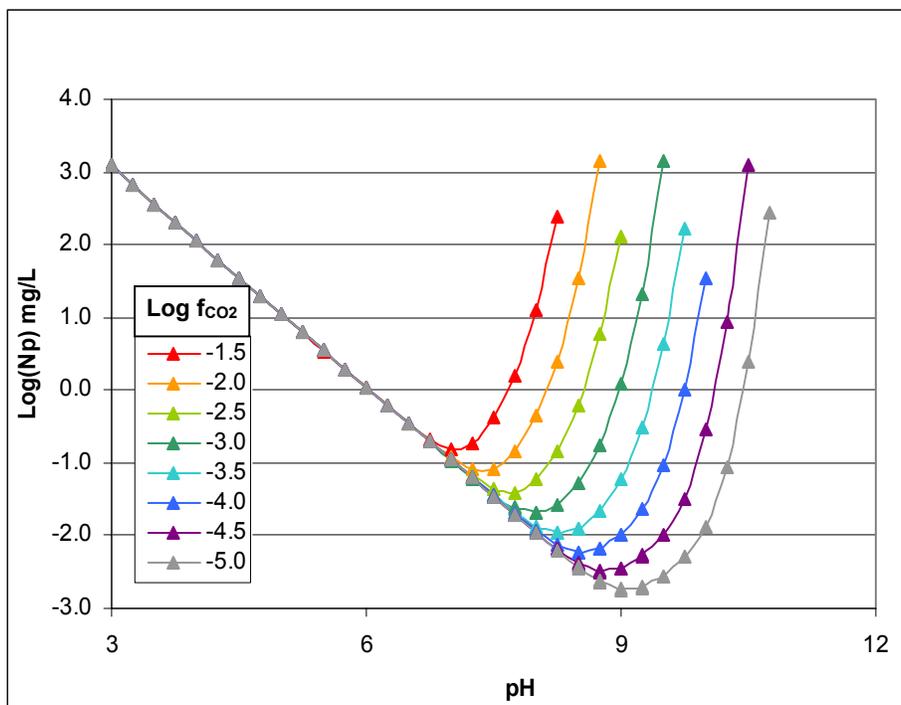
Table 6.6-5. Calculated NpO₂ Solubility (mg/L)

pH	log f _{CO2}							
	-1.50	-2.00	-2.50	-3.00	-3.50	-4.00	-4.50	-5.00
3.00	1.24E+03	1.24E+03	1.24E+03	1.24E+03	1.24E+03	1.24E+03	1.24E+03	1.24E+03
3.25	6.63E+02	6.63E+02	6.63E+02	6.63E+02	6.63E+02	6.63E+02	6.63E+02	6.63E+02
3.50	3.63E+02	3.63E+02	3.63E+02	3.63E+02	3.63E+02	3.63E+02	3.63E+02	3.63E+02
3.75	2.01E+02	2.01E+02	2.01E+02	2.01E+02	2.01E+02	2.01E+02	2.01E+02	2.01E+02
4.00	1.12E+02	1.12E+02	1.12E+02	1.12E+02	1.12E+02	1.12E+02	1.12E+02	1.12E+02
4.25	6.26E+01	6.26E+01	6.26E+01	6.26E+01	6.26E+01	6.26E+01	6.26E+01	6.26E+01
4.50	3.51E+01	3.51E+01	3.51E+01	3.51E+01	3.51E+01	3.51E+01	3.51E+01	3.51E+01
4.75	1.97E+01	1.97E+01	1.97E+01	1.97E+01	1.97E+01	1.97E+01	1.97E+01	1.97E+01
5.00	1.11E+01	1.11E+01	1.11E+01	1.11E+01	1.11E+01	1.11E+01	1.11E+01	1.11E+01
5.25	6.22E+00	6.22E+00	6.22E+00	6.22E+00	6.22E+00	6.22E+00	6.22E+00	6.22E+00
5.50	3.50E+00	3.50E+00	3.50E+00	3.50E+00	3.50E+00	3.50E+00	3.50E+00	3.50E+00
5.75	1.97E+00	1.97E+00	1.97E+00	1.97E+00	1.97E+00	1.97E+00	1.97E+00	1.97E+00
6.00	1.11E+00	1.11E+00	1.11E+00	1.11E+00	1.11E+00	1.11E+00	1.11E+00	1.11E+00
6.25	6.24E-01	6.22E-01						
6.50	3.57E-01	3.51E-01	3.50E-01	3.50E-01	3.50E-01	3.50E-01	3.50E-01	3.50E-01
6.75	2.16E-01	2.01E-01	1.98E-01	1.97E-01	1.97E-01	1.97E-01	1.97E-01	1.97E-01
7.00	1.59E-01	1.19E-01	1.13E-01	1.11E-01	1.11E-01	1.11E-01	1.11E-01	1.11E-01
7.25	1.88E-01	8.17E-02	6.66E-02	6.34E-02	6.26E-02	6.23E-02	6.22E-02	6.22E-02
7.50	4.20E-01	8.19E-02	4.39E-02	3.73E-02	3.57E-02	3.52E-02	3.50E-02	3.50E-02
7.75	1.60E+00	1.47E-01	3.92E-02	2.42E-02	2.10E-02	2.01E-02	1.98E-02	1.97E-02
8.00	1.26E+01	4.46E-01	5.84E-02	2.01E-02	1.35E-02	1.18E-02	1.13E-02	1.11E-02
8.25	2.43E+02	2.53E+00	1.44E-01	2.60E-02	1.08E-02	7.53E-03	6.62E-03	6.35E-03
8.50		3.36E+01	6.11E-01	5.33E-02	1.27E-02	5.93E-03	4.22E-03	3.72E-03
8.75		1.44E+03	5.90E+00	1.76E-01	2.24E-02	6.60E-03	3.28E-03	2.37E-03
9.00			1.31E+02	1.25E+00	5.97E-02	1.05E-02	3.54E-03	1.83E-03
9.25				2.16E+01	3.15E-01	2.35E-02	5.32E-03	1.94E-03
9.50				1.44E+03	4.40E+00	9.39E-02	1.05E-02	2.81E-03
9.75					1.64E+02	1.05E+00	3.29E-02	5.10E-03
10.00						3.45E+01	2.87E-01	1.32E-02
10.25							8.73E+00	8.84E-02
10.50							1.22E+03	2.45E+00
10.75								2.69E+02

Sources: Microsoft Excel spreadsheet NpO2 solubility.xls in Spreadsheets.zip (Attachment I)

NOTES: Some cells have no data because the EQ3NR calculations do not converge.

Runs with ionic strengths > 1.0 are outside the range of validation, and are not reported in this table.



Source: Microsoft Excel spreadsheet NpO₂ Solubility.xls in Spreadsheets.zip (Attachment I)

Figure 6.6-2. NpO₂ Solubility Modeled as a Function of pH and log f_{CO_2}

6.6.3.3 Abstraction

As the independent variables (pH and log f_{CO_2}) are both in log scale, solubility entries in the look-up table for TSPA to use should also be in log scale. Table 6.6-6 gives log[Np] in units of mg/L. For those calculations that do not converge or are not valid, a big number (500) is entered to flag that under such pH and f_{CO_2} conditions solubility of neptunium are not defined or the calculation results are outside the valid range of the computing tool. The user of the look-up table needs to ensure that when the flag (500) is encountered, the inventory concentrations calculated according to the dissolution rate of waste forms, water volume, and radionuclide inventory should be used instead of the flag itself. For any conditions that fall between a valid solubility and a flag of 500, the flag should be used. In addition, for any conditions outside of the 3.0-11.0 pH range, the -1.5 to -5.0 f_{CO_2} range, or with an ionic strength greater than 1.0 molal, the inventory concentrations calculated according to the dissolution rate of waste forms, water volume, and radionuclide inventory should be used.

Table 6.6-6. NpO₂ Solubility Look-up Table (log[Np], mg/L)

pH	log f _{CO2}							
	-1.50	-2.00	-2.50	-3.00	-3.50	-4.00	-4.50	-5.00
3.00	3.09E+00	3.09E+00	3.09E+00	3.09E+00	3.09E+00	3.09E+00	3.09E+00	3.09E+00
3.25	2.82E+00	2.82E+00	2.82E+00	2.82E+00	2.82E+00	2.82E+00	2.82E+00	2.82E+00
3.50	2.56E+00	2.56E+00	2.56E+00	2.56E+00	2.56E+00	2.56E+00	2.56E+00	2.56E+00
3.75	2.30E+00	2.30E+00	2.30E+00	2.30E+00	2.30E+00	2.30E+00	2.30E+00	2.30E+00
4.00	2.05E+00	2.05E+00	2.05E+00	2.05E+00	2.05E+00	2.05E+00	2.05E+00	2.05E+00
4.25	1.80E+00	1.80E+00	1.80E+00	1.80E+00	1.80E+00	1.80E+00	1.80E+00	1.80E+00
4.50	1.55E+00	1.55E+00	1.55E+00	1.55E+00	1.55E+00	1.55E+00	1.55E+00	1.55E+00
4.75	1.29E+00	1.29E+00	1.29E+00	1.29E+00	1.29E+00	1.29E+00	1.29E+00	1.29E+00
5.00	1.04E+00	1.04E+00	1.04E+00	1.04E+00	1.04E+00	1.04E+00	1.04E+00	1.04E+00
5.25	7.94E-01	7.94E-01	7.94E-01	7.94E-01	7.94E-01	7.94E-01	7.94E-01	7.94E-01
5.50	5.44E-01	5.44E-01	5.44E-01	5.44E-01	5.44E-01	5.44E-01	5.44E-01	5.44E-01
5.75	2.93E-01	2.94E-01						
6.00	4.37E-02	4.36E-02						
6.25	-2.05E-01	-2.06E-01						
6.50	-4.48E-01	-4.54E-01	-4.56E-01	-4.56E-01	-4.56E-01	-4.56E-01	-4.56E-01	-4.56E-01
6.75	-6.65E-01	-6.98E-01	-7.04E-01	-7.06E-01	-7.06E-01	-7.06E-01	-7.06E-01	-7.06E-01
7.00	-8.00E-01	-9.24E-01	-9.48E-01	-9.54E-01	-9.56E-01	-9.56E-01	-9.56E-01	-9.56E-01
7.25	-7.26E-01	-1.09E+00	-1.18E+00	-1.20E+00	-1.20E+00	-1.21E+00	-1.21E+00	-1.21E+00
7.50	-3.77E-01	-1.09E+00	-1.36E+00	-1.43E+00	-1.45E+00	-1.45E+00	-1.46E+00	-1.46E+00
7.75	2.05E-01	-8.33E-01	-1.41E+00	-1.62E+00	-1.68E+00	-1.70E+00	-1.70E+00	-1.71E+00
8.00	1.10E+00	-3.51E-01	-1.23E+00	-1.70E+00	-1.87E+00	-1.93E+00	-1.95E+00	-1.95E+00
8.25	2.39E+00	4.02E-01	-8.43E-01	-1.59E+00	-1.97E+00	-2.12E+00	-2.18E+00	-2.20E+00
8.50	500	1.53E+00	-2.14E-01	-1.27E+00	-1.90E+00	-2.23E+00	-2.37E+00	-2.43E+00
8.75	500	3.16E+00	7.71E-01	-7.55E-01	-1.65E+00	-2.18E+00	-2.48E+00	-2.63E+00
9.00	500	500	2.12E+00	9.62E-02	-1.22E+00	-1.98E+00	-2.45E+00	-2.74E+00
9.25	500	500	500	1.33E+00	-5.02E-01	-1.63E+00	-2.27E+00	-2.71E+00
9.50	500	500	500	3.16E+00	6.43E-01	-1.03E+00	-1.98E+00	-2.55E+00
9.75	500	500	500	500	2.21E+00	2.13E-02	-1.48E+00	-2.29E+00
10.00	500	500	500	500	500	1.54E+00	-5.42E-01	-1.88E+00
10.25	500	500	500	500	500	500	9.41E-01	-1.05E+00
10.50	500	500	500	500	500	500	3.09E+00	3.90E-01
10.75	500	500	500	500	500	500	500	2.43E+00

Source: Microsoft Excel spreadsheet NpO₂ solubility.xls in Spreadsheets.zip (Attachment I)

NOTES: Some cells have no valid data because the EQ3NR calculations do not converge, and those results are reported as 500 in this table.

Runs with ionic strengths > 1.0 are outside the range of validation, and are reported as 500 in this table.

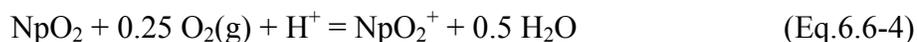
6.6.3.4 Uncertainty

6.6.3.4.1 Uncertainties in log K Values of Controlling Solid and Aqueous Species

The uncertainty in solubility involves uncertainties in the thermodynamic properties of both the controlling solid and significant dissolved species. The rationale behind the evaluation and combination of these uncertainties are discussed in some detail in Section 6.3.3.1.

The dissolved species accounting for more than 5 percent of the dissolved neptunium were found by examining the EQ3NR output for selected runs representing the range of conditions modeled. They are NpO_2^+ , $\text{NpO}_2\text{SO}_4(\text{aq})$, $\text{NpO}_2(\text{SO}_4)_2^{2-}$, $\text{NpO}_2(\text{CO}_3)_2^{2-}$, $\text{NpO}_2\text{CO}_3^-$, and $\text{NpO}_2(\text{CO}_3)_3^{4-}$. The uncertainties for species except $\text{NpO}_2(\text{CO}_3)_2^{2-}$ are ± 0.1 or less. For $\text{NpO}_2(\text{CO}_3)_2^{2-}$ the uncertainty is high, ± 0.7 , because it is based on only one, very sparse, experimental data set (Lemire 2001, Section 12.1.2.1.2.b).

After an extensive review, Lemire (2001) recommended -1021.731 ± 2.514 kJ/mol for the Gibbs free energy of formation of NpO_2 , based on calorimetric studies. Following the procedure outlined in Section 6.3.3.1 leads to log K of 0.81 with a 2σ uncertainty of ± 1.1 (at 25°C) for the reaction:



The evaluation of reactions from NpO_2 to each of the six dissolved species noted above leads to a maximum uncertainty in log K for reaction to $\text{NpO}_2(\text{CO}_3)_2^{2-}$, ± 1.31 . This is a 2σ uncertainty, so the 1σ uncertainty to be applied to $\log[\text{Np}]$ is ± 0.7 .

6.6.3.4.2 Uncertainty from Fluoride Concentration

Table 6.6-7 lists the calculated NpO_2 solubilities at the base-case value and higher concentrations (10 times and 200 times of the base-case value) of fluoride, along with their differences in log scale. The fugacity of CO_2 is set to $10^{-3.00}$. The differences between the base-case results and the uncertainty case results vary with pH. The maximum difference between the base-case results and the 10 times fluoride results is 0.0431. This is the uncertainty term of $\log[\text{Np}]$ for CSNF waste packages ($\varepsilon_2^{\text{CSNF}}$), which obeys a triangular distribution, with $a = b = 0.00$, and $c = 0.0431$. For codisposal waste packages and the invert, the uncertainty term $\varepsilon_2^{\text{CO-IN}}$ associated with fluoride concentration also obeys a triangular distribution but with a c value equal to 0.887.

Table 6.6-7. The Effects of Variations in Fluoride Concentration on NpO₂ Solubility

pH	Base Case (1× F ⁻)	CSNF (10× F ⁻)	Codisposal (200× F ⁻)	CSNF Difference	Codisposal Difference
	[Np mg/L]			$\log[\text{Np}_{\text{CSNF}}] - \log[\text{Np}_{\text{Base Case}}]$	$\log[\text{Np}_{\text{Codisp}}] - \log[\text{Np}_{\text{Base Case}}]$
3.00	1.24E+03	1.35E+03	3.80E+03	3.67E-02	4.87E-01
3.25	6.63E+02	7.32E+02	2.78E+03	4.27E-02	6.23E-01
3.50	3.63E+02	4.01E+02	2.06E+03	4.31E-02	7.53E-01
3.75	2.01E+02	2.19E+02	1.42E+03	3.73E-02	8.50E-01
4.00	1.12E+02	1.20E+02	8.64E+02	2.83E-02	8.87E-01
4.25	6.26E+01	6.56E+01	4.40E+02	1.98E-02	8.46E-01
4.50	3.51E+01	3.62E+01	1.91E+02	1.37E-02	7.35E-01
4.75	1.97E+01	2.02E+01	7.71E+01	9.76E-03	5.93E-01
5.00	1.11E+01	1.13E+01	3.18E+01	7.39E-03	4.58E-01
5.25	6.22E+00	6.31E+00	1.39E+01	6.00E-03	3.49E-01
5.50	3.50E+00	3.54E+00	6.51E+00	5.20E-03	2.70E-01
5.75	1.97E+00	1.99E+00	3.24E+00	4.75E-03	2.17E-01
6.00	1.11E+00	1.12E+00	1.69E+00	4.49E-03	1.85E-01
6.25	6.22E-01	6.28E-01	9.09E-01	4.34E-03	1.65E-01
6.50	3.50E-01	3.53E-01	4.98E-01	4.25E-03	1.54E-01
6.75	1.97E-01	1.99E-01	2.76E-01	4.21E-03	1.47E-01
7.00	1.11E-01	1.12E-01	1.55E-01	4.16E-03	1.43E-01
7.25	6.34E-02	6.40E-02	8.75E-02	4.05E-03	1.40E-01
7.50	3.73E-02	3.77E-02	5.10E-02	3.76E-03	1.35E-01
7.75	2.42E-02	2.43E-02	3.24E-02	2.25E-03	1.26E-01
8.00	2.01E-02	2.04E-02	2.60E-02	5.48E-03	1.11E-01
8.25	2.60E-02	2.64E-02	3.30E-02	7.56E-03	1.03E-01
8.50	5.33E-02	5.43E-02	7.24E-02	8.51E-03	1.33E-01
8.75	1.76E-01	1.81E-01	2.89E-01	1.23E-02	2.16E-01
9.00	1.25E+00	1.29E+00	2.34E+00	1.53E-02	2.73E-01
9.25	2.16E+01	2.22E+01	3.62E+01	1.20E-02	2.25E-01
9.50	1.44E+03	1.47E+03	2.35E+03	9.68E-03	2.13E-01
			Maximum:	4.31E-02	8.87E-01
			Minimum:	2.25E-03	1.03E-01
			Average:	1.32E-02	3.53E-01

Source: Microsoft Excel spreadsheet NpO₂ solubility.xls in Spreadsheets.zip (Attachment I)NOTE: $\log f_{\text{CO}_2} = -3.0$

6.6.3.5 Summary of NpO₂ Solubility Model

The NpO₂ solubility model can be summarized by the following equation:

$$\log[Np] = S(pH, \log f_{CO_2}) + \varepsilon_1 + \varepsilon_2^i \quad (\text{Eq. 6.6-7})$$

where:

$S(pH, \log f_{CO_2})$ is given by Table 6.6-6

ε_1 is the uncertainty term associated with uncertainty in log Ks

ε_2^i is the uncertainty term associated with variations in fluoride concentration

i corresponds to either CSNF or codisposal waste package and the invert

The distribution properties of these uncertainty terms are listed in Table 6.6-8.

Table 6.6-8. Uncertainty Terms of log[Np] of NpO₂ Model

Uncertainty Term	Associated With	Distribution Type	Distribution Parameter	Applicable to
ε_1	Uncertainties in log K	Normal	$\mu = 0, \sigma = 0.7$	
ε_2^{CSNF}	Fluoride concentration in CSNF waste packages	Triangular	$a = b = 0, c = 0.0431$	CSNF waste packages
ε_2^{CO-IN}	Fluoride concentration in codisposal waste packages	Triangular	$a = b = 0, c = 0.887$	Codisposal waste packages and the invert

6.6.4 Alternative Neptunium Solubility Models II: Secondary Phase Model

6.6.4.1 Concentrating Factor of Neptunium

The experimental data described in Section 6.6.1.2 show that the neptunium concentrations in solutions degrading spent fuel are considerably lower than concentrations controlled by pure neptunium solids. An empirical neptunium solubility limit was developed based on drip test measurements which does not rely on the identification of neptunium-bearing phases or assumptions about neptunium retention mechanisms (Chen 2001; BSC 2001f, Section 5.1; Chen et al. 2002).

The concentrating factor of neptunium in solution is defined as:

$$F_c = \frac{(Np/U)_{soln}}{(Np/U)_{fuel}} \quad (\text{Eq. 6.6-8})$$

where $(Np/U)_{soln}$ denotes the ratio of neptunium to uranium in solution and $(Np/U)_{fuel}$ the same ratio in spent fuel. The concentrating factor (F_c) of neptunium describes the degree of neptunium being concentrated in solution relative to the spent fuel with which it is in contact.

Re-arranging Eq. 6.6-8 yields:

$$[Np] = F_c (Np/U)_{fuel} [U] \quad (\text{Eq. 6.6-9})$$

where [Np] and [U] denote the concentrations of neptunium and uranium in solution, respectively.

Note that Eq. 6.6-9 says neptunium concentration is proportional to uranium concentration and the proportionality constant is a product of a known value of the ratio of neptunium and uranium in the fuel and an uncertain concentrating factor, F_c , which can be obtained from spent fuel dissolution experimental data.

6.6.4.2 Simple Estimation of F_c of Neptunium Using Data from ANL Drip Tests

Unsaturated spent fuel dissolution tests have been described in detail in several journal articles (Finn et al. 1994; Finn et al. 1997) and in *Secondary Uranium-Phase Paragenesis and Incorporation of Radionuclides into Secondary Phases* (BSC 2001g). Based on the rates of water added to the spent fuel samples, those experiments were grouped into three categories: high drip-rate tests, low drip-rate tests, and vapor tests. All other environmental conditions were constant. The tests are designed to simulate the evolution of spent nuclear fuel and the release of radionuclides in the repository. The concentrations of several radionuclides in the leachate were measured and reported (CRWMS M&O 2000d; CRWMS M&O 2000e; DTN: LL991001251021.090).

Two types of commercial spent fuels, approved testing material (ATM)-103 with a burn-up of 30 MW-d/kgU and ATM-106 with a burn-up of 43 MW-d/kgU (Finn et al. 1994), were used in the experiments. The calculated neptunium-237/uranium-238 ratios in those two fuels are listed in Table 6.6-9 using the inventory tables given by Guenther et al. (1988a; 1988b), assuming 15 years out of the reactor (see Section 5).

Table 6.6-9. Calculated Mole Ratio of Neptunium-237 to Uranium-238 in the Fuels Used in ANL Experiments

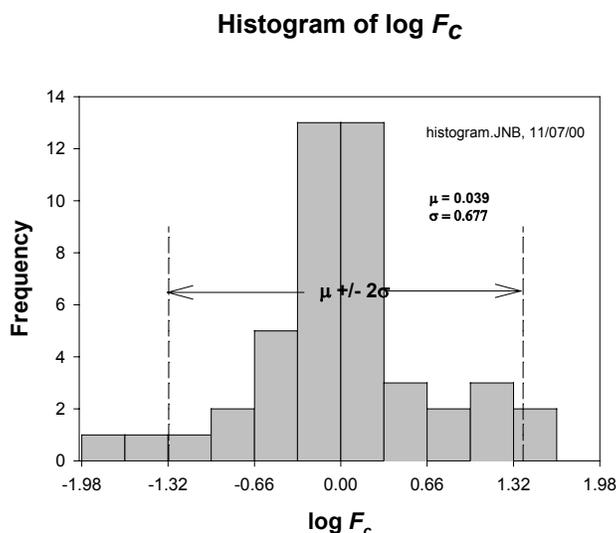
	ATM-103	ATM-106
Burnup	30 MW-d/kgU	43 MW-d/kgU
Np-237/U-238	4.20E-04	6.44E-04

Source: Microsoft Excel spreadsheet ANL6dripdata.xls in Spreadsheets.zip (Attachment I)

There are 46 concentration values of neptunium-237 and uranium-238 available from the high drip-rate and low drip-rate tests (DTN: LL991001251021.090; CRWMS M&O 2000e). Because isotope fractionation is not expected to change significantly the isotopic ratios of the leachate from that of the fuel, it is concluded that:

$$F_c = \frac{(Np/U)_{soln}}{(Np/U)_{fuel}} = \frac{(Np^{237}/U^{238})_{soln}}{(Np^{237}/U^{238})_{fuel}} \quad (\text{Eq. 6.6-10})$$

Figure 6.6-3 is a histogram of the $\log F_c$ values calculated from the 46 sets of experiments reported. It appears that $\log F_c$ has a normal distribution with a mode around 0.0 (i.e., F_c has a mode of 1.0).



Source: F_c histogram.jnb in SigmaPlots.zip (Attachment I)

NOTE: It appears that $\log F_c$ has a normal distribution, with a mode around 0.0 (i.e., F_c has a mode of 1.0).

Figure 6.6-3. Histogram of F_c on a log Scale

Table 6.6-10 lists the statistical description of F_c for neptunium determined from the ANL high and low drip tests. Of the 46 data points, the geometric mean of F_c is 1.094, very close to 1. In other words, the arithmetic mean of $\log F_c$ is 0.039, very close to 0. The standard deviation of $\log F_c$ is 0.667. With a confidence level of 95.5 percent, the upper and lower statistical limits ($\mu \pm 2\sigma$) of $\log F_c$ are 1.394 and -1.316, respectively. In other words, the probability for $\log F_c$ falling between (-1.316, 1.394) is 95.5 percent. Translated back to F_c , the upper and lower limits of F_c are 24.787 and 0.048, respectively. That is the range of uncertainty in F_c of neptunium from ANL high-drip and low-drip tests. It spans less than 3 orders of magnitude.

The fact that the average of $\log F_c$ is very close to 0.0 and has a mode of 0.0 strongly suggests that the neptunium/uranium values in the solutions are very close to the neptunium/uranium values in the fuels. In other words, uranium and neptunium are released from the fuel coherently.

In fact, the coherent relation between uranium and neptunium has also been observed in other spent fuel dissolution experiments. For example, based on PNNL's Series 2 and Series 3 steady-state test results (Wilson 1990a; Wilson 1990b; CRWMS M&O 1998a) states that "the data suggest that Np enters the aqueous phase congruently with uranium as the fuel dissolves." The calculated F_c for Series 2 tests ranges from 0.44 to 2.59, with a geometric mean of 1.13 (see Microsoft Excel spreadsheet PNL-wilson.xls in Spreadsheets.zip of Attachment I). The calculated F_c for Series 3 tests ranges from 3.38 to 11.73, with a geometric mean of 5.90 (see Microsoft Excel spreadsheet PNL-wilson.xls in Spreadsheets.zip of Attachment I).

Table 6.6-10. Statistics of F_c of Neptunium from High and Low Drip Tests

	F_c	$\log F_c$
Number of Samples	46	46
Maximum	30.260	1.481
Minimum	0.015	-1.833
Arithmetic Mean (μ)	3.363	0.039
Geometric Mean	1.094	
Std Dev (σ)		0.677
$\mu + 2\sigma$		1.394
$\mu - 2\sigma$		-1.316
Upper Limit of 95% Confidence Level (UL = $10^{\mu+2\sigma}$)	24.787	
Lower Limit of 95% Confidence Level (LL = $10^{\mu-2\sigma}$)	0.048	
Ratio of Upper to Lower Limit	513.407	

Source: Microsoft Excel spreadsheet ANL6dripdata.xls in Spreadsheets.zip (Attachment I)

Bruno et al. (1998) have also observed the coherent relation between neptunium and uranium in spent fuel dissolution experiments in the Spanish Nuclear Waste Program as shown in Table 6.6-11.

Table 6.6-11. Neptunium/uranium Ratios in Spent Fuel and Its Solution

	Fuel Inventory	Solution
Np/U	4.88E-4	5.25E-4

Source: Bruno et al. 1998

It is unlikely that the coherent relation between uranium and neptunium is a coincidence. Rather, it reflects the similarity of geochemical behaviors of U(VI) and Np(V). Incorporation of neptunium into uranyl minerals is the most reasonable explanation for this relation, as discussed in Section 6.6.1.2.

In summary, based on the simple statistics of ANL drip test data, F_c was a log-normal random variable, with a mean of 1.094. At a confidence level of 95.5 percent, it ranges from 0.048 to 24.787, an uncertainty range of less than 3 orders of magnitude.

6.6.4.3 Trend Analysis of F_c of Neptunium Using Data from ANL Drip Tests

The previous section discussed the conventional statistics of F_c of neptunium. This section further analyzes the variation of F_c in time.

Figure 6.6-4 shows the F_c of neptunium in ANL's high-drip tests as a function of time. The low-drip results are shown in Figure 6.6-5. The solid lines are tests with ATM-103 fuel, while the dashed lines are tests for ATM-106 fuel. They show that in those 4 tests, F_c of neptunium fluctuates around 1. Moreover, in all the 4 tests, the highest F_c occurs in the first sample, and then F_c decreases and reaches the lowest value within 2 years. In other words, the big variations

in F_c occur in the first 2 years, and decrease with time. This suggests that the coherent relation between neptunium and uranium will become more obvious as time increases, and the spikes of F_c s observed in the first 2 years are transient phenomena in the drip tests. The rapid release of neptunium at the early stage of experiments has also been observed in PNNL's Series 2 and Series 3 tests (Wilson 1990a, Figure 3.5, p. 3.18; Wilson 1990b, Figure 3.19, p. 3.39). Early transient phenomena are thought to be due to fuel fines and supersaturation effects and have no TSPA implications. Because TSPA focuses on the long-term performance of the repository, these spikes may not be important. Therefore, it is reasonable to exclude the early data from ANL's drip tests when F_c is estimated.

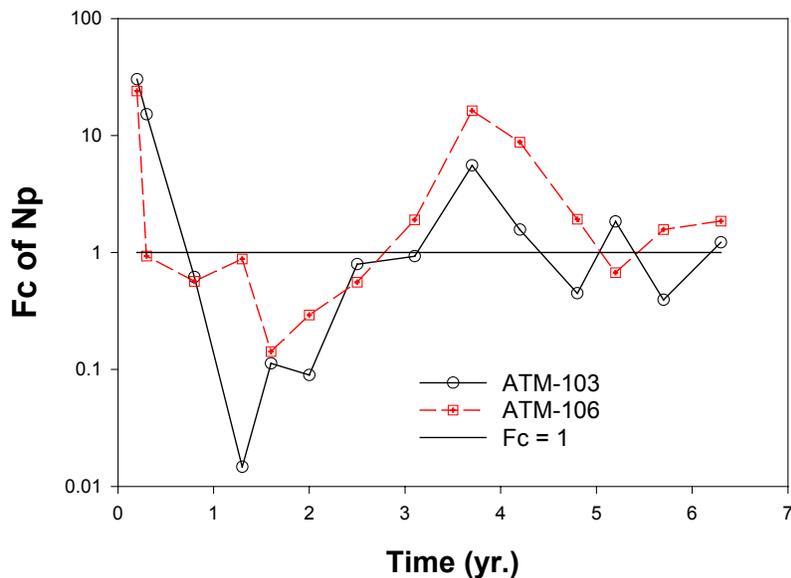
Excluding those data points measured at time less than 2 years, subset data (containing 28 data points) of the 4 drip tests were obtained. Table 6.6-12 presents the statistical results for the subset data. The geometric mean of this reduced dataset is still close to 1.0 (1.142), but with a smaller standard deviation. The upper and lower limits of F_c at a confidence level of 95.5 percent now are 10.653 and 0.122, respectively. The dataset spans less than 2 orders of magnitude.

Table 6.6-12. Statistics of F_c of Neptunium from the Subset of High and Low Drip Tests ($t \geq 2$ yr.)

	F_c	$\log F_c$
Number of Samples	28	28
Maximum	16.347	1.213
Minimum	0.032	-1.048
Arithmetic Mean (μ)	1.954	0.058
Geometric Mean	1.142	
Std Dev (σ)		0.485
$\mu + 2\sigma$		1.027
$\mu - 2\sigma$		-0.912
Upper Limit of 95% Confidence Level (UL = $10^{\mu+2\sigma}$)	10.653	
Lower Limit of 95% Confidence Level (LL = $10^{\mu-2\sigma}$)	0.122	
Ratio of Upper Limit to Lower Limit	86.974	

Source: Microsoft Excel spreadsheet ANL6dripdata.xls in Spreadsheets.zip (Attachment I)

ANL's High-Drip Results

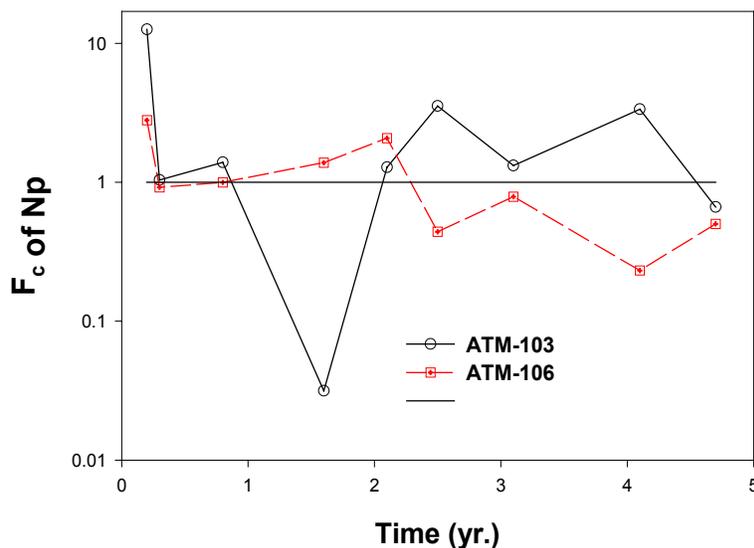


Source: HighDrip-Fc.jnb in SigmaPlots.zip (Attachment I)

NOTE: The figure shows that F_c of neptunium fluctuates around 1 and appears to damp to 1 as time increases.

Figure 6.6-4. F_c s of Neptunium in ANL's High-Drip Tests as a Function of Time

ANL's Low-Drip Results



Source: LowDrip-Fc.jnb in SigmaPlots.zip (Attachment I)

NOTE: Similar to Figure 4, F_c of neptunium fluctuates around 1 and appears to damp to 1 as time increases.

Figure 6.6-5. F_c s of Neptunium in ANL's Low-Drip Tests as a Function of Time

In summary, excluding the early data points that represent the transient period, F_c was estimated with a geometric mean of 1.142. It ranges from 0.122 to 10.653.

6.6.4.4 Abstracted Neptunium Solubility Based on F_c

As discussed in Section 6.6.4.1, neptunium solubility $[Np]$ can be calculated from uranium solubility, F_c , and the neptunium/uranium ratio of the fuel.

As discussed in the previous section, F_c is around 1.0, with an uncertainty range of about 2 orders of magnitude. So, it is proposed that F_c has a geometric mean of 1.0, ranging from 0.1 to 10.0.

The ratio of neptunium/uranium in the fuel can be calculated from the waste inventory. It is worthwhile to note that in order to have long-term predictive capability, the effect of decay-chain in-growth on $(Np/U)_{fuel}$ should be considered. Otherwise, the calculated neptunium solubility could be nonconservative. For example, for ATM-103 fuel with a burnup of 30 MWd/kg and 10 years storage, $(Np/U)_{fuel}$ is $4.15E-4$ (see Microsoft Excel spreadsheet ANL6dripdata.xls). However, if the in-growth from americium-241 and plutonium-241 decay are included, $(Np/U)_{fuel}$ should be $1.68E-3$ (see Microsoft Excel spreadsheet ANL6dripdata.xls), an increase of a factor of 4.04. Using the average waste inventory (DTN: SN0011T0810599.023) with adjustment for decay of americium-241, for CSNF waste packages, the ratio equals $1.93E-3$ (see Microsoft Excel spreadsheet ANL6dripdata.xls).

Using schoepite as the uranium solubility-controlling solid, uranium solubility was represented as a look-up table with pH and $\log f_{CO_2}$ (Section 6.7, Table 6.7-2), with uncertainty terms given in Table 6.7-4.

Using the values of F_c , $(Np/U)_{fuel}$, and $[U]$ described above, the abstracted neptunium solubility is given by Table 6.6-13. The difference between the atomic weights of uranium and neptunium is very small and is neglected.

The user of the look-up table needs to ensure that when the flag (500) is encountered, the inventory concentrations calculated according to the dissolution rate of waste forms, water volume, and radionuclide inventory should be used instead of the flag itself. For any conditions that fall between a valid solubility and a flag of 500, the flag should be used. In addition, for any conditions outside of the 3.0-11.0 pH range, the -1.5 to -5.0 f_{CO_2} range, or with an ionic strength greater than 1.0 molal, the inventory concentrations calculated according to the dissolution rate of waste forms, water volume, and radionuclide inventory should be used.

The uncertainty terms given to uranium solubility model in Table 6.7-4 also apply to this neptunium solubility model. In addition, this neptunium solubility has an additional uncertainty term, ϵ_3 , which represents the uncertainty in F_c . ϵ_3 obeys a normal distribution with $\mu = 0$ and a standard deviation of ± 0.5 .

This model was mainly developed for CSNF waste packages. For codisposal waste packages, some adjustment may be needed to account for the difference of isotope inventory between the two types of waste packages. However, as an alternative model, this model can be used as a first order approximation for codisposal waste packages also.

Table 6.6-13. Look-up Table of Secondary Phase Neptunium Solubility Model (log[Np] (mg/L))

pH	Logf _{CO2}							
	-1.50	-2.00	-2.50	-3.00	-3.50	-4.00	-4.50	-5.00
3.50	1.70E+00	1.70E+00	1.70E+00	1.70E+00	1.70E+00	1.70E+00	1.70E+00	1.70E+00
3.75	8.43E-01	8.42E-01						
4.00	1.56E-01	1.56E-01	1.56E-01	1.56E-01	1.56E-01	1.56E-01	1.56E-01	1.56E-01
4.25	-3.76E-01	-3.78E-01	-3.79E-01	-3.79E-01	-3.79E-01	-3.79E-01	-3.79E-01	-3.79E-01
4.50	-7.84E-01	-7.90E-01	-7.92E-01	-7.93E-01	-7.93E-01	-7.93E-01	-7.93E-01	-7.93E-01
4.75	-1.09E+00	-1.11E+00	-1.11E+00	-1.12E+00	-1.12E+00	-1.12E+00	-1.12E+00	-1.12E+00
5.00	-1.36E+00	-1.39E+00	-1.40E+00	-1.40E+00	-1.41E+00	-1.41E+00	-1.41E+00	-1.41E+00
5.25	-1.61E+00	-1.68E+00	-1.71E+00	-1.71E+00	-1.72E+00	-1.72E+00	-1.72E+00	-1.72E+00
5.50	-1.78E+00	-1.95E+00	-2.01E+00	-2.04E+00	-2.04E+00	-2.05E+00	-2.05E+00	-2.05E+00
5.75	-1.81E+00	-2.09E+00	-2.24E+00	-2.30E+00	-2.32E+00	-2.33E+00	-2.33E+00	-2.33E+00
6.00	-1.68E+00	-2.08E+00	-2.33E+00	-2.46E+00	-2.51E+00	-2.52E+00	-2.53E+00	-2.53E+00
6.25	-1.46E+00	-1.95E+00	-2.30E+00	-2.50E+00	-2.59E+00	-2.63E+00	-2.64E+00	-2.64E+00
6.50	-1.19E+00	-1.75E+00	-2.18E+00	-2.46E+00	-2.61E+00	-2.67E+00	-2.69E+00	-2.70E+00
6.75	-8.47E-01	-1.50E+00	-2.00E+00	-2.36E+00	-2.58E+00	-2.68E+00	-2.71E+00	-2.73E+00
7.00	-3.83E-01	-1.20E+00	-1.77E+00	-2.21E+00	-2.50E+00	-2.66E+00	-2.72E+00	-2.74E+00
7.25	500	-8.23E-01	-1.51E+00	-2.01E+00	-2.38E+00	-2.60E+00	-2.70E+00	-2.74E+00
7.50	500	-1.74E-01	-1.19E+00	-1.78E+00	-2.22E+00	-2.51E+00	-2.67E+00	-2.73E+00
7.75	500	500	-7.29E-01	-1.50E+00	-2.01E+00	-2.38E+00	-2.60E+00	-2.70E+00
8.00	500	500	500	-1.13E+00	-1.77E+00	-2.21E+00	-2.50E+00	-2.65E+00
8.25	500	500	500	-4.43E-01	-1.47E+00	-2.00E+00	-2.36E+00	-2.57E+00
8.50	500	500	500	500	-9.83E-01	-1.75E+00	-2.18E+00	-2.45E+00
8.75	500	500	500	500	500	-1.37E+00	-1.96E+00	-2.29E+00
9.00	500	500	500	500	500	-5.98E-01	-1.67E+00	-2.10E+00
9.25	500	500	500	500	500	500	-1.13E+00	-1.85E+00
9.50	500	500	500	500	500	500	500	-1.47E+00
9.75	500	500	500	500	500	500	500	-6.30E-01

Source: Microsoft Excel spreadsheet Np 2ndPhase Solubility.xls in Spreadsheets.zip (Attachment I)

NOTES: Some cells have no valid data because the EQ3NR calculations do not converge, and those results are reported as 500 in this table.

Runs with ionic strengths > 1.0 are outside the range of validation, and are reported as 500 in this table.

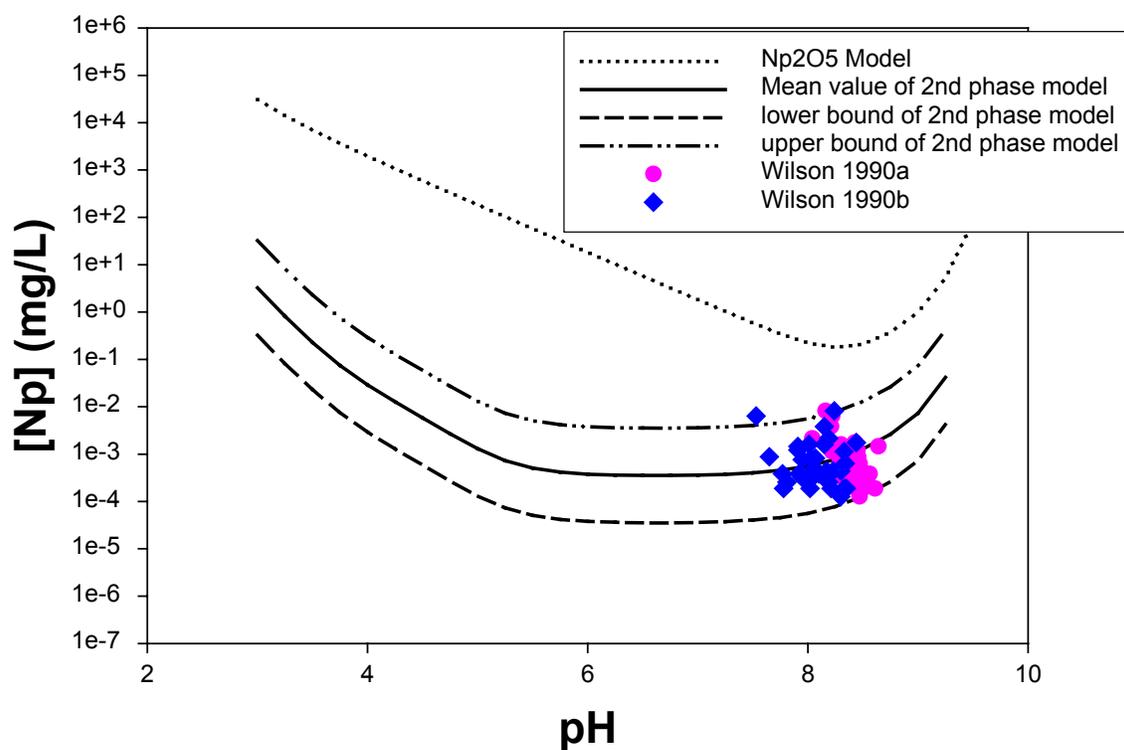
6.6.4.5 Model Corroboration

The secondary phase neptunium solubility model developed in previous sections is an alternative model and is not recommended for the TSPA-LA base-case analyses because a weakness exists in the model's bases, as discussed in Sections 6.6.1 and 6.6.4.6. Therefore, it has no impact on the estimate of mean annual dose. According to Appendix B of *Scientific Processes Guidelines Manual* (BSC 2002d, p. B-1), no model validation is required for this model. This section describes corroboration activities to enhance the confidence in the model.

Figure 6.6-6 compares the model (which was presented without decay train in-growth adjustment to match the neptunium/uranium ratio in the spent fuel), and the Np₂O₅ solubility model developed in Sections 6.6.2 with spent fuel corrosion experimental data (Wilson 1990a; Wilson 1990b). The solid curve is the mean value at T = 90°C and log f_{CO2} = -3.5. The double-dot

dashed curve and the dashed curve are ten times and one tenth of the mean value, respectively, which correspond to adding $\pm 2\sigma$ of $\log F_c$ to the log of neptunium solubility. Note that the cited experimental results were not used in the development of this model. The figure clearly shows that the secondary phase model captures the experimental results, and the fluctuations in the experimental measurements are well within the uncertainty range of the model. In contrast, the Np_2O_5 solubility model does not match the experimental results. The agreement between this model and the experimental results corroborates this model.

A mechanistic model has been developed (CRWMS M&O 1998b; Chen et al. 1999), based on the concept that neptunium is incorporated into secondary uranyl minerals). The model is a reactive-transport model and it considers both equilibrium reactions and kinetic dissolution/precipitation reactions of solids under flow conditions. The modeling results have been compared against laboratory measurements and observations of natural analogs. For repository conditions, the model predicted that neptunium solubility ranges from $1.0\text{E-}9$ to $1.0\text{E-}6$ mol/L, about 2 orders of magnitude lower than the value used for the TSPA-VA base case. A TSPA sensitivity study used this solubility range and showed that the peak neptunium dose rate was reduced by a factor of 45 from the base case (DOE 1998, Section 5.5.3).



Data Source: Wilson 1990a; Wilson 1990b; (see Microsoft Excel spreadsheet PNL-Wilson.xls in Spreadsheets.zip of Attachment I)

Source: SigmaPlot file Np2ndphase modelvalid.jnb

Figure 6.6-6. Comparison of Secondary Phase Neptunium Solubility Model (without inventory adjustment) with PNNL's and ANL's Measurements and Calculated Np_2O_5 Solubility

An enhanced reactive-transport modeling study of the release of neptunium during the process of spent fuel corrosion has been published in *Computers & Geosciences* (Chen 2003). This study considers several scenarios of neptunium release from spent nuclear fuel corrosion. The simulation results shows that experimental observations are consistent with the hypothesis that neptunium is incorporated into every uranyl mineral (including schoepite). This study further supports the conceptual model of neptunium incorporation into uranyl minerals.

In summary, the above corroborative activities demonstrate that the secondary phase neptunium solubility model has its merits, though a couple of issues in its technical bases remain to be resolved.

6.6.4.6 Summary of Secondary-Phase Neptunium Solubility Model

The secondary phase neptunium solubility model can be summarized by the following equation:

$$\log[Np] = S(pH, \log f_{CO_2}) + \varepsilon_1 + \varepsilon_2^i + \varepsilon_3 \quad (\text{Eq. 6.6-11})$$

where

$S(pH, \log f_{CO_2})$ is given by Table 6.6-13

ε_1 is the uncertainty term associated with uncertainty in log Ks of the uranium solubility model

ε_2^i is the uncertainty term associated with variations in fluoride concentration

i corresponds to either CSNF or codisposal waste package and the invert

ε_3 is the uncertainty term in F_c

The distribution properties of these uncertainty terms are listed in Table 6.6-14.

Table 6.6-14. Uncertainty Terms of $\log[Np]$ of the Secondary Phase Neptunium Solubility Model

Uncertainty Term	Associated With	Distribution Type	Distribution Parameter	Applicable to
ε_1	Uncertainties in log K	Normal	$\mu = 0, \sigma = 0.5$	
ε_2^{CSNF}	Fluoride concentration in CSNF waste packages	Triangular	$a = b = 0, c = 1.03$	CSNF waste packages
ε_2^{CO-IN}	Fluoride concentration in codisposal waste packages	Triangular	$a = b = 0, c = 2.82$	Codisposal waste packages and the invert
ε_3	Uncertainty in F_c	Normal	$\mu = 0, \sigma = 0.5$	

6.6.5 Recommendations

It is recommended that Np_2O_5 solubility (Table 6.6-2 and uncertainty terms defined in Table 6.6-4) be used for the base case of performance analyses. This phase has been definitely identified as forming from aqueous solutions at 25°C.

$NpO_2(cr)$ is considered an alternative controlling phase. It has not been observed to form at temperature conditions relevant to the repository. Even if it could precipitate at such temperature

conditions, it would be a difficult and time/resource consuming task to prove that it could form within 100 to 1000 years under the expected repository conditions. Although it gives lower solubility than the Np_2O_5 solubility model does, the difference is about 1 order of magnitude. Weighting the potential gains in the calculated performance of the repository from this solubility model with the required experimental work to validate this model, this model is not recommended for the base case of performance calculations.

An alternative model of incorporation of neptunium into uranyl minerals has also been considered. The results produced by these alternative models capture experimental results very well (Section 6.6.4.5). It eliminates the built-in conservatism in the conventional pure phase solubility approach and thus gives more realistic source terms. Moreover, the understanding about radionuclide migration and the performance of the repository was enhanced. However, experimental studies on whether schoepite, the critical secondary uranyl phase, can incorporate sufficient neptunium and immobilize it during spent fuel corrosion do not provide a solid basis for recommending this model to be used in the TSPA-LA model. Experimental work leading to data bearing on this model is under continuous review and may lead to an amended recommendation to adopt neptunium concentrations based on the co-precipitation model.

6.7 URANIUM SOLUBILITY

6.7.1 Introduction

Data0.ymp.R2 (DTN: MO0302SPATHDYN.000) incorporates uranium thermodynamic data compiled by the NEA Thermodynamic Data Project (Grenthe et al. 1992; Silva and Nitsche 1995). This database was used to calculate uranium solubility and uncertainty terms that account for the effects of temperature and fluoride concentration.

6.7.2 Controlling Solid

Once a waste package is breached and water enters, the waste form will react with the incoming water or water vapor. As a result, uranyl (UO_2^{2+}) solids will precipitate under oxidizing conditions. Laboratory experiments and field observations show that the most common secondary uranyl solids expected to form in the repository are schoepite, soddyite, uranophane, and/or Na-boltwoodite. Schoepite is chosen as the controlling solid for this analysis for several reasons:

1. Schoepite is the first solid to be formed during the process of spent fuel corrosion (Wronkiewicz et al. 1992, Section 4.2).
2. Field observations and modeling studies show that schoepite can last more than 10,000 years, albeit thermodynamically unstable for the repository conditions and will be replaced by uranyl silicates (CRWMS M&O 1998b, Section 6.4.3.2; Finch et al. 1996, Table 1; Murphy 1997; Percy et al. 1994, pp. 718 and 719; Wronkiewicz et al. 1992).
3. For the reference water (Table 6.4-1), schoepite is more soluble than the other above mentioned solids (as confirmed by EQ3NR calculations discussed in Section 7.4); using it as the controlling phase will make this analysis conservative for uranium solubility.

6.7.3 Chemical Conditions

See Table 6.4-1 for the chemical conditions for the uranium calculations.

6.7.4 Results

Figure 6.7-1 and Table 6.7.1 give the calculated uranium solubility (with Table 6.7.2 giving the log of the solubility), along with the conditions for the 298 cases run (164 of which converged). The calculated uranium solubility ranges from 9.29E-1 mg/L (at pH = 7.25 and log f_{CO_2} = 5.00) to 2.55E+4 mg/L (at pH = 3.50 and log f_{CO_2} = -1.50), with an average of 1.48E+3 mg/L.

A few data points are out of the range the code can handle, i.e., the calculation cannot generate a converging solution or the ionic strength of the solution exceeded the range of validation (1 molal) for the database. Thus, there are several blank entries in Table 6.7-1. The convergence problems occur at either high pH and high f_{CO_2} or low pH (none of the runs below a pH of 3.5 converged), due to computational limits of the geochemical modeling tool, which imposes restrictions on the ranges of conditions the model calculations can address.

Table 6.7-1. Calculated Uranium Solubility (mg/L)

pH	log f _{CO2}							
	-1.50	-2.00	-2.50	-3.00	-3.50	-4.00	-4.50	-5.00
3.50	2.55E+04	2.55E+04	2.55E+04	2.55E+04	2.55E+04	2.55E+04	2.55E+04	2.55E+04
3.75	3.57E+03	3.57E+03	3.57E+03	3.57E+03	3.57E+03	3.57E+03	3.57E+03	3.57E+03
4.00	7.35E+02	7.34E+02						
4.25	2.16E+02	2.15E+02	2.14E+02	2.14E+02	2.14E+02	2.14E+02	2.14E+02	2.14E+02
4.50	8.43E+01	8.31E+01	8.27E+01	8.26E+01	8.25E+01	8.25E+01	8.25E+01	8.25E+01
4.75	4.13E+01	3.99E+01	3.95E+01	3.93E+01	3.93E+01	3.93E+01	3.93E+01	3.93E+01
5.00	2.25E+01	2.09E+01	2.04E+01	2.02E+01	2.02E+01	2.01E+01	2.01E+01	2.01E+01
5.25	1.27E+01	1.07E+01	1.01E+01	9.89E+00	9.83E+00	9.81E+00	9.81E+00	9.80E+00
5.50	8.53E+00	5.82E+00	4.98E+00	4.72E+00	4.63E+00	4.61E+00	4.60E+00	4.60E+00
5.75	8.03E+00	4.16E+00	2.93E+00	2.55E+00	2.43E+00	2.39E+00	2.38E+00	2.38E+00
6.00	1.07E+01	4.22E+00	2.38E+00	1.78E+00	1.60E+00	1.54E+00	1.52E+00	1.51E+00
6.25	1.76E+01	5.73E+00	2.59E+00	1.61E+00	1.31E+00	1.21E+00	1.18E+00	1.17E+00
6.50	3.32E+01	9.13E+00	3.39E+00	1.77E+00	1.26E+00	1.09E+00	1.04E+00	1.03E+00
6.75	7.30E+01	1.63E+01	5.16E+00	2.26E+00	1.36E+00	1.08E+00	9.89E-01	9.61E-01
7.00	2.12E+02	3.24E+01	8.67E+00	3.17E+00	1.62E+00	1.13E+00	9.81E-01	9.32E-01
7.25		7.72E+01	1.60E+01	4.99E+00	2.16E+00	1.29E+00	1.01E+00	9.29E-01
7.50		3.44E+02	3.33E+01	8.56E+00	3.11E+00	1.59E+00	1.10E+00	9.53E-01
7.75			9.57E+01	1.62E+01	4.97E+00	2.12E+00	1.29E+00	1.02E+00
8.00				3.76E+01	8.68E+00	3.14E+00	1.63E+00	1.15E+00
8.25				1.85E+02	1.75E+01	5.10E+00	2.22E+00	1.39E+00
8.50					5.33E+01	9.22E+00	3.36E+00	1.82E+00
8.75						2.18E+01	5.58E+00	2.61E+00
9.00						1.30E+02	1.11E+01	4.08E+00
9.25							3.78E+01	7.18E+00
9.50								1.73E+01
9.75								1.20E+02

Source: Microsoft Excel spreadsheet uranium solubility.xls in Spreadsheets.zip (Attachment I)

NOTES: Some cells have no data because the EQ3NR calculations do not converge.

Runs with ionic strengths > 1.0 are outside the range of validation, and are not reported in this table.

Table 6.7-2. Look-up Table for Uranium Solubility (log U [mg/L])

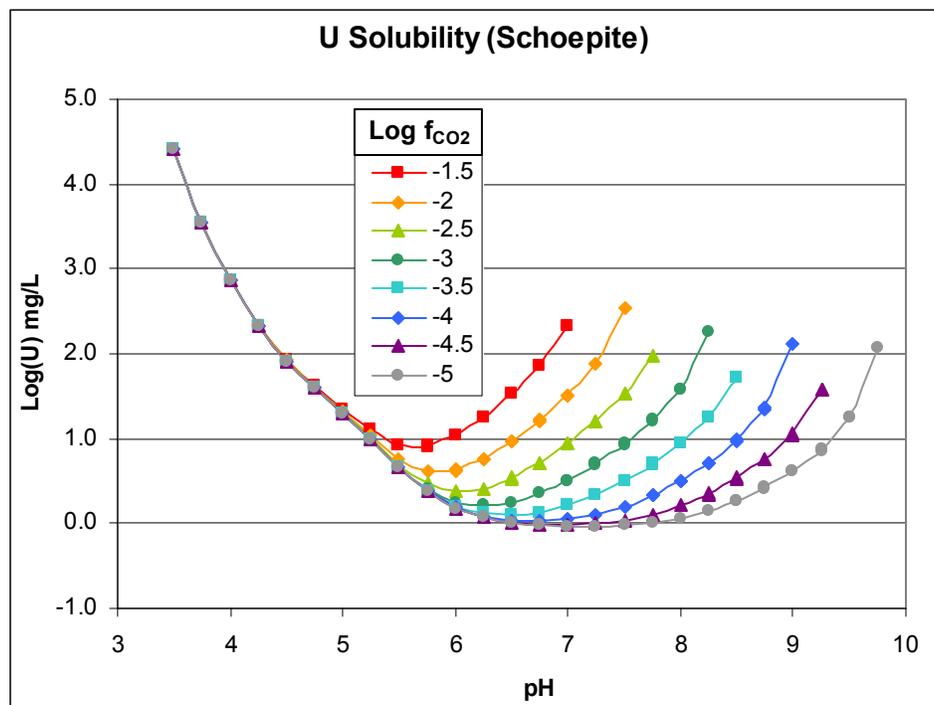
pH	log f_{CO_2}							
	-1.50	-2.00	-2.50	-3.00	-3.50	-4.00	-4.50	-5.00
3.50	4.41E+00	4.41E+00	4.41E+00	4.41E+00	4.41E+00	4.41E+00	4.41E+00	4.41E+00
3.75	3.55E+00	3.55E+00	3.55E+00	3.55E+00	3.55E+00	3.55E+00	3.55E+00	3.55E+00
4.00	2.87E+00	2.87E+00	2.87E+00	2.87E+00	2.87E+00	2.87E+00	2.87E+00	2.87E+00
4.25	2.33E+00	2.33E+00	2.33E+00	2.33E+00	2.33E+00	2.33E+00	2.33E+00	2.33E+00
4.50	1.93E+00	1.92E+00	1.92E+00	1.92E+00	1.92E+00	1.92E+00	1.92E+00	1.92E+00
4.75	1.62E+00	1.60E+00	1.60E+00	1.59E+00	1.59E+00	1.59E+00	1.59E+00	1.59E+00
5.00	1.35E+00	1.32E+00	1.31E+00	1.31E+00	1.30E+00	1.30E+00	1.30E+00	1.30E+00
5.25	1.10E+00	1.03E+00	1.00E+00	9.95E-01	9.93E-01	9.92E-01	9.92E-01	9.91E-01
5.50	9.31E-01	7.65E-01	6.97E-01	6.74E-01	6.66E-01	6.63E-01	6.63E-01	6.62E-01
5.75	9.05E-01	6.19E-01	4.67E-01	4.07E-01	3.86E-01	3.79E-01	3.77E-01	3.76E-01
6.00	1.03E+00	6.26E-01	3.76E-01	2.51E-01	2.03E-01	1.87E-01	1.82E-01	1.80E-01
6.25	1.25E+00	7.58E-01	4.13E-01	2.07E-01	1.17E-01	8.36E-02	7.27E-02	6.92E-02
6.50	1.52E+00	9.60E-01	5.30E-01	2.48E-01	9.90E-02	3.93E-02	1.87E-02	1.19E-02
6.75	1.86E+00	1.21E+00	7.12E-01	3.53E-01	1.32E-01	3.21E-02	-4.74E-03	-1.71E-02
7.00	2.33E+00	1.51E+00	9.38E-01	5.01E-01	2.11E-01	5.47E-02	-8.42E-03	-3.04E-02
7.25	500	1.89E+00	1.20E+00	6.98E-01	3.34E-01	1.09E-01	6.00E-03	-3.21E-02
7.50	500	2.54E+00	1.52E+00	9.32E-01	4.92E-01	2.00E-01	4.29E-02	-2.10E-02
7.75	500	500	1.98E+00	1.21E+00	6.96E-01	3.26E-01	1.09E-01	7.58E-03
8.00	500	500	500	1.58E+00	9.38E-01	4.97E-01	2.12E-01	6.04E-02
8.25	500	500	500	2.27E+00	1.24E+00	7.07E-01	3.47E-01	1.45E-01
8.50	500	500	500	500	1.73E+00	9.65E-01	5.26E-01	2.59E-01
8.75	500	500	500	500	500	1.34E+00	7.47E-01	4.16E-01
9.00	500	500	500	500	500	2.11E+00	1.04E+00	6.11E-01
9.25	500	500	500	500	500	500	1.58E+00	8.56E-01
9.50	500	500	500	500	500	500	500	1.24E+00
9.75	500	500	500	500	500	500	500	2.08E+00

Source: Microsoft Excel spreadsheet U solubility.xls in Spreadsheets.zip (Attachment I)

NOTES: Some cells have no valid data because the EQ3NR calculations do not converge, and those results are reported as 500 in this table.

Runs with ionic strengths > 1.0 are outside the range of validation, and are reported as 500 in this table.

The user of the look-up table needs to ensure that when the flag (500) is encountered, the inventory concentrations calculated according to the dissolution rate of waste forms, water volume, and radionuclide inventory should be used instead of the flag itself. For any conditions that fall between a valid solubility and a flag of 500, the flag should be used. In addition, for any conditions outside of the 3.0-11.0 pH range, the -1.5 to -5.0 f_{CO_2} range, or with an ionic strength greater than 1.0 molal, the inventory concentrations calculated according to the dissolution rate of waste forms, water volume, and radionuclide inventory should be used.



Source: Uranium Solubility.xls in Spreadsheets.zip (Attachment I)

Figure 6.7-1. Uranium Solubility Modeled as a Function of pH and log f_{CO_2}

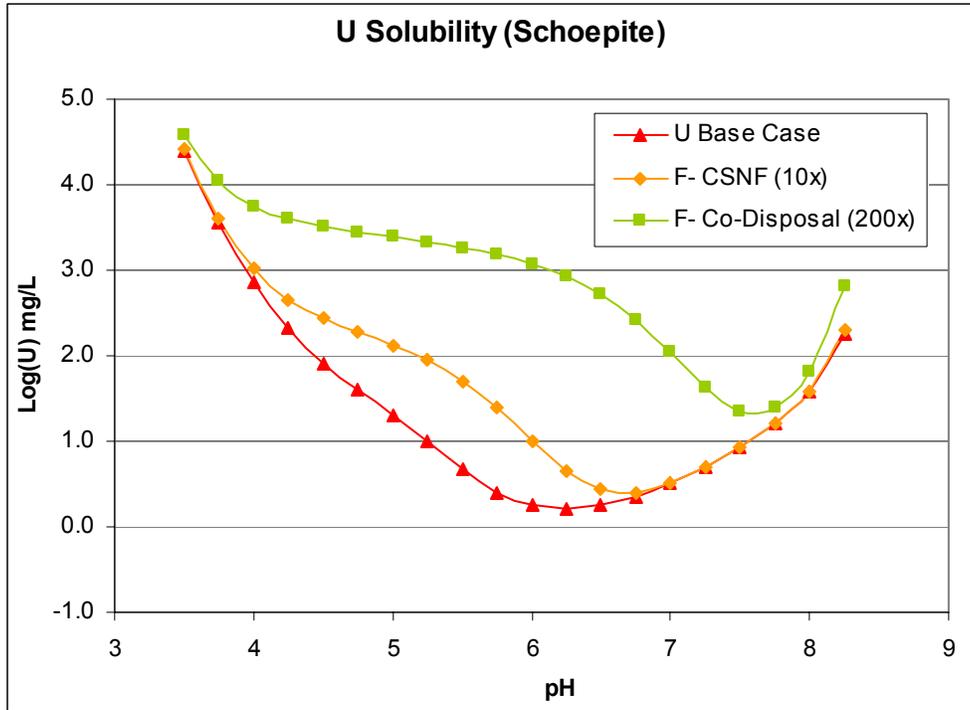
6.7.5 Uncertainty

6.7.5.1 Uncertainty in log K Values of the Controlling Solid and Aqueous Species.

This type of uncertainty in solubility involves uncertainties in both the thermodynamic properties of the controlling solid and those for the dissolved species. The evaluation and combination of these uncertainties are discussed in some detail in Section 6.3.3.1, and 1σ uncertainty of ± 0.5 applicable uniformly to log [U] was given there.

6.7.5.2 Uncertainty from Fluoride Concentration

Sensitivity studies conducted to determine the effect fluoride concentration on the solubility of uranium were conducted at $\log f_{CO_2} = -3.0$. Two fluoride sensitivity studies were performed: one to account for the maximum amount of fluoride expected in the CSNF waste package, which is ten times more than the fluoride in the base case, and another to account for the codisposal waste package, which is two hundred times the amount in the base case. The results of these studies are presented in Figure 6.7-2 and Table 6.7-3.



Source: Microsoft Excel spreadsheet Uncertainty.xls in Spreadsheets.zip (Attachment I)

NOTE: $\log f_{CO_2} = -3$

Figure 6.7-2. Schoepite Solubility at $\log f_{CO_2} = -3.0$ as a Function of pH and F^- Concentrations

Table 6.7-3. The Effects of Variations in Fluoride Concentration on Uranium Solubility

pH	Base Case (1× F ⁻)	CSNF (10× F ⁻)	Codisposal (200× F ⁻)	CSNF Difference	Codisposal Difference
	[U mg/L]			$\log[U_{\text{CSNF}}] - \log[U_{\text{Base Case}}]$	$\log[U_{\text{Codisp}}] - \log[U_{\text{Base Case}}]$
3.50	2.55E+04	2.61E+04	3.71E+04	1.00E-02	1.64E-01
3.75	3.57E+03	3.99E+03	1.10E+04	4.88E-02	4.90E-01
4.00	7.34E+02	1.03E+03	5.66E+03	1.48E-01	8.87E-01
4.25	2.14E+02	4.48E+02	3.96E+03	3.20E-01	1.27E+00
4.50	8.26E+01	2.72E+02	3.21E+03	5.17E-01	1.59E+00
4.75	3.93E+01	1.89E+02	2.76E+03	6.81E-01	1.85E+00
5.00	2.02E+01	1.33E+02	2.43E+03	8.18E-01	2.08E+00
5.25	9.89E+00	8.76E+01	2.13E+03	9.47E-01	2.33E+00
5.50	4.72E+00	5.04E+01	1.83E+03	1.03E+00	2.59E+00
5.75	2.55E+00	2.42E+01	1.52E+03	9.78E-01	2.77E+00
6.00	1.78E+00	1.02E+01	1.19E+03	7.58E-01	2.82E+00
6.25	1.61E+00	4.50E+00	8.44E+02	4.46E-01	2.72E+00
6.50	1.77E+00	2.72E+00	5.19E+02	1.86E-01	2.47E+00
6.75	2.26E+00	2.54E+00	2.62E+02	5.18E-02	2.07E+00
7.00	3.17E+00	3.29E+00	1.10E+02	1.69E-02	1.54E+00
7.25	4.99E+00	5.07E+00	4.30E+01	7.37E-03	9.35E-01
7.50	8.56E+00	8.69E+00	2.21E+01	6.32E-03	4.13E-01
7.75	1.62E+01	1.65E+01	2.46E+01	8.28E-03	1.81E-01
8.00	3.76E+01	3.89E+01	6.57E+01	1.55E-02	2.43E-01
8.25	1.85E+02	1.99E+02	6.48E+02	3.30E-02	5.45E-01
			Maximum:	1.03E+00	2.82E+00
			Minimum:	6.32E-03	1.64E-01
			Average:	3.51E-01	1.50E+00

Source: Microsoft Excel spreadsheet U Solubility.xls in Spreadsheets.zip (Attachment I)

NOTE: $\log f_{\text{CO}_2} = -3.0$

The solubility in the codisposal case (200× F⁻ concentration) is higher than the corresponding CSNF case (10× F⁻ concentration), which is also higher than the corresponding base case (1× F⁻ concentration), which indicates that the solubility of uranium increases with an increase in fluoride concentration. The maximum difference between the logs of the CSNF results and the base-case results, 1.03 (left column in Table 6.7-3), and the maximum difference between the logs of the codisposal results and the base-case results, 2.82, are chosen to represent the uncertainty terms associated with fluoride variation.

6.7.6 Summary

The uranium solubility is given by the following equation:

$$\log[U] = S(pH, \log f_{\text{CO}_2}) + \varepsilon_1 + \varepsilon_2 \quad (\text{Eq.6.7-1})$$

where $S(pH, \log f_{CO_2})$ is given in Table 6.7-2; and the ϵ 's are given in Table 6.7-4.

Table 6.7-4. Uncertainty Terms of log[U]

Uncertainty Term	Associated with	Distribution Type	Distribution Parameter	Applicable to
ϵ_1	log K of controlling solid and aqueous species	Normal	$\mu = 0, \sigma = 0.5$	
ϵ_2^{CSNF}	Fluoride concentration in CSNF waste packages	Triangular	a = b = 0, c = 1.03	CSNF waste packages
ϵ_2^{CO-IN}	Fluoride concentration in codisposal waste packages	Triangular	a = b = 0, c = 2.82	Codisposal waste packages and the invert

6.8 THORIUM SOLUBILITY

6.8.1 Introduction

Data0.ymp.R2 (DTN: MO0302SPATHDYN.000) includes thorium data from a variety of sources. These have been used with EQ3NR to calculate the thorium concentrations discussed in this section.

6.8.2 Controlling Mineral

ThO₂(am) was chosen as the controlling phase for the full range of pH and f_{CO_2} values. Data0.ymp.R2 also includes data for the ThO₂ mineral thorianite and for a number of other thorium solids. Thorianite is about 5.5 log units more stable (less soluble) than ThO₂(am). However, as discussed by Hummel et al. (2002, Section 5.21.2), solubilities as low as those predicted using thorianite are measured only at pH values below about 5. Calculations using ThO₂(am) leads to dissolved thorium concentrations like those commonly measured in solubility studies, as discussed in Section 7.4 below.

Several other solids in Data0.ymp.R2 are less soluble than ThO₂(am) in the nominal reference water under certain conditions of pH and f_{CO_2} . Th_{0.75}PO₄ is less soluble under acid conditions. However, because of the amount of uranium available in the waste package environment, phosphate concentrations there are likely to be very low, as discussed in Section 6.4.2.5. Thus, Th_{0.75}PO₄ is excluded. Th(SO₄)₂, ThF₄, and ThF₄·2.5H₂O are also less soluble than ThO₂(am) under acid conditions, with Th(SO₄)₂ particularly insoluble at the lowest pH values where SO₄²⁻ concentrations are high because of the use of this anion for charge balance of the modeled solutions. Data for ThF₄·2.5H₂O and Th(SO₄)₂ are taken from a previous compilation of data (Wagman et al. 1982). Hummel et al. (2002, Sections 5.21.6 and 7) in reviewing these data note that the properties of ThF₄·2.5H₂O are based on an estimate and could not determine the original source for the properties of Th(SO₄)₂. Thus these two solids are also excluded from consideration. The relevant F⁻ concentrations are uncertain, so ThF₄ is also excluded.

The uncertainty associated with the properties of the controlling phase will be addressed in Section 6.8.5.

6.8.3 Chemical Conditions

See Table 6.4-1 for the chemical conditions for the thorium calculations.

6.8.4 Results

Table 6.8-1 and Figure 6.8-1 show the thorium concentrations calculated in mg/L for the reference water using $\text{ThO}_2(\text{am})$ as the controlling mineral for pH values from 3.25 to 10.75 and $\log f_{\text{CO}_2}$ values from -1.5 to -5.0. The figure illustrates the generally observed pattern of thorium solubility: increasing solubility with decreasing pH under acid conditions and increasing solubility with increasing f_{CO_2} and pH under alkaline conditions.

Calculations did not converge for conditions outside this range and where blanks appear in the table. In the high f_{CO_2} and pH region, increasing CO_3^{2-} concentrations favor the formation of complexes such as $\text{Th}(\text{CO}_3)_5^{6-}$ and $\text{Th}(\text{OH})_3\text{CO}_3^-$. This is evident in the sharp increases in the thorium concentrations in the highest pH point of each f_{CO_2} line. Even sharper increases at the next pH or f_{CO_2} step of the modeling is what prevents EQ3NR from converging.

At pH values below 3.25, the modeling instability is due to the rapid increases in total thorium and SO_4 concentrations due to the strength of the $\text{Th}(\text{SO}_4)_2(\text{aq})$ ion pair and the addition of SO_4^{2-} as the charge-balancing anion. Instability from this cause occurs in calculations on other actinides as well, and has a particularly strong effect on the calculations of americium solubilities (Section 6.9.4).

Table 6.8-2 give the same values as in Table 6.8-1 in units of log mg/L. It is included as the look-up table for use in the TSPA modeling for LA. The second table includes the value "500" for those ranges of conditions for which no concentrations were given in Table 6.8-1. This value is intended as a flag to indicate that release rates rather than concentration limits for thorium should be selected for these conditions in the TSPA modeling. For any conditions that fall between a valid solubility and a flag of 500, the flag should be used. In addition, for any conditions outside of the 3.0-11.0 pH range, the -1.5 to -5.0 f_{CO_2} range, or with an ionic strength greater than 1.0 molal, the inventory concentrations calculated according to the dissolution rate of waste forms, water volume, and radionuclide inventory should be used.

Table 6.8-1. Thorium Solubility (mg/L)—ThO₂(am)

pH	log f _{CO2}							
	-1.50	-2.00	-2.50	-3.00	-3.50	-4.00	-4.50	-5.00
3.25	6.94E+03	6.95E+03						
3.50	3.45E+02	3.45E+02	3.45E+02	3.45E+02	3.45E+02	3.45E+02	3.45E+02	3.45E+02
3.75	4.12E+01	4.12E+01	4.12E+01	4.12E+01	4.12E+01	4.12E+01	4.12E+01	4.12E+01
4.00	1.37E+01	1.37E+01	1.37E+01	1.37E+01	1.37E+01	1.37E+01	1.37E+01	1.37E+01
4.25	8.73E+00	8.73E+00	8.73E+00	8.73E+00	8.73E+00	8.73E+00	8.73E+00	8.73E+00
4.50	5.52E+00	5.52E+00	5.52E+00	5.52E+00	5.52E+00	5.52E+00	5.52E+00	5.52E+00
4.75	2.41E+00	2.41E+00	2.41E+00	2.41E+00	2.41E+00	2.41E+00	2.41E+00	2.41E+00
5.00	5.10E-01	5.08E-01	5.07E-01	5.07E-01	5.07E-01	5.07E-01	5.07E-01	5.07E-01
5.25	6.69E-02	6.27E-02	6.14E-02	6.10E-02	6.08E-02	6.08E-02	6.08E-02	6.08E-02
5.50	1.77E-02	1.03E-02	7.93E-03	7.19E-03	6.96E-03	6.89E-03	6.86E-03	6.86E-03
5.75	2.04E-02	7.33E-03	3.18E-03	1.87E-03	1.46E-03	1.32E-03	1.28E-03	1.27E-03
6.00	3.48E-02	1.15E-02	4.10E-03	1.76E-03	1.03E-03	7.92E-04	7.18E-04	6.95E-04
6.25	6.03E-02	1.98E-02	6.69E-03	2.54E-03	1.22E-03	8.09E-04	6.78E-04	6.36E-04
6.50	1.07E-01	3.47E-02	1.14E-02	4.02E-03	1.68E-03	9.46E-04	7.13E-04	6.39E-04
6.75	1.92E-01	6.03E-02	1.98E-02	6.67E-03	2.52E-03	1.21E-03	7.93E-04	6.62E-04
7.00	3.47E-01	1.07E-01	3.47E-02	1.14E-02	4.01E-03	1.68E-03	9.40E-04	7.07E-04
7.25	6.28E-01	1.93E-01	6.03E-02	1.98E-02	6.67E-03	2.52E-03	1.21E-03	7.90E-04
7.50	1.14E+00	3.47E-01	1.07E-01	3.47E-02	1.14E-02	4.01E-03	1.68E-03	9.39E-04
7.75	2.10E+00	6.28E-01	1.93E-01	6.03E-02	1.98E-02	6.67E-03	2.52E-03	1.20E-03
8.00	3.89E+00	1.15E+00	3.47E-01	1.07E-01	3.47E-02	1.14E-02	4.01E-03	1.68E-03
8.25	1.09E+01	2.10E+00	6.29E-01	1.93E-01	6.03E-02	1.98E-02	6.67E-03	2.52E-03
8.50		3.95E+00	1.15E+00	3.47E-01	1.08E-01	3.47E-02	1.14E-02	4.01E-03
8.75		2.56E+01	2.12E+00	6.31E-01	1.93E-01	6.04E-02	1.98E-02	6.66E-03
9.00			4.25E+00	1.16E+00	3.49E-01	1.08E-01	3.41E-02	1.14E-02
9.25			4.17E+02	2.15E+00	6.36E-01	1.94E-01	6.06E-02	1.97E-02
9.50				8.90E+00	1.18E+00	3.53E-01	1.09E-01	3.43E-02
9.75					2.41E+00	6.52E-01	1.96E-01	6.10E-02
10.00						1.25E+00	3.63E-01	1.10E-01
10.25						4.64E+01	6.91E-01	2.03E-01
10.50							4.37E+00	3.86E-01
10.75								1.01E+00

Source: Microsoft Excel spreadsheet Th solubility.xls in Spreadsheets.zip (Attachment I)

NOTES: Some cells have no data because the EQ3NR calculations do not converge.

Runs with ionic strengths > 1.0 are outside the range of validation, and are not reported in this table.

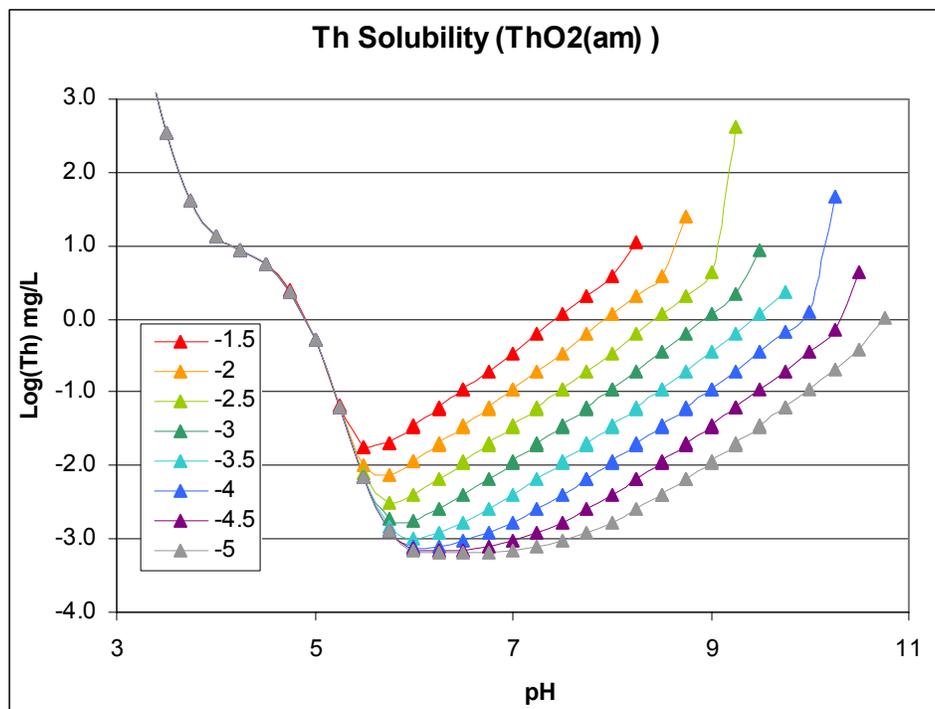
Table 6.8-2. Thorium Solubility Look-up Table (log[Th] mg/L)

pH	log f _{CO2}							
	-1.50	-2.00	-2.50	-3.00	-3.50	-4.00	-4.50	-5.00
3.25	3.84E+00	3.84E+00	3.84E+00	3.84E+00	3.84E+00	3.84E+00	3.84E+00	3.84E+00
3.50	2.54E+00	2.54E+00	2.54E+00	2.54E+00	2.54E+00	2.54E+00	2.54E+00	2.54E+00
3.75	1.61E+00	1.61E+00	1.62E+00	1.62E+00	1.62E+00	1.62E+00	1.62E+00	1.62E+00
4.00	1.14E+00	1.14E+00	1.14E+00	1.14E+00	1.14E+00	1.14E+00	1.14E+00	1.14E+00
4.25	9.41E-01	9.41E-01	9.41E-01	9.41E-01	9.41E-01	9.41E-01	9.41E-01	9.41E-01
4.50	7.42E-01	7.42E-01	7.42E-01	7.42E-01	7.42E-01	7.42E-01	7.42E-01	7.42E-01
4.75	3.82E-01	3.82E-01	3.82E-01	3.82E-01	3.82E-01	3.82E-01	3.82E-01	3.82E-01
5.00	-2.92E-01	-2.94E-01	-2.95E-01	-2.95E-01	-2.95E-01	-2.95E-01	-2.95E-01	-2.95E-01
5.25	-1.17E+00	-1.20E+00	-1.21E+00	-1.21E+00	-1.22E+00	-1.22E+00	-1.22E+00	-1.22E+00
5.50	-1.75E+00	-1.99E+00	-2.10E+00	-2.14E+00	-2.16E+00	-2.16E+00	-2.16E+00	-2.16E+00
5.75	-1.69E+00	-2.13E+00	-2.50E+00	-2.73E+00	-2.84E+00	-2.88E+00	-2.89E+00	-2.90E+00
6.00	-1.46E+00	-1.94E+00	-2.39E+00	-2.75E+00	-2.99E+00	-3.10E+00	-3.14E+00	-3.16E+00
6.25	-1.22E+00	-1.70E+00	-2.17E+00	-2.60E+00	-2.91E+00	-3.09E+00	-3.17E+00	-3.20E+00
6.50	-9.69E-01	-1.46E+00	-1.94E+00	-2.40E+00	-2.77E+00	-3.02E+00	-3.15E+00	-3.19E+00
6.75	-7.16E-01	-1.22E+00	-1.70E+00	-2.18E+00	-2.60E+00	-2.92E+00	-3.10E+00	-3.18E+00
7.00	-4.60E-01	-9.69E-01	-1.46E+00	-1.94E+00	-2.40E+00	-2.78E+00	-3.03E+00	-3.15E+00
7.25	-2.02E-01	-7.16E-01	-1.22E+00	-1.70E+00	-2.18E+00	-2.60E+00	-2.92E+00	-3.10E+00
7.50	5.88E-02	-4.60E-01	-9.69E-01	-1.46E+00	-1.94E+00	-2.40E+00	-2.78E+00	-3.03E+00
7.75	3.22E-01	-2.02E-01	-7.15E-01	-1.22E+00	-1.70E+00	-2.18E+00	-2.60E+00	-2.92E+00
8.00	5.90E-01	5.91E-02	-4.60E-01	-9.69E-01	-1.46E+00	-1.94E+00	-2.40E+00	-2.78E+00
8.25	1.04E+00	3.23E-01	-2.01E-01	-7.15E-01	-1.22E+00	-1.70E+00	-2.18E+00	-2.60E+00
8.50	500	5.96E-01	6.01E-02	-4.59E-01	-9.68E-01	-1.46E+00	-1.94E+00	-2.40E+00
8.75	500	1.41E+00	3.25E-01	-2.00E-01	-7.14E-01	-1.22E+00	-1.70E+00	-2.18E+00
9.00	500	500	6.29E-01	6.31E-02	-4.57E-01	-9.67E-01	-1.47E+00	-1.94E+00
9.25	500	500	2.62E+00	3.33E-01	-1.96E-01	-7.12E-01	-1.22E+00	-1.70E+00
9.50	500	500	500	9.49E-01	7.17E-02	-4.53E-01	-9.65E-01	-1.47E+00
9.75	500	500	500	500	3.81E-01	-1.86E-01	-7.07E-01	-1.21E+00
10.00	500	500	500	500	500	9.60E-02	-4.41E-01	-9.58E-01
10.25	500	500	500	500	500	1.67E+00	-1.61E-01	-6.93E-01
10.50	500	500	500	500	500	500	6.41E-01	-4.13E-01
10.75	500	500	500	500	500	500	500	4.71E-03

Source: Microsoft Excel spreadsheet Th solubility.xls in Spreadsheets.zip (Attachment I)

NOTES: Some cells have no valid data because the EQ3NR calculations do not converge, and those results are reported as 500 in this table.

Runs with ionic strengths > 1.0 are outside the range of validation, and are reported as 500 in this table.



Source: Microsoft Excel spreadsheet Th Solubility.xls in Spreadsheets.zip (Attachment I)

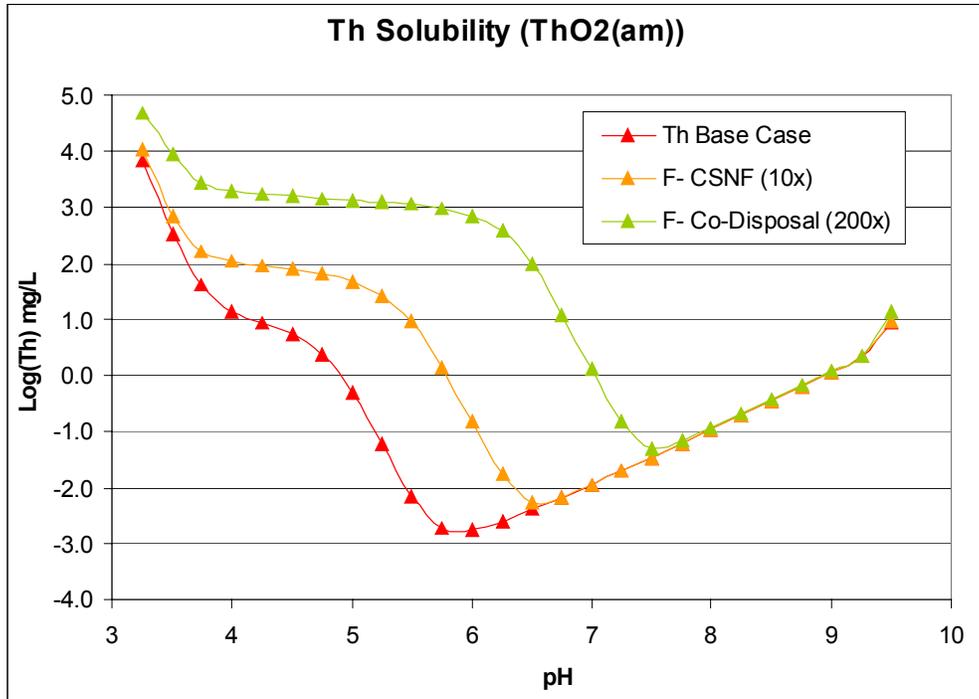
Figure 6.8-1. ThO₂(am) Solubility Modeled as a Function of f_{CO_2} and pH

6.8.5 Uncertainty

As described in Section 6.3.3, uncertainty in the solubilities has been evaluated considering uncertainties in the thermodynamic data for the solubility-controlling phase and uncertainties in the fluoride content of the matrix fluid.

The uncertainty in thorium solubility due to uncertainties in thermodynamic data was calculated as described in Section 6.3.3.1, allowing for uncertainties in log K values of both the controlling solid and the important aqueous thorium species, and 1σ uncertainty of 0.7 applicable uniformly to log [Th] was given there.

Calculations of the effects of uncertainties in fluoride concentrations were made for a range of pH values at a log f_{CO_2} of -3.0. The results are displayed in Figure 6.8-2, and the differences of these results from the base-case solubilities are given in Table 6.8-3. As the figure and table show at fluoride concentrations $10\times$ the base-case value (CSNF value), the maximum difference from the base-case concentration is +3.10 log[Th mg/L] units. At a fluoride concentrations $200\times$ the base case (codisposal and invert value), the solubility is higher by a maximum value of +5.72 log[Th mg/L].



Source: Microsoft Excel spreadsheet Th Solubility.xls in Spreadsheets.zip (Attachment I)

Figure 6.8-2. ThO₂(am) Solubility at log f_{CO2} = -3.0 as a Function of pH and F⁻ Concentrations

Table 6.8-3. The Effects in Variation in Fluoride Concentration on Th Solubility

pH	Base Case (1× F)	CSNF (10× F)	Codisposal (200× F)	CSNF Difference	Codisposal Difference
	[Th mg/L]			$\log[\text{Th}_{\text{CSNF}}] - \log[\text{Th}_{\text{Base Case}}]$	$\log[\text{Th}_{\text{Codisp}}] - \log[\text{Th}_{\text{Base Case}}]$
3.25	6.95E+03	1.08E+04	4.98E+04	1.93E-01	8.56E-01
3.50	3.45E+02	6.86E+02	8.85E+03	2.98E-01	1.41E+00
3.75	4.12E+01	1.64E+02	2.67E+03	6.00E-01	1.81E+00
4.00	1.37E+01	1.09E+02	1.95E+03	9.02E-01	2.15E+00
4.25	8.73E+00	9.17E+01	1.73E+03	1.02E+00	2.30E+00
4.50	5.52E+00	7.83E+01	1.58E+03	1.15E+00	2.46E+00
4.75	2.41E+00	6.42E+01	1.47E+03	1.43E+00	2.78E+00
5.00	5.07E-01	4.73E+01	1.37E+03	1.97E+00	3.43E+00
5.25	6.10E-02	2.72E+01	1.27E+03	2.65E+00	4.32E+00
5.50	7.19E-03	9.02E+00	1.15E+03	3.10E+00	5.20E+00
5.75	1.87E-03	1.39E+00	9.80E+02	2.87E+00	5.72E+00
6.00	1.76E-03	1.50E-01	7.18E+02	1.93E+00	5.61E+00
6.25	2.54E-03	1.75E-02	3.74E+02	8.39E-01	5.17E+00
6.50	4.02E-03	5.51E-03	9.70E+01	1.37E-01	4.38E+00
6.75	6.67E-03	6.74E-03	1.24E+01	4.20E-03	3.27E+00
7.00	1.14E-02	1.13E-02	1.29E+00	-5.25E-03	2.06E+00
7.25	1.98E-02	1.95E-02	1.50E-01	-5.28E-03	8.79E-01
7.50	3.47E-02	3.44E-02	5.01E-02	-4.15E-03	1.60E-01
7.75	6.03E-02	6.08E-02	6.72E-02	4.05E-03	4.70E-02
8.00	1.07E-01	1.08E-01	1.17E-01	3.54E-03	3.70E-02
8.25	1.93E-01	1.94E-01	2.08E-01	2.92E-03	3.34E-02
8.50	3.47E-01	3.49E-01	3.72E-01	2.27E-03	2.91E-02
8.75	6.31E-01	6.33E-01	6.66E-01	1.64E-03	2.38E-02
9.00	1.16E+00	1.16E+00	1.20E+00	1.05E-03	1.77E-02
9.25	2.15E+00	2.16E+00	2.23E+00	7.45E-04	1.51E-02
9.50	8.90E+00	9.07E+00	1.39E+01	8.42E-03	1.93E-01
			Maximum:	3.10E+00	5.72E+00
			Minimum:	7.45E-04	1.51E-02
			Average:	7.35E-01	2.09E+00

Source: Microsoft Excel spreadsheet Th Solubility.xls in Spreadsheets.zip (Attachment I)

NOTE: $f_{\text{CO}_2} = -3.0$

6.8.6 Summary

The uncertainties in thorium solubilities are summarized in the following equation:

$$\log[Th] = S(pH, \log f_{\text{CO}_2}) + \varepsilon_1 + \varepsilon_2^i \quad (\text{Eq. 6.8-1})$$

where $S(pH, \log f_{\text{CO}_2})$ is given in Table 6.8-2 and the ε 's are given in Table 6.8-4.

Table 6.8-4. Uncertainty Terms of log[Th]

Uncertainty Term	Associated with	Distribution Type	Distribution Parameter	Applicable to
ε_1	log K of controlling solid and aqueous species	Normal	$\mu = 0, \sigma = 0.7$	
ε_2^{CSNF}	Fluoride concentration in CSNF waste packages	Triangular	a = b = 0, c = 3.10	CSNF waste packages
ε_2^{CO-IN}	Fluoride concentration in codisposal waste packages	Triangular	a = b = 0, c = 5.72	Codisposal waste packages and the invert

6.9 AMERICIUM SOLUBILITY

6.9.1 Introduction

Data0.ymp.R2 includes americium data from the NEA compilation by Silva et al. (1995). Under the reference conditions only Am(III) is significant.

The database includes a number of americium solids: the oxide and hydroxides AmO_2 , Am(OH)_3 , and $\text{Am(OH)}_3(\text{am})$, the carbonate and hydroxy carbonate $\text{Am}_2(\text{CO}_3)_2$ and AmOHCO_3 , the fluoride AmF_3 and the phosphate $\text{AmPO}_4(\text{am})$. Under none of the conditions modeled were $\text{Am}_2(\text{CO}_3)_2$ or AmF_3 oversaturated, so these can be discounted as solubility-controlling phases. $\text{AmPO}_4(\text{am})$ was oversaturated under all conditions. However, as discussed in Section 6.4.2.5, because of the amount of uranium available in the waste package environment, the phosphate concentrations there are likely to be very low. Thus, $\text{AmPO}_4(\text{am})$ is also excluded from consideration. This is conservative because concentrations would be lower if solubility control by this solid was selected. The solubilities of the oxides and hydroxides increase in the order: $\text{AmO}_2 < \text{Am(OH)}_3 < \text{Am(OH)}_3(\text{am})$. According to Hummel et al. (2002, Section 5.2.3.2), the properties of AmO_2 are based on thermochemical studies and no solubility data are available to assess whether this phase ever actually controls dissolved Am concentrations under the conditions modeled. Thus it is also excluded as a possible controlling phase. The remaining solids AmOHCO_3 , Am(OH)_3 and $\text{Am(OH)}_3(\text{am})$ are considered as controlling or alternative controlling phases.

6.9.2 Controlling Phase

AmOHCO_3 was chosen as the controlling solid phase in all calculations. The choice of this mineral is based on the studies by Nitsche et al. (1993a; 1993b, p. 1494), which identify AmOHCO_3 as the solid phase precipitated from water corresponding to the water used in these calculations at a pH range from 5.9 to 8.4 and temperatures from 25 to 90°C. This is the most likely controlling phase under the range of environmental variables of interest to this analysis.

As discussed in Section 6.3.3.1, the uncertainty of the solubility product of this mineral is given by Silva et al. (1995, Table III.2) as ± 1.4 log K units.

6.9.3 Chemical Conditions

See Table 6.4-1 for the chemical conditions for the americium calculations.

6.9.4 Results

Table 6.9-1 and Figure 6.9-1 give the americium concentrations using AmOHCO_3 as the controlling mineral for pH values from 5.5 to 10.75, and $\log f_{\text{CO}_2}$ values from -2.5 to -5.0. Calculations for conditions outside this range and where blanks appear in the table either did not converge or led to solution ionic strengths above 1 mol, outside the range of validity of EQ3NR. At the low pH values, the modeling instability was due to the rapid increases in total americium and SO_4 concentrations due to the strength of the AmSO_4^+ ion pair and the addition of SO_4^{2-} as the charge-balancing anion. At high pH and f_{CO_2} values the instability was due to rapid increases in total americium and Na^+ concentrations due to the strength of the $\text{Am}(\text{CO}_3)_3^{3-}$ complexes and the addition of Na^+ as the cation balancing the increasing CO_3^{2-} concentrations at these conditions. Instability from this cause occurs in calculations on other actinides as well, but the SO_4^{2-} -linked instability at lower pH and f_{CO_2} values is specific to americium and thorium. It results from the fact that these elements are present as Am(III) and Th(IV) while the other actinides occur principally in the (V) or higher oxidation states. The SO_4^{2-} complexes of M(III) and M(IV) species are relatively stronger than those of higher oxidation states.

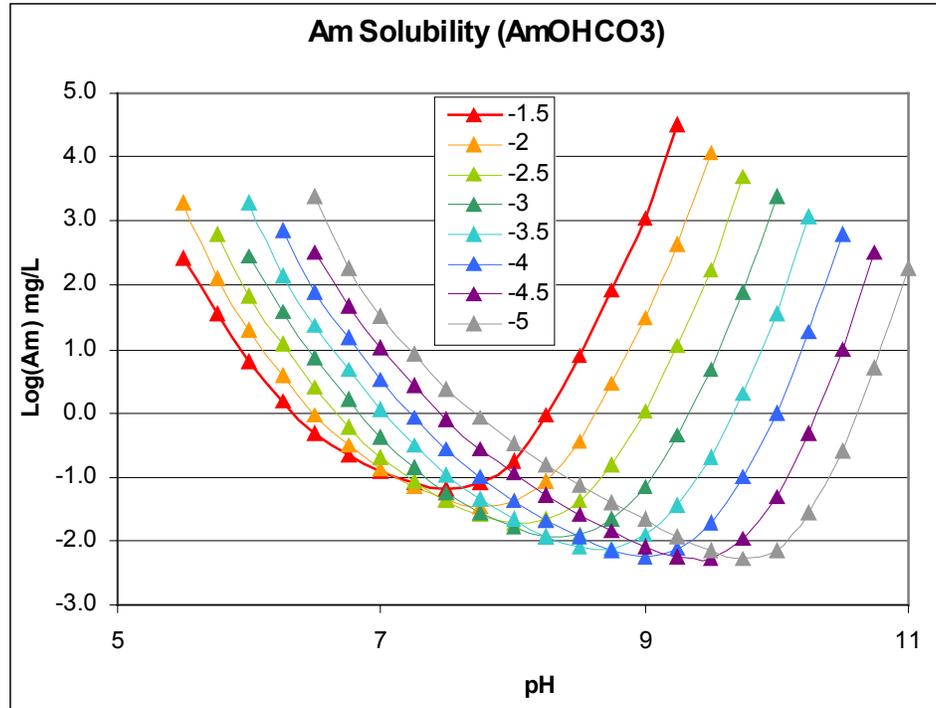
Table 6.9-1. Americium Solubility (mg/L) Calculated with AmOHCO_3 as Controlling Solid

pH	log f_{CO_2}							
	-1.50	-2.00	-2.50	-3.00	-3.50	-4.00	-4.50	-5.00
5.50	2.52E+02	1.88E+03						
5.75	3.42E+01	1.26E+02	6.25E+02					
6.00	6.30E+00	2.00E+01	6.77E+01	2.72E+02	2.00E+03			
6.25	1.45E+00	3.92E+00	1.19E+01	3.84E+01	1.38E+02	6.90E+02		
6.50	4.37E-01	9.38E-01	2.44E+00	7.25E+00	2.29E+01	7.78E+01	3.17E+02	2.37E+03
6.75	2.18E-01	3.02E-01	6.08E-01	1.58E+00	4.67E+00	1.46E+01	4.81E+01	1.76E+02
7.00	1.22E-01	1.27E-01	1.97E-01	4.13E-01	1.10E+00	3.27E+00	1.02E+01	3.30E+01
7.25	7.79E-02	6.98E-02	8.30E-02	1.37E-01	3.08E-01	8.52E-01	2.58E+00	8.07E+00
7.50	6.28E-02	4.38E-02	4.15E-02	5.65E-02	1.06E-01	2.65E-01	7.69E-01	2.36E+00
7.75	7.67E-02	3.46E-02	2.54E-02	2.78E-02	4.43E-02	9.88E-02	2.72E-01	8.21E-01
8.00	1.80E-01	4.06E-02	1.96E-02	1.59E-02	2.14E-02	4.28E-02	1.12E-01	3.31E-01
8.25	9.20E-01	8.42E-02	2.21E-02	1.17E-02	1.18E-02	2.08E-02	5.18E-02	1.51E-01
8.50	7.84E+00	3.62E-01	4.18E-02	1.25E-02	7.90E-03	1.12E-02	2.60E-02	7.44E-02
8.75	8.49E+01	2.80E+00	1.54E-01	2.18E-02	7.63E-03	6.89E-03	1.39E-02	3.88E-02
9.00		3.02E+01	1.07E+00	7.10E-02	1.20E-02	5.55E-03	8.05E-03	2.11E-02
9.25		4.31E+02	1.14E+01	4.44E-01	3.49E-02	7.25E-03	5.38E-03	1.18E-02
9.50			1.75E+02	4.62E+00	1.99E-01	1.83E-02	5.29E-03	7.14E-03
9.75				7.66E+01	2.03E+00	9.57E-02	1.04E-02	5.25E-03
10.00					3.59E+01	9.62E-01	4.90E-02	7.02E-03
10.25						1.79E+01	4.84E-01	2.67E-02
10.50							9.33E+00	2.55E-01
10.75								5.02E+00

Source: Microsoft Excel spreadsheet Am solubility.xls in Spreadsheets.zip (Attachment I)

NOTES: Some cells have no data because the EQ3NR calculations do not converge.

Runs with ionic strengths > 1.0 are outside the range of validation, and are not reported in this table.



Source: Microsoft Excel spreadsheet Am Solubility.xls in Spreadsheets.zip (Attachment I)

Figure 6.9-1. AmOHCO₃ Solubility Modeled as a Function of f_{CO2} and pH

Table 6.9-2 gives the same values as in Table 6.9-1 in units of log mg/L. It is included as the look-up table for use in the TSPA modeling for LA. The second table includes the value “500” for those ranges of conditions for which no concentrations were given in Table 6.9-1. This value is intended as a flag to indicate that release rates rather than concentration limits for americium should be selected for these conditions in the TSPA modeling. For any conditions that fall between a valid solubility and a flag of 500, the flag should be used. In addition, for any conditions outside of the 3.0-11.0 pH range, the -1.5 to -5.0 f_{CO2} range, or with an ionic strength greater than 1.0 molal, the inventory concentrations calculated according to the dissolution rate of waste forms, water volume, and radionuclide inventory should be used.

Table 6.9-2. Americium Solubility Look-up Table (log[Am] mg/L)

pH	log f _{CO2}							
	-1.50	-2.00	-2.50	-3.00	-3.50	-4.00	-4.50	-5.00
5.50	2.40E+00	3.27E+00	500	500	500	500	500	500
5.75	1.53E+00	2.10E+00	2.80E+00	500	500	500	500	500
6.00	7.99E-01	1.30E+00	1.83E+00	2.43E+00	3.30E+00	500	500	500
6.25	1.60E-01	5.93E-01	1.07E+00	1.58E+00	2.14E+00	2.84E+00	500	500
6.50	-3.60E-01	-2.76E-02	3.88E-01	8.60E-01	1.36E+00	1.89E+00	2.50E+00	3.37E+00
6.75	-6.62E-01	-5.20E-01	-2.16E-01	1.98E-01	6.69E-01	1.16E+00	1.68E+00	2.25E+00
7.00	-9.13E-01	-8.97E-01	-7.05E-01	-3.84E-01	3.99E-02	5.14E-01	1.01E+00	1.52E+00
7.25	-1.11E+00	-1.16E+00	-1.08E+00	-8.65E-01	-5.11E-01	-6.96E-02	4.11E-01	9.07E-01
7.50	-1.20E+00	-1.36E+00	-1.38E+00	-1.25E+00	-9.73E-01	-5.76E-01	-1.14E-01	3.74E-01
7.75	-1.12E+00	-1.46E+00	-1.60E+00	-1.56E+00	-1.35E+00	-1.01E+00	-5.65E-01	-8.59E-02
8.00	-7.46E-01	-1.39E+00	-1.71E+00	-1.80E+00	-1.67E+00	-1.37E+00	-9.51E-01	-4.80E-01
8.25	-3.64E-02	-1.07E+00	-1.66E+00	-1.93E+00	-1.93E+00	-1.68E+00	-1.29E+00	-8.22E-01
8.50	8.95E-01	-4.41E-01	-1.38E+00	-1.90E+00	-2.10E+00	-1.95E+00	-1.58E+00	-1.13E+00
8.75	1.93E+00	4.47E-01	-8.11E-01	-1.66E+00	-2.12E+00	-2.16E+00	-1.86E+00	-1.41E+00
9.00	500	1.48E+00	3.02E-02	-1.15E+00	-1.92E+00	-2.26E+00	-2.09E+00	-1.68E+00
9.25	500	2.63E+00	1.06E+00	-3.53E-01	-1.46E+00	-2.14E+00	-2.27E+00	-1.93E+00
9.50	500	500	2.24E+00	6.65E-01	-7.01E-01	-1.74E+00	-2.28E+00	-2.15E+00
9.75	500	500	500	1.88E+00	3.08E-01	-1.02E+00	-1.98E+00	-2.28E+00
10.00	500	500	500	500	1.56E+00	-1.70E-02	-1.31E+00	-2.15E+00
10.25	500	500	500	500	500	1.25E+00	-3.16E-01	-1.57E+00
10.50	500	500	500	500	500	500	9.70E-01	-5.94E-01
10.75	500	500	500	500	500	500	500	7.01E-01

Source: Microsoft Excel spreadsheet Am solubility.xls in Spreadsheets.zip (Attachment I)

NOTES: Some cells have no valid data because the EQ3NR calculations do not converge, and those results are reported as 500 in this table.

Runs with ionic strengths > 1.0 are outside the range of validation, and are reported as 500 in this table.

6.9.5 Alternative Conceptual Model

As mentioned in Section 6.9.1, other solids with properties specified in Data0.ymp.R2 are potential controls on americium solubility. Hummel et al. (2002, Section 5.2.3.2) describe experimental observations of solids with properties ranging from those of Am(OH)₃ to those of Am(OH)₃(am). The less stable solid appears to form first in many experiments and to invert to the more stable solid with time. However, with additional time, the stable solid becomes less stable once again, presumably as a result of self-irradiation. An alternative controlling phase could be chosen conservatively to have properties of Am(OH)₃(am).

Examination of the EQ3NR output files shows that Am(OH)₃(am) becomes oversaturated under conditions of the lowest f_{CO2}, but under the remaining conditions modeled it is more soluble than AmOHCO₃, the controlling phase selected.

6.9.6 Uncertainty

As described in Section 6.3.3, uncertainties in the solubilities have been evaluated considering uncertainties in thermodynamic data, and uncertainties in the fluoride content of the matrix fluid. The uncertainty due to uncertainties in thermodynamic data was calculated as described in Section 6.3.3.1, allowing for uncertainties in log K values of both the controlling solid and the important aqueous americium species.

As described in Section 6.3.3, uncertainty in the solubilities have been evaluated considering uncertainties in thermodynamic data, and uncertainties in the fluoride content of the matrix fluid. The uncertainty due to uncertainties in thermodynamic data was calculated as described in Section 6.3.3.1, allowing for uncertainties in log K values of both the controlling solid and the important aqueous americium species.

The principal dissolved americium species accounting for more than 5 percent of the total dissolved americium were found by examining the EQ3NR output for selected runs representing the range of conditions modeled. They are: $\text{Am}(\text{CO}_3)_3^{3-}$, $\text{Am}(\text{CO}_3)_2^-$, AmCO_3^+ , $\text{Am}(\text{OH})_2^+$, AmOH^{2+} , AmSO_4^+ , $\text{Am}(\text{SO}_4)_2^-$ and Am^{3+} . Uncertainties for log K values of these species given by Silva et al. (1995, Table III.2) range from ± 0.03 to ± 0.8 . Uncertainty in the log K of AmOHCO_3 , the controlling solid, also taken from *Chemical Thermodynamics of Americium* (Silva et al. 1995, Table III.2), is ± 1.4 . The largest log K uncertainty was found for the reaction to $\text{Am}(\text{SO}_4)_2^-$, ± 1.97 . This represents a 2σ value. The 1σ uncertainty assigned to the log[Am] values is ± 1.0 .

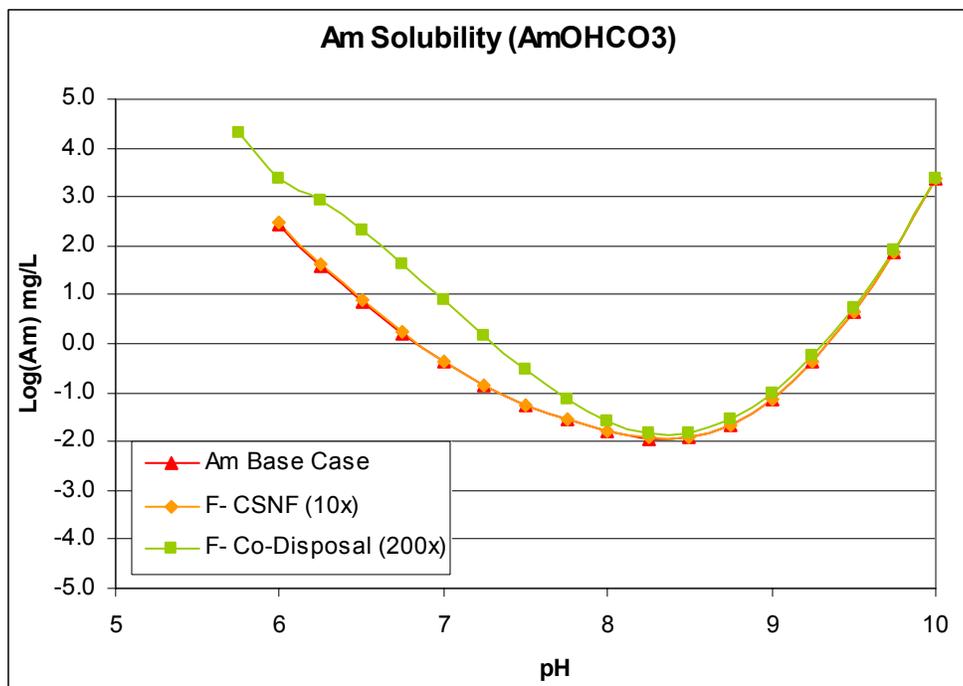
Calculations of the effects of uncertainties in fluoride concentrations were made for a range of pH values at a log f_{CO_2} of -3.0. The results are displayed in Figure 6.9-2, and the differences of these results from the base-case solubilities are given in Tables 6.9-3. As the figure and tables show, at fluoride concentrations 10× the base-case value (CSNF value) the maximum difference from the base-case concentration is only 0.0591 log (Am mg/L) units. At a fluoride concentrations 200× the base case (codisposal and invert value), the solubility is higher at lower pH values by a maximum value of +1.46 log (Am mg/L) at pH 6.5.

Table 6.9-3. The Effects of Variations in Fluoride Concentrations on Americium Solubility

pH	Base Case (25°C)	CSNF (10× F)	Codisposal (200× F)	CSNF Difference	Codisposal Difference
	[Am mg/L]			$\log[\text{Am}_{\text{CSNF}}] - \log[\text{Am}_{\text{Base Case}}]$	$\log[\text{Am}_{\text{Codisp}}] - \log[\text{Am}_{\text{Base Case}}]$
6.00	2.72E+02	3.12E+02	2.29E+03	5.91E-02	9.25E-01
6.25	3.84E+01	4.30E+01	8.19E+02	4.89E-02	1.33E+00
6.50	7.25E+00	7.99E+00	2.10E+02	4.21E-02	1.46E+00
6.75	1.58E+00	1.70E+00	4.13E+01	3.34E-02	1.42E+00
7.00	4.13E-01	4.34E-01	7.64E+00	2.18E-02	1.27E+00
7.25	1.37E-01	1.40E-01	1.44E+00	1.06E-02	1.02E+00
7.50	5.65E-02	5.69E-02	2.93E-01	3.18E-03	7.15E-01
7.75	2.78E-02	2.77E-02	7.23E-02	-1.58E-03	4.15E-01
8.00	1.59E-02	1.61E-02	2.52E-02	6.98E-03	2.02E-01
8.25	1.17E-02	1.18E-02	1.43E-02	4.33E-03	8.84E-02
8.50	1.25E-02	1.26E-02	1.44E-02	3.95E-03	6.36E-02
8.75	2.18E-02	2.21E-02	2.72E-02	5.70E-03	9.64E-02
9.00	7.10E-02	7.22E-02	9.63E-02	7.48E-03	1.33E-01
9.25	4.44E-01	4.51E-01	5.82E-01	6.25E-03	1.17E-01
9.50	4.62E+00	4.66E+00	5.44E+00	3.55E-03	7.12E-02
9.75	7.66E+01	7.68E+01	8.18E+01	1.36E-03	2.89E-02
			Maximum:	5.91E-02	1.46E+00
			Minimum:	1.36E-03	2.89E-02
			Average:	1.61E-02	5.85E-01

Source: Microsoft Excel spreadsheet Am Solubility.xls in Spreadsheets.zip (Attachment I)

NOTE: $\log f_{\text{CO}_2} = -3.0$



Source: Microsoft Excel spreadsheet Uncertainty.xls in Spreadsheets.zip (Attachment I)

Figure 6.9-2. Sensitivity of Americium Solubility at $\log f_{CO_2} = -3.0$ to Variations of Fluoride Concentrations

6.9.7 Summary

The uncertainties in americium solubilities are summarized in the following equation:

$$\log[Am] = S(pH, \log f_{CO_2}) + \varepsilon_1 + \varepsilon_2^i \quad (\text{Eq. 6.9-1})$$

where $S(pH, \log f_{CO_2})$ is given in Table 6.9-2 and the ε 's are given in Table 6.9-5.

Table 6.9-5. Uncertainty Terms of $\log[Am]$

Uncertainty Term	Associated With:	Distribution Type	Distribution Parameter	Applicable To:
ε_1	log K of controlling solid and aqueous species	Normal	$\mu = 0, \sigma = 1.0$	
ε_2^{CSNF}	Fluoride concentration in CSNF waste packages	Triangular	$a = b = 0, c = 5.91E-2$	CSNF waste packages
ε_2^{CO-IN}	Fluoride concentration in codisposal waste packages	Triangular	$a = b = 0, c = 1.46$	Codisposal waste packages and the invert

6.10 ACTINIUM SOLUBILITY

6.10.1 Introduction

No thermodynamic data for actinium are included in Data0.ymp.R2, so actinium solubilities cannot be calculated. It is an established chemical principle that properties of elements are consistent with their position in the periodic table. Thus, for example, corresponding solids of elements of similar positions in the table should also have similar solubilities. This chemical principle has been used to develop solubility values for actinium.

6.10.2 Solubility Development

Properties of elements in solution can be related to their charge (z) and ionic radius (r) (see, for example, Hummel et al. 2002, Figures 3.1.1 through 3.1.5). Figure 6.10-1 is a plot of z^2/r of selected cations against the $\log K(25)$ of dissociation of their monohydroxyl solution complexes, i. e.,



This figure illustrates the correlation of chemical properties—in this case solute complexation behavior—with charge and size. The sources of the $\log K(25)$ values are given in the figure caption.

This graph shows what would be expected from inspection of the periodic table, that Ac(III) behavior is similar to that of Y(III) and members of the lanthanide and actinide series in their trivalent states. Solubility calculations for Am(III), one of the elements which Ac(III) resembles, have been made as part of this report (Section 6.9). In the absence of data for actinium in Data0.ymp.R2, the actinium concentrations given here will be based on those calculated for americium. To do this, it is necessary to evaluate the differences between actinium and americium solubilities based on the few actinium data that are available in the literature.

Only an upper limiting value is available for $\log K(\text{AcOH}^{2+})$, so the correct value will be lower and more consistent with the $\log K$ values for the corresponding complexes of its neighbors in the periodic table, La and Y. This places it in the upper part of the range of values for M(III) elements. The value for the corresponding Am(III) complex is in the lower part of this range.

Figure 6.10-2 illustrates the relationship between the solubility products of $\text{Ac}(\text{OH})_3$, $\text{La}(\text{OH})_3$, $\text{Eu}(\text{OH})_3$ and $\text{Am}(\text{OH})_3$ solids, that is, the $\log K$ values for the reaction:



The sources of the $\log K(25)$ values are given in the figure caption. Values for both lower solubility (cr or aged) and higher solubility (amorphous or fresh) variants of these solids are shown for all but $\text{Eu}(\text{OH})_3$, for which only data for one unspecified variant are given in Data0.ymp.R2.

This figure illustrates that the solubility products for the $\text{Ac}(\text{OH})_3$ solids are close to those of $\text{La}(\text{OH})_3$, as expected because they are adjacent in the periodic table, and about six log units higher

than the corresponding Eu and Am(III) solubilities. Am(III) solubilities have been calculated for this report (Section 6.9) and will be used as the bases for the actinium values.

No data are available for an AcOHCO_3 solid analogous to AmOHCO_3 , the solid controlling the modeled americium solubilities. In the absence of such data, the difference between the Ac(OH)_3 and Am(OH)_3 solids is taken as the difference between AcOHCO_3 and AmOHCO_3 .

6.10.3 Chemical Conditions

Because the actinium solubility is based on the americium calculations, the chemical conditions given in Table 6.4-1 and used for the americium calculations also apply to the actinium values.

6.10.4 Results

Table 6.10-1 give the actinium solubilities in mg/L. They are 10^6 times those of the corresponding americium concentrations given in Table 6.9-1. The actinium table covers a smaller range of pH and f_{CO_2} values than are given in the americium table. For consistency with the limit of applicability of EQ3NR and the data0.ymp.R2 database, solubilities greater than 1 mol/L have not been included.

Table 6.10-1. Actinium Solubility (mg/L) Taken as 10^6 Times Americium Solubilities

pH	log f_{CO_2}							
	-1.50	-2.00	-2.50	-3.00	-3.50	-4.00	-4.50	-5.00
5.50								
5.75								
6.00								
6.25								
6.50								
6.75	2.18E+05							
7.00	1.22E+05	1.27E+05	1.97E+05					
7.25	7.79E+04	6.98E+04	8.30E+04	1.37E+05				
7.50	6.28E+04	4.38E+04	4.15E+04	5.65E+04	1.06E+05			
7.75	7.67E+04	3.46E+04	2.54E+04	2.78E+04	4.43E+04	9.88E+04		
8.00	1.80E+05	4.06E+04	1.96E+04	1.59E+04	2.14E+04	4.28E+04	1.12E+05	
8.25		8.42E+04	2.21E+04	1.17E+04	1.18E+04	2.08E+04	5.18E+04	1.51E+05
8.50			4.18E+04	1.25E+04	7.90E+03	1.12E+04	2.60E+04	7.44E+04
8.75			1.54E+05	2.18E+04	7.63E+03	6.89E+03	1.39E+04	3.88E+04
9.00				7.10E+04	1.20E+04	5.55E+03	8.05E+03	2.11E+04
9.25					3.49E+04	7.25E+03	5.38E+03	1.18E+04
9.50					1.99E+05	1.83E+04	5.29E+03	7.14E+03
9.75						9.57E+04	1.04E+04	5.25E+03
10.00							4.90E+04	7.02E+03
10.25								2.67E+04
10.50								
10.75								
11.00								

Source: Microsoft Excel spreadsheet Ac solubility.xls in Spreadsheets.zip (Attachment I)

NOTES: Some cells have no data because the EQ3NR calculations do not converge.
Runs with ionic strengths > 1.0 are outside the range of validation, and are not reported in this table.
Range was truncated so solubilities do not Exceed 1 mol/L.

Table 6.10-2 gives values from Table 6.10-1 in units of log mg/L. It is included as the look-up table for use in the TSPA modeling for LA. The second table includes the value "500" for those ranges of conditions for which no concentrations were given in Table 6.10-1. This value is intended as a flag to indicate that release rates rather than concentration limits for actinium should be selected for these conditions in the TSPA modeling. For any conditions that fall between a valid solubility and a flag of 500, the flag should be used. In addition, for any conditions outside of the 3.0-11.0 pH range, the -1.5 to -5.0 f_{CO_2} range, or with an ionic strength greater than 1.0 molal, the inventory concentrations calculated according to the dissolution rate of waste forms, water volume, and radionuclide inventory should be used.

Table 6.10-2. Actinium Solubility Look-up Table (log[Ac] mg/L) Taken as 10^6 Times Americium Solubilities

pH	log f _{co2}							
	-1.50	-2.00	-2.50	-3.00	-3.50	-4.00	-4.50	-5.00
5.50	500	500	500	500	500	500	500	500
5.75	500	500	500	500	500	500	500	500
6.00	500	500	500	500	500	500	500	500
6.25	500	500	500	500	500	500	500	500
6.50	500	500	500	500	500	500	500	500
6.75	5.34E+00	500	500	500	500	500	500	500
7.00	5.09E+00	5.10E+00	5.29E+00	500	500	500	500	500
7.25	4.89E+00	4.84E+00	4.92E+00	5.14E+00	500	500	500	500
7.50	4.80E+00	4.64E+00	4.62E+00	4.75E+00	5.03E+00	500	500	500
7.75	4.88E+00	4.54E+00	4.40E+00	4.44E+00	4.65E+00	4.99E+00	500	500
8.00	5.26E+00	4.61E+00	4.29E+00	4.20E+00	4.33E+00	4.63E+00	5.05E+00	500
8.25	500	4.93E+00	4.34E+00	4.07E+00	4.07E+00	4.32E+00	4.71E+00	5.18E+00
8.50	500	500	4.62E+00	4.10E+00	3.90E+00	4.05E+00	4.41E+00	4.87E+00
8.75	500	500	5.19E+00	4.34E+00	3.88E+00	3.84E+00	4.14E+00	4.59E+00
9.00	500	500	500	4.85E+00	4.08E+00	3.74E+00	3.91E+00	4.32E+00
9.25	500	500	500	500	4.54E+00	3.86E+00	3.73E+00	4.07E+00
9.50	500	500	500	500	5.30E+00	4.26E+00	3.72E+00	3.85E+00
9.75	500	500	500	500	500	4.98E+00	4.02E+00	3.72E+00
10.00	500	500	500	500	500	500	4.69E+00	3.85E+00
10.25	500	500	500	500	500	500	500	4.43E+00
10.50	500	500	500	500	500	500	500	500
10.75	500	500	500	500	500	500	500	500
11.00	500	500	500	500	500	500	500	500

Source: Microsoft Excel spreadsheet Ac Solubility.xls in Spreadsheets.zip (Attachment I)

NOTES: Some cells have no valid data because the EQ3NR calculations do not converge, and those results are reported as 500 in this table.

Runs with ionic strengths > 1.0 are outside the range of validation, and are reported as 500 in this table.
Range was truncated so solubilities do not Exceed 1 mol/L

6.10.5 Alternative Conceptual Model

As pointed out above, actinium is more closely analogous to lanthanum than to americium. Lanthanum solubilities could be calculated using EQ3NR and the Data0.ymp.R2 database and could be used directly as actinium solubilities. As a result, the uncertainty could be reduced.

6.10.6 Uncertainty

The uncertainty of the actinium solubilities includes the uncertainty of the americium concentrations and additional uncertainty in the factor used to convert americium to actinium solubilities. Actinium data are so sparse it is difficult to develop a rational approach to estimate this additional uncertainty. Thus, a factor of 1 log unit has arbitrarily added to the uncertainty of the log K of the controlling americium solid.

6.10.7 Summary

The uncertainties in actinium solubilities are summarized in the following equation:

$$\log[Ac] = S(pH, \log f_{CO_2}) + \varepsilon_1 + \varepsilon_2^i \quad (\text{Eq. 6.10-3})$$

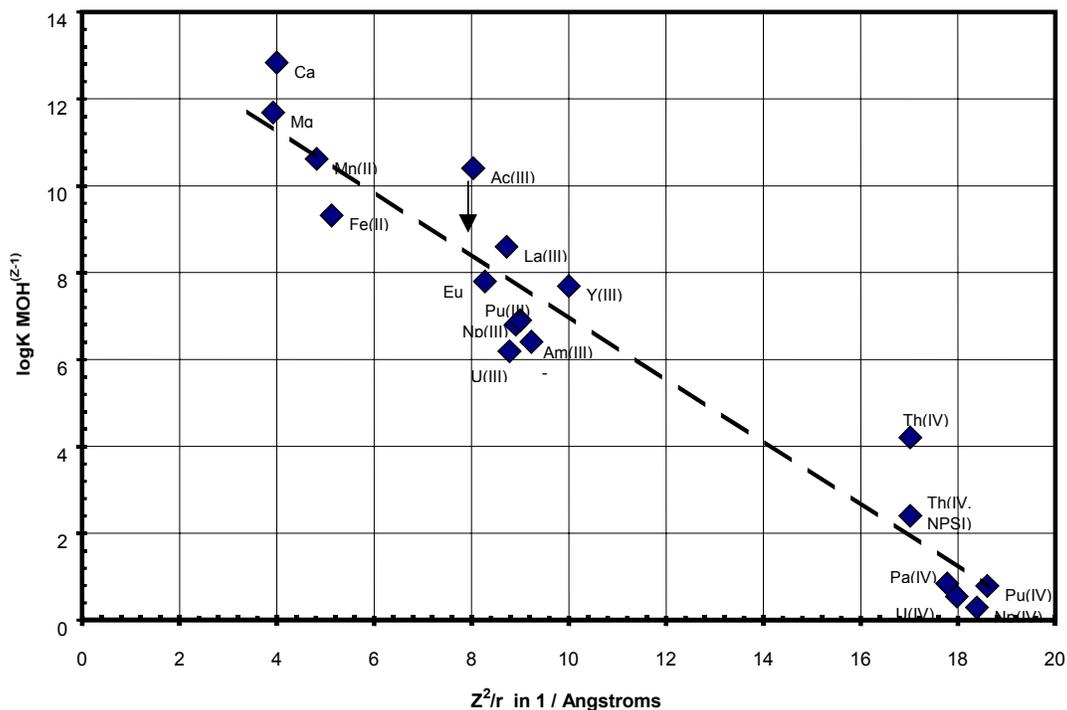
where $S(pH, \log f_{CO_2})$ is given in Table 6.10-2 and the ε 's are given in Table 6.10-3.

Table 6.10-3. Uncertainty Terms of log[Ac]

Uncertainty Term	Associated with	Distribution Type	Distribution Parameter	Applicable to
ε_1	Uncertainty in log Ks	Normal	$\mu = 0, \sigma = 2.0$	
ε_2^{CSNF}	Fluoride concentration in CSNF waste packages	Triangular	$a = b = 0, c = 0.04$	CSNF waste packages
ε_2^{CO-IN}	Fluoride concentration in codisposal waste packages	Triangular	$a = b = 0, c = 1.46$	Codisposal waste packages and the invert

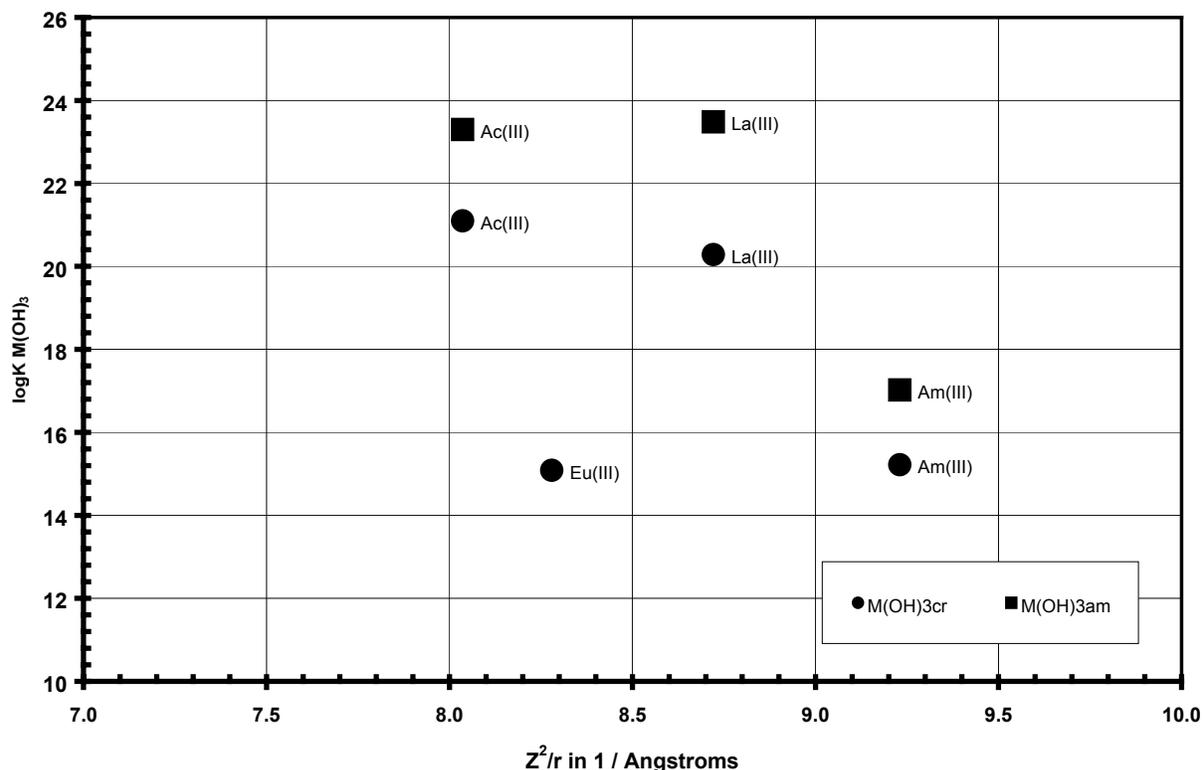
Data Sources: Values for r are from Shannon 1976, Table 1. log K(25) values are from Data0.ymp.R2, except those for Ac(III) and Pa(IV), which are from Baes and Mesmer 1986 (Tables 7.2 and 9.1, respectively) and Th(IV, NPSI), which is from Hummel et al. 2002, Table 5.21.1.

Source: Microsoft Excel spreadsheet Fig 6_10-1_2 data and plots.xls in Spreadsheets.zip (Attachment I)



NOTES: z = charge and r = ionic radius in Ångstroms
 The value for Ac(III) is a maximum value. The arrow in the figure that the correct value would be lower than the value plotted.

Figure 6.10-1. Correlation Between z^2/r and log K(25) for the Formation of the Monohydroxyl Complex of Selected Ions



Data Sources: Values for r are from Shannon 1976, Table 1. $\log K(25)$ values are from Data0.ymp.R2, except those for Ac(III), which are from Baes and Mesmer 1986, Table 7.2.

Source: Microsoft Excel spreadsheet Fig 6_10-1_2 data and plots.xls in Spreadsheets.zip (Attachment I)

NOTES: z = charge and r = ionic radius in Ångstroms

Values for both lower solubility (cr, or aged) and higher solubility (amorphous or fresh) variants of these solids are shown for all but Eu(OH)_3 , for which only data for one unspecified variant are given in Data0.ymp.R2.

Figure 6.10-2. Correlation Between z^2/r and $\log K(25)$ for the Dissolution of Aged or Crystalline and Fresh or Amorphous Solid Hydroxides of Selected Trivalent Ions

6.11 PROTACTINIUM SOLUBILITIES

6.11.1 Introduction

No thermodynamic data for protactinium are included in Data0.ymp.R2, so protactinium solubilities cannot be calculated using EQ3NR. It is an established chemical principle that properties of elements are consistent with their position in the periodic table. Thus, corresponding solids of elements of similar positions in the table should also have similar solubilities. This chemical principle was used to develop solubility values for actinium, for example (Section 6.10), and has been used for protactinium as well.

Some experimental protactinium data are available and have been interpreted to extract thermodynamic data by Baes and Mesmer (1986, Section 9.1) and Shibutani et al. (1998).

Protactinium appears to occur in aqueous solution as both Pa(IV) and Pa(V). As illustrated in Figure 6.10-1, the solution properties of Pa(IV) are similar to those of other actinides in their (IV) oxidation state. Thus, if protactinium occurred only as Pa(IV), its solubility would resemble that of thorium (Section 6.8).

Baes and Mesmer (1986, Section 9.1.2) also derive values for several Pa(V) reactions. These can be compared with data for analogous reactions of Np(V) as follows:

Table 6.11-1. Comparison of Analogous Neptunium and Protactinium Reactions

Reaction	log K - Np(V) ^a	log K - Pa(V) ^b
$\text{MO}_2\text{OH}(\text{aq}) + \text{H}^+ = \text{MO}_2^+ + \text{H}_2\text{O}$	11.3	4.5
$\text{M}_2\text{O}_5 + 2\text{H}^+ = 2\text{MO}_2^+ + 2\text{H}_2\text{O}$	3.7	< -4

Sources: ^a Data0.ymp.R2

^b Baes and Mesmer 1986, Table 9.1.

The stability of the Pa(V) solid appears to be greater than that of the analogous Np(V) solid while that of the Pa(V) aqueous complex is lower. This indicates that if protactinium occurred only as Pa(V), its solubility would be less than that of neptunium. Baes and Mesmer (1986, Section 9.1.2) describe experimental difficulties in maintaining protactinium in a stable oxidation state in solution, so calculations of the protactinium oxidation state required to calculate solubilities would be unreliable.

6.11.2 Solubility Development

Based on the considerations of chemical analogy in the previous section, protactinium solubility should range from below that of thorium to below that of Np(V). Figure 6.11-1 shows the difference between the solubilities of Np₂O₅ and ThO₂(am). Under the widest range of pH and f_{CO2} conditions, Np₂O₅ solubility is greater than that of ThO₂(am). The base case protactinium solubility is taken equal to that of Np₂O₅ with the difference to the ThO₂(am) solubility accommodated in the uncertainty term.

6.11.3 Chemical Conditions

Because the protactinium solubility is based on the neptunium and thorium calculations, the chemical conditions given in Table 6.4-1 and used for the neptunium and thorium calculations also apply to the protactinium values.

6.11.4 Results

Table 6.11-2 gives the protactinium concentrations in mg/L. It is equivalent to the corresponding tables for Np₂O₅.

Table 6.11-2. Base-Case Protactinium Solubility (mg/L)

pH	log f _{CO2}							
	-1.50	-2.00	-2.50	-3.00	-3.50	-4.00	-4.50	-5.00
3.00	3.07E+04	3.07E+04	3.07E+04	3.07E+04	3.07E+04	3.07E+04	3.07E+04	3.07E+04
3.25	1.40E+04	1.40E+04	1.40E+04	1.40E+04	1.40E+04	1.40E+04	1.40E+04	1.40E+04
3.50	6.95E+03	6.95E+03	6.95E+03	6.95E+03	6.95E+03	6.95E+03	6.95E+03	6.95E+03
3.75	3.64E+03	3.64E+03	3.64E+03	3.64E+03	3.64E+03	3.64E+03	3.64E+03	3.64E+03
4.00	1.96E+03	1.96E+03	1.96E+03	1.96E+03	1.96E+03	1.96E+03	1.96E+03	1.96E+03
4.25	1.07E+03	1.07E+03	1.07E+03	1.07E+03	1.07E+03	1.07E+03	1.07E+03	1.07E+03
4.50	5.91E+02	5.91E+02	5.91E+02	5.91E+02	5.91E+02	5.91E+02	5.91E+02	5.91E+02
4.75	3.29E+02	3.29E+02	3.29E+02	3.29E+02	3.29E+02	3.29E+02	3.29E+02	3.29E+02
5.00	1.84E+02	1.84E+02	1.84E+02	1.84E+02	1.84E+02	1.84E+02	1.84E+02	1.84E+02
5.25	1.03E+02	1.03E+02	1.03E+02	1.03E+02	1.03E+02	1.03E+02	1.03E+02	1.03E+02
5.50	5.77E+01	5.77E+01	5.77E+01	5.77E+01	5.77E+01	5.77E+01	5.77E+01	5.77E+01
5.75	3.24E+01	3.24E+01	3.24E+01	3.24E+01	3.24E+01	3.24E+01	3.24E+01	3.24E+01
6.00	1.82E+01	1.82E+01	1.82E+01	1.82E+01	1.82E+01	1.82E+01	1.82E+01	1.82E+01
6.25	1.03E+01	1.02E+01						
6.50	5.83E+00	5.78E+00	5.76E+00	5.76E+00	5.76E+00	5.75E+00	5.75E+00	5.75E+00
6.75	3.56E+00	3.30E+00	3.25E+00	3.24E+00	3.24E+00	3.24E+00	3.24E+00	3.24E+00
7.00	2.61E+00	1.95E+00	1.86E+00	1.83E+00	1.82E+00	1.82E+00	1.82E+00	1.82E+00
7.25	3.09E+00	1.34E+00	1.10E+00	1.04E+00	1.03E+00	1.03E+00	1.02E+00	1.02E+00
7.50	6.92E+00	1.35E+00	7.18E-01	6.14E-01	5.87E-01	5.79E-01	5.77E-01	5.76E-01
7.75	2.66E+01	2.42E+00	6.45E-01	3.99E-01	3.45E-01	3.30E-01	3.26E-01	3.24E-01
8.00	2.33E+02	7.35E+00	9.61E-01	3.29E-01	2.22E-01	1.94E-01	1.86E-01	1.83E-01
8.25		4.26E+01	2.37E+00	4.28E-01	1.78E-01	1.24E-01	1.09E-01	1.04E-01
8.50		1.04E+03	1.01E+01	8.77E-01	2.08E-01	9.75E-02	6.95E-02	6.13E-02
8.75			1.07E+02	2.90E+00	3.69E-01	1.09E-01	5.40E-02	3.90E-02
9.00				2.10E+01	9.84E-01	1.72E-01	5.83E-02	3.01E-02
9.25				6.00E+02	5.21E+00	3.88E-01	8.66E-02	3.19E-02
9.50					8.00E+01	1.55E+00	1.73E-01	4.56E-02
9.75						1.77E+01	5.41E-01	8.40E-02
10.00						1.68E+03	4.76E+00	2.18E-01
10.25							1.70E+02	1.46E+00
10.50								4.23E+01

Source: Microsoft Excel spreadsheet Np2O5 solubility.xls in Spreadsheets.zip (Attachment I)

NOTES: Some cells have no data because the EQ3NR calculations do not converge.
Runs with ionic strengths > 1.0 are outside the range of validation, and are not reported in this table.
Equivalent to calculated Np₂O₅ Solubility.

Table 6.11-2 gives the same values as in Table 6.11-1 in units of log mg/L. It is included as the look-up table for use in the TSPA modeling for LA. The second table includes the value “500” for those ranges of conditions for which no concentrations were given in Table 6.11-1. This value is intended as a flag to indicate that release rates rather than concentration limits for protactinium should be selected for these conditions in the TSPA modeling. For any conditions that fall between a valid solubility and a flag of 500, the flag should be used. In addition, for any conditions outside of the 3.0-11.0 pH range, the -1.5 to -5.0 log f_{CO2} range, or with an ionic

strength greater than 1.0 molal, the inventory concentrations calculated according to the dissolution rate of waste forms, water volume, and radionuclide inventory should be used.

Table 6.11-3. Base-Case Protactinium Solubility Look-up Table (log[Pa], mg/L)

pH	log f _{CO2}							
	-1.50	-2.00	-2.50	-3.00	-3.50	-4.00	-4.50	-5.00
3.00	4.49E+00	4.49E+00	4.49E+00	4.49E+00	4.49E+00	4.49E+00	4.49E+00	4.49E+00
3.25	4.15E+00	4.15E+00	4.15E+00	4.15E+00	4.15E+00	4.15E+00	4.15E+00	4.15E+00
3.50	3.84E+00	3.84E+00	3.84E+00	3.84E+00	3.84E+00	3.84E+00	3.84E+00	3.84E+00
3.75	3.56E+00	3.56E+00	3.56E+00	3.56E+00	3.56E+00	3.56E+00	3.56E+00	3.56E+00
4.00	3.29E+00	3.29E+00	3.29E+00	3.29E+00	3.29E+00	3.29E+00	3.29E+00	3.29E+00
4.25	3.03E+00	3.03E+00	3.03E+00	3.03E+00	3.03E+00	3.03E+00	3.03E+00	3.03E+00
4.50	2.77E+00	2.77E+00	2.77E+00	2.77E+00	2.77E+00	2.77E+00	2.77E+00	2.77E+00
4.75	2.52E+00	2.52E+00	2.52E+00	2.52E+00	2.52E+00	2.52E+00	2.52E+00	2.52E+00
5.00	2.26E+00	2.26E+00	2.26E+00	2.26E+00	2.26E+00	2.26E+00	2.26E+00	2.26E+00
5.25	2.01E+00	2.01E+00	2.01E+00	2.01E+00	2.01E+00	2.01E+00	2.01E+00	2.01E+00
5.50	1.76E+00	1.76E+00	1.76E+00	1.76E+00	1.76E+00	1.76E+00	1.76E+00	1.76E+00
5.75	1.51E+00	1.51E+00	1.51E+00	1.51E+00	1.51E+00	1.51E+00	1.51E+00	1.51E+00
6.00	1.26E+00	1.26E+00	1.26E+00	1.26E+00	1.26E+00	1.26E+00	1.26E+00	1.26E+00
6.25	1.01E+00	1.01E+00	1.01E+00	1.01E+00	1.01E+00	1.01E+00	1.01E+00	1.01E+00
6.50	7.66E-01	7.62E-01	7.61E-01	7.60E-01	7.60E-01	7.60E-01	7.60E-01	7.60E-01
6.75	5.51E-01	5.19E-01	5.12E-01	5.11E-01	5.10E-01	5.10E-01	5.10E-01	5.10E-01
7.00	4.17E-01	2.89E-01	2.69E-01	2.63E-01	2.61E-01	2.60E-01	2.60E-01	2.60E-01
7.25	4.90E-01	1.28E-01	3.98E-02	1.87E-02	1.27E-02	1.09E-02	1.03E-02	1.01E-02
7.50	8.40E-01	1.30E-01	-1.44E-01	-2.11E-01	-2.31E-01	-2.37E-01	-2.39E-01	-2.40E-01
7.75	1.42E+00	3.83E-01	-1.90E-01	-3.99E-01	-4.62E-01	-4.81E-01	-4.87E-01	-4.89E-01
8.00	2.37E+00	8.66E-01	-1.73E-02	-4.82E-01	-6.54E-01	-7.13E-01	-7.31E-01	-7.37E-01
8.25	500	1.63E+00	3.74E-01	-3.69E-01	-7.49E-01	-9.07E-01	-9.63E-01	-9.81E-01
8.50	500	3.01E+00	1.00E+00	-5.70E-02	-6.83E-01	-1.01E+00	-1.16E+00	-1.21E+00
8.75	500	500	2.03E+00	4.62E-01	-4.32E-01	-9.64E-01	-1.27E+00	-1.41E+00
9.00	500	500	500	1.32E+00	-7.19E-03	-7.63E-01	-1.23E+00	-1.52E+00
9.25	500	500	500	2.78E+00	7.17E-01	-4.12E-01	-1.06E+00	-1.50E+00
9.50	500	500	500	500	1.90E+00	1.90E-01	-7.63E-01	-1.34E+00
9.75	500	500	500	500	500	1.25E+00	-2.67E-01	-1.08E+00
10.00	500	500	500	500	500	3.22E+00	6.78E-01	-6.62E-01
10.25	500	500	500	500	500	500	2.23E+00	1.64E-01
10.50	500	500	500	500	500	500	500	1.63E+00

Source: Microsoft Excel spreadsheet Np2O5 solubility.xls in Spreadsheets.zip (Attachment I)

NOTES: Some cells have no valid data because the EQ3NR calculations do not converge, and those results are reported as 500 in this table.

Runs with ionic strengths > 1.0 are outside the range of validation, and are reported as 500 in this table. Equivalent to Np₂O₅ solubility look-up table.

6.11.5 Uncertainty

It is difficult to assign formal uncertainty to the protactinium solubility because the values are based on chemical analogy rather than on thermodynamic data and are supported by only one experimental study made in waters unlike those used for modeling the solubilities of other elements.

Because protactinium data are so sparse that even the choice of best analogous element is uncertain, the uncertainty in the protactinium solubility is taken as the difference between the solubilities of the two possible elements. That is, the uncertainty is taken as a uniform distribution in $\log[\text{Pa mg/L}]$ ranging from neptunium and thorium solubilities. As Figure 6.11-1 illustrates, these differences range from +3.04 to -1.02 in $\log \text{mg/L}$.

The uncertainty in protactinium solubilities due to fluoride contents is also unknown. It is taken as the larger of the corresponding uncertainty of the Np_2O_5 or $\text{ThO}_2(\text{am})$ solubilities.

The distribution properties of these uncertainty terms are listed in Table 6.11-4.

Table 6.11-4. Uncertainty Terms of $\log[\text{Pa}]$

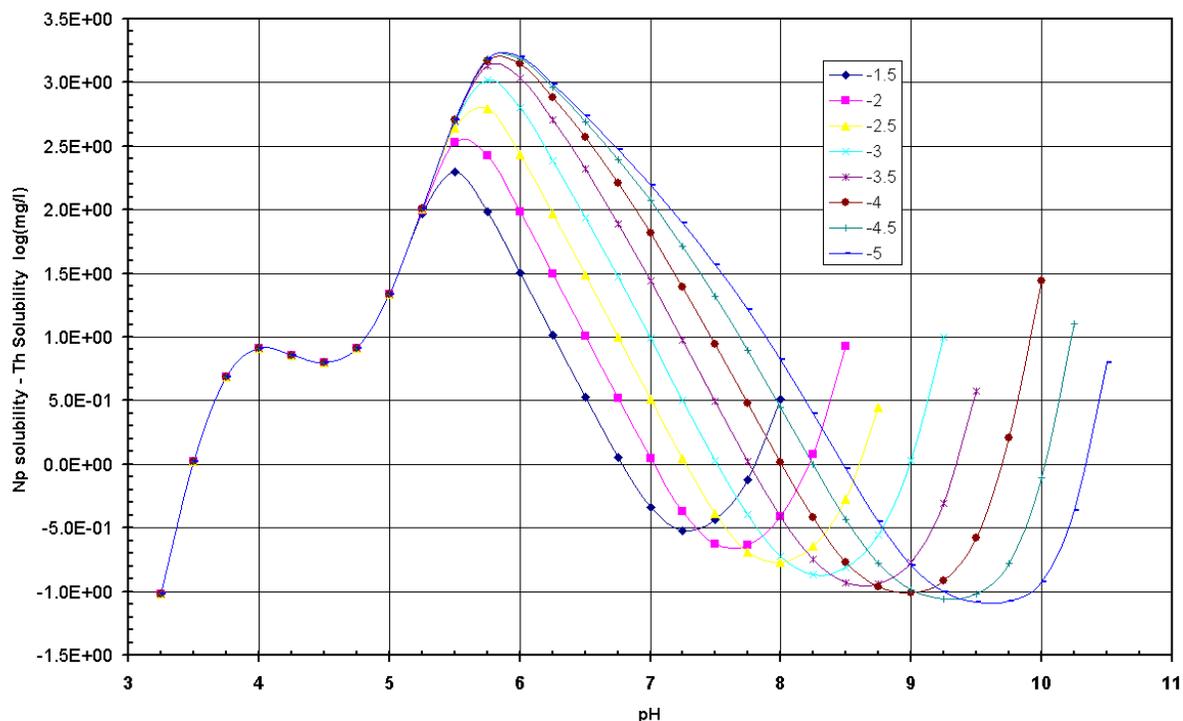
Uncertainty Term	Associated With	Distribution Type	Distribution Parameter	Applicable to
ε_1	Analogs	Uniform	Over an interval [-1.02, 3.04]	
$\varepsilon_2^{\text{CSNF}}$	Fluoride concentration in CSNF waste packages	Triangular	a = b = 0, c = 3.10	CSNF waste packages
$\varepsilon_2^{\text{CO-IN}}$	Fluoride concentration in codisposal waste packages	Triangular	a = b = 0, c = 5.79	Codisposal waste packages and the invert

6.11.6 Summary

The protactinium solubility model can be summarized by the following equation:

$$\log[\text{Pa}] = S(pH, \log f_{\text{CO}_2}) + \varepsilon_1 + \varepsilon_2^i \quad (\text{Eq 6.11-1})$$

where $S(pH, \log f_{\text{CO}_2})$ is given by Table 6.11-3; ε_1 is the uncertainty term associated with uncertainty in the analogs; ε_2^i is the uncertainty term associated with variations in fluoride concentration, i equals to CSNF or CODISP.



Source: Microsoft Excel spreadsheet Pa-Np-Th Solubility.xls in Spreadsheets.zip (Attachment I)

Figure 6.11-1. Differences Between Np_2O_5 and $ThO_2(am)$ Solubilities (log mg/L) as Functions of pH and f_{CO_2}

6.12 RADIUM SOLUBILITY

Radium solubility has been studied briefly in *Pure Phase Solubility Limits – LANL* (CRWMS M&O 2001b, Section 6.3.7). EQ3NR runs (see EQ3NR output files in Ra.zip of Attachment I) at $\log f_{CO_2} = -3.0$ indicate that the solubility controlling phase, if solid solutions with $BaSO_4$ or $SrSO_4$ are not taken into account, will be $RaSO_4$. Accordingly, the solubility will depend primarily on the concentration of free SO_4^{2-} in the solution. (Free means not combined with other elements in complexes or ion pairs.) The free SO_4^{2-} is expected to vary over a wide range for two reasons. First, acid conditions may arise from the oxidation of sulfur to SO_4^{2-} during the corrosion of steel (see Section 6.4.3.4). Such an increase in SO_4^{2-} will repress the solubility of $RaSO_4$. Second, under alkaline conditions ion pairs, such as $NaSO_4^-$ or $CaSO_4(aq)$ should form thereby limiting the reducing free SO_4^{2-} and enhancing the solubility.

For slightly alkaline (J-13 water) and acidified Yucca Mountain waters, the calculated radium solubility ranges from $9.1E-03$ to $1.9E-02$ mg/L. A constant solubility of $2.0E-02$ mg/L is recommended for radium for pH 7.75 or less. Under more alkaline conditions, pHs from 8.0 to 9.75, the calculated solubility ranges from $7.1E-02$ to 1.2 mg/L. For this pH range a constant value of 1.2 mg/L is recommended. These values are recommended for both CSNF and codisposal waste packages. If these solubilities are determined to be controlling parameters in determining individual dose, further work could provide a more realistic model.

At pH at or above 10 the rate of release of radium from the waste must be used. A higher pH cannot be achieved at equilibrium with the specified values of f_{CO_2} because any attempt to do so, e.g., adding NaOH to the solution, will simply result in the precipitation of sodium bicarbonate or carbonate. Similarly, the addition of any other cation, such as Ca^{2+} , would result in the supersaturation and precipitation of the corresponding carbonate, or an oxide or hydroxide. Already the EQ3NR runs show that the solution becomes supersaturated in a sodium-calcium carbonate (gaylussite) and several calcium and/or magnesium carbonates at pH 7.75.

Field studies have shown that radium concentrations in some natural waters are orders of magnitude below levels corresponding to $RaSO_4$ saturation. Radium concentrations more probably correspond to the solubilities of radium in solid solution in more common sulfate solids such as $SrSO_4$ or $BaSO_4$ (Langmuir and Riese 1985). A radium concentration based on pure $RaSO_4$ solubility is, therefore, a conservative value.

The recommended radium solubility limits are summarized below:

Table 6.12-1. Radium Solubility Values

pH Range	Radium Solubility (mg/L)
3.0 to 7.75	2.0E-2
7.75 to 9.75	1.2
> 9.75	500 (not controlled by solubility)

6.13 LEAD SOLUBILITY

Lead is one of the least mobile of heavy metals as it forms a number of sparingly soluble mineral phases and sorbs strongly to many mineral surfaces. The formation of $Pb_3(CO_3)_2(OH)_2$ can limit dissolved lead levels to 50 ppb or less under neutral to alkaline conditions (e.g., Hem 1985, p. 144). Under sulfate-rich, acidic conditions lead sulfate forms. Low-solubility lead phosphate formation limits dissolved lead levels in some soils. Lead ion (Pb^{2+}) forms complexes with carbonate, hydroxyls, and sulfate. It also interacts strongly with a number of organic acids.

Surface waters containing 1 ppb lead are reasonably common. Waters with lead loads greater than 10 ppb are less common and tend to possess lead in particulate, mineral-associated form, as opposed to dissolved lead (Hem 1985, p. 144).

Because in-package fluids are expected to be either low-pH, sulfate-rich waters or neutral to alkaline, carbonate-rich waters, or some combination of the two, there is a strong likelihood that dissolved lead levels will be limited by either lead sulfate or lead hydroxycarbonate formation. Uptake by corrosion products is also expected to be substantial. Because the lead sinks in the waste package environment are similar to a number of those that control lead in the environment, it is reasonable to expect dissolved lead levels to roughly reflect natural distributions (i.e., levels between 1 and 100 ppb). This corresponds to a range of $4.8E-9$ to $4.8E-7$ M. It is therefore recommended that TSPA use a log-uniform distribution, with a minimum of $4.8E-9$, and a maximum of $4.8E-7$ mol/L, to constrain lead solubility.

6.14 TECHNETIUM SOLUBILITY

Under the repository conditions, it is expected that no solubility-controlling solid exists for technetium. Therefore, technetium solubility is undefined and it is flagged by the default value of 500. In TSPA modeling for LA, the release of technetium should be controlled by the dissolution rate of waste forms rather than by solubility.

6.15 CARBON SOLUBILITY

Although under neutral or high pH, calcite may control the solubility of carbon; under pH as low as 3.6, calcite is not stable (Langmuir 1997, Figure 6.6, p. 202). Therefore, carbon solubility is undefined and it is flagged by the default value of 500. In TSPA modeling for LA, the release of carbon should be controlled by the dissolution rate of waste forms rather than by solubility.

6.16 IODINE SOLUBILITY

Under the repository conditions, it is expected that no solubility-controlling solid exists for iodine. Therefore, iodine solubility is undefined and it is flagged by the default value of 500. In TSPA modeling for LA, the release of iodine should be controlled by the dissolution rate of waste forms rather than by solubility.

6.17 CESIUM SOLUBILITY

Under the repository conditions, it is expected that no solubility-controlling solid exists for cesium. Therefore, cesium solubility is undefined and it is flagged by the default value of 500. In TSPA modeling for LA, the release of cesium should be controlled by the dissolution rate of waste forms rather than by solubility.

6.18 STRONTIUM SOLUBILITY

Strontium is quite soluble. The most likely solids to precipitate under the repository conditions are carbonate (strontianite, SrCO_3) or sulfate (celestite, SrSO_4). It is conservatively assumed that under the repository conditions, no solubility-controlling solid exists for strontium. Therefore, strontium solubility is undefined and it is flagged by the default value of 500. In TSPA modeling for LA, the release of strontium should be controlled by the dissolution rate of waste forms rather than by solubility. A strontium solubility can be developed using strontianite or celestite as its solubility controlling solid.

6.19 CONSIDERATION OF ALTERNATIVE CONCEPTUAL MODELS

Alternative conceptual models were considered in developing the solubility models reported for many of the elements included in this report. These alternative models were described explicitly or implicitly in the discussions of each element given above. Some elements were assigned arbitrarily high solubilities so that the control on their concentrations will be release rates from the waste form rather than solubility control. No alternative conceptual models were considered for these elements.

The alternative conceptual models considered are summarized in Table 6.19-1.

Table 6.19-1. Summary of Alternative Conceptual Models

Element	Alternative Conceptual Model	Model Bases	Screening Assessment and Basis
Pu	None explicit. Alternative conceptual model implicit in consideration of two end-member controlling solids	Controlling solid will become more stable than rapidly-precipitated PuO ₂ (hyd, aged) during aging but will not reach stability of crystalline PuO ₂ because of self irradiation.	Laboratory data show rapidly precipitated PuO ₂ (hyd, aged) does age toward more stable solids. Other laboratory data also show that initially crystalline PuO ₂ becomes more soluble with time due to self irradiation. Long-term control by solid of intermediate properties chosen.
Np	Solubility control by NpO ₂	Pure phase solid controlling neptunium concentration will be NpO ₂ rather than Np ₂ O ₅ .	Laboratory experiments show neptunium control by Np ₂ O ₅ formation at T < 100°C and by NpO ₂ at higher temperatures. More soluble Np ₂ O ₅ chosen for conservatism.
	Neptunium incorporation into uranyl secondary phases	Neptunium concentration controlled by solid solution rather than by pure phases.	Experimental studies on whether schoepite, the critical secondary uranyl phase, can incorporate sufficient neptunium and immobilize it during spent fuel corrosion do not provide a solid basis for recommending this model to be used in the TSPA-LA model.
U	Solubility control by uranyl silicate minerals	With time, initially formed UO ₃ ·2H ₂ O will convert to more stable uranyl silicate minerals.	UO ₃ ·2H ₂ O formation is observed in laboratory experiments and in natural analogs. Uranyl silicates also observed in natural analogs and to a lesser extent in laboratory experiments. More soluble UO ₃ ·2H ₂ O chosen for conservatism.
Th	Solubility control by other Th phases included in thermodynamic modeling data base including ThO ₂ (thorianite), Th _{0.75} PO ₄ , Th(SO ₄) ₂ , ThF ₄ , ThF ₄ ·2H ₂ O	That solubility of thermodynamically most stable phase will control concentrations; that thermodynamic data are impeccable.	Solubilities calculated with ThO ₂ (am) are most consistent with measured Th solubility in pure water. Other phases may be less soluble under only certain conditions or may be based on questionable data. More soluble ThO ₂ (am) chosen for conservatism.
Am	Solubility control by phase with properties between Am(OH) ₃ (am) to Am(OH) ₃ .	That initially formed Am(OH) ₃ (am) will invert to more stable Am(OH) ₃ with time. Am(OH) ₃ stability decreases with time from self irradiation.	AmOHCO ₃ is formed in americium solubility experiments under Yucca Mountain conditions. Under some conditions, Am(OH) ₃ may be less soluble, but generally choosing AmOHCO ₃ is conservative.
Ac	Of the elements in Data0, but not modeled, lanthanum may be a better analogue for actinium than americium.	That lanthanum is a better analogue for actinium than americium.	Actinium is commonly assumed to be directly analogous to americium. Adoption of 10 ⁶ factor is conservative.
Pa	Solubility is same as that of ThO ₂ (am)	Thorium is also a good analogue to protactinium and was modeled in this report.	Solubility of Np ₂ O ₅ was chosen because it is lower than that of ThO ₂ (am) under most conditions modeled, so its choice is conservative.
Ra	None	N/A	Chemistry of in-package and invert waters will not be so far outside the normal range of natural waters to cause different radium solubilities.
Pb	None	N/A	Chemistry of in-package and invert waters will not be so far outside the normal range of natural waters to cause different lead solubilities.
Tc	None	N/A	No solubility was defined and inventory release should be in control.

Element	Alternative Conceptual Model	Model Bases	Screening Assessment and Basis
C	None	N/A	No solubility was defined and inventory release should be in control.
I	None	N/A	No solubility was defined and inventory release should be in control.
Cs	None	N/A	No solubility was defined and inventory release should be in control.
Sr	Solubility controlled by SrCO ₃ or SrSO ₄	N/A	No solubility was defined and inventory release should be in control. This is a conservative approach.

7. MODEL VALIDATION

The purpose of this model report is to evaluate solubility limits of radioactive elements based on geochemical modeling calculations using geochemical modeling tools and thermodynamic databases and measurements collected from laboratory experiments and field work.

The scope of this modeling activity is to produce solubility limits as look-up tables, distributions, or constants for all radioactive elements transported outside breached waste packages identified by *Radionuclide Screening* (BSC 2002b). Fourteen radioelements were identified as important to dose for the time period from 10² to 2x10⁴ years; they are actinium, americium, carbon, cesium, iodine, lead, neptunium, plutonium, protactinium, radium, strontium, technetium, thorium, and uranium. TSPA will use the results of this report to constrain the release of these elements.

Technical Work Plan for Waste Form Degradation Modeling, Testing, and Analyses in Support of SR and LA (BSC 2002a, p. 18) lists seven criteria to be used to determine that the required level of confidence in model validation has been obtained. As noted in Section 1, Criterion 8 will be added to the list of model validation criteria in the technical work plan (BSC 2002a). These criteria are given in Table 7-1.

Table 7-1. Model Validation Criteria

Criterion One	Is the waste form degradation model consistent with the experimental data generated for YMP at various laboratories? When the model is not consistent, are there physical or phenomenological reasons why the differences are observed?
Criterion Two	Is the database of waste form degradation rates in the model consistent with the rates published in the peer-reviewed or industrial literature?
Criterion Three	Has the model been corroborated with results from an alternative mathematical model?
Criterion Four	Has the model been corroborated by a Peer Review per AP-2.12Q, <i>Peer Review</i> , or with technical review in a refereed professional journal?
Criterion Five	Has the model been technically reviewed by an international or other technical or organizational entity and their review documented in the open literature?
Criterion Six	Have the abstraction models been corroborated by comparison with the results of validated process models from which the abstraction was derived?
Criterion Seven	Has the model been validated with pre-test predictions that were later compared with test data?
Criterion Eight	Has the model been validated by demonstrating that it is conservative?

The level of confidence required for actinium, americium, carbon, cesium, iodine, lead, radium, strontium, technetium, thorium, and uranium is low; therefore, at least one of these criteria must be met. It also requires that plutonium and neptunium solubility models to be validated with a higher level of confidence than other solubility models, which means two criteria should be met to achieve the required level of confidence.

As pointed out in Section 6.3, solubility evaluation involves several technical aspects including (1) the thermodynamic database and a modeling tool, (2) the environmental conditions, (3) the construction of the conceptual model, and (4) the calculation of solubility limits using a geochemical modeling tool based on the conceptual model. Because both the thermodynamic database used in this report and the EQ3/6 code are controlled products (Steinborn et al. 2003; DTN: MO0302SPATHDYN.000) and this report uses them within their valid ranges, Aspects (1) and (4) are exempted from model validation. Aspect 2 is inputs to this report; thus, no model validation is necessary. Therefore, model validation discussed in this report focuses on Aspect 3: whether the conceptual model (i.e., the selection of solubility-controlling mechanism) is appropriate.

The selection of the solubility-controlling solids, as documented in individual subsections of Section 6, was based on laboratory and/or field observations when they are available and conclusive. Otherwise, a conservative approach based on the Ostwald Step Rule was adopted as discussed in Section 6.3. In other words, the conceptual model is either supported by direct observations or is conservative as documented below. This meets Criterion One given by the technical work plan (BSC 2002a, p. 18).

In addition, the technical work plan specifically requires (BSC 2002a, p. 20) that the plutonium and neptunium solubility models should be validated “through corroboration with laboratory measurements or relevant observations not previously used to develop the model” (i.e., to meet Criterion Seven). These corroborative activities are documented in Sections 7.1 and 7.2.

Two alternative neptunium solubility models (the NpO_2 model developed in Section 6.6.3 and the secondary phase model developed in Section 6.6.4) were not recommended for the TSPA-LA base-case analyses, because there are weaknesses in their foundations, as discussed in Sections 6.6.1 and 6.6.4.5. Therefore, they have no impact on the estimate of mean annual dose. According to Appendix B of *Scientific Processes Guidelines Manual* (BSC 2002d, p. B-1), model validation is not required for these models.

Corroborative data used in this section to validate solubility models were summarized in Table 7-2.

The post-validation models are summarized in Section 8. No further activities are needed to complete this model validation for its intended use.

Table 7-2. Corroborative Data Used for Model Validation

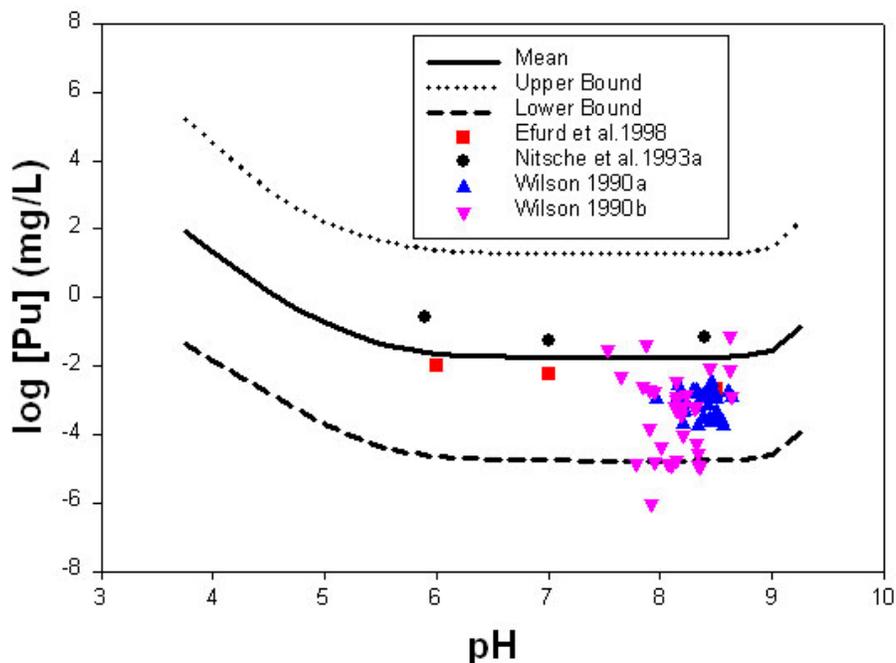
Model	Source	Note
Plutonium Solubility	Efurd et al. 1998, Table 4, p. 3897	Plutonium solubility measured at 25°C.
	Nitsche et al. 1993a, Table XVI, p. 54	Plutonium solubility measured at 25°C.
	Wilson 1990a (see Microsoft Excel spreadsheet PNL-Wilson.xls in spreadsheets.xls of Attachment I)	Plutonium concentrations measured at spent fuel corrosion experiments
	Wilson 1990b (see Microsoft Excel spreadsheet PNL-Wilson.xls in Spreadsheets.zip of Attachment I)	Plutonium concentrations measured at spent fuel corrosion experiments
Base-Case Np ₂ O ₅ Solubility	Wilson 1990a (see Microsoft Excel spreadsheet PNL-Wilson.xls in Spreadsheets.zip of Attachment I)	Neptunium concentrations measured at spent fuel corrosion experiments
	Wilson 1990b (see Microsoft Excel spreadsheet PNL-Wilson.xls in Spreadsheets.zip of Attachment I)	Neptunium concentrations measured at spent fuel corrosion experiments
	CRWMS M&O 2000d and CRMWS M&O 2000e for ANL-high drip and low drip tests (see Microsoft Excel spreadsheet ANL6dripData.xls in Spreadsheets.zip of Attachment I)	Neptunium concentrations measured at spent fuel corrosion experiments
Thorium Solubility	Hummel et al. 2002, Section 5.21	Thorium solubilities
Protactinium Solubility	Berry et al. 1989	Protactinium solubility

7.1 VALIDATION OF PLUTONIUM SOLUBILITY MODEL

Criteria One and Seven (see Table 7-1) were selected for validating the plutonium solubility model developed in Section 6.5.

The selection of the solubility controlling solid for this model is based on laboratory experiments. This satisfies Criterion One set forth in the technical work plan (BSC 2002a, p. 18).

Figure 7-1 presents the abstracted plutonium solubility model developed in Section 6.5 for log $f_{\text{CO}_2} = -3.5$ bars. The solid line represents the geometric mean values; the dotted line and the dashed line represent upper and lower bounds, respectively. Four sets of experimental data are also plotted in Figure 7-1. Two of them are plutonium solubilities measured at 25°C in plutonium experiments conducted by Nitsche et al. (1993a, Table XVI, p. 54) and by Efurd et al. (1998, Table 4, p. 3897). The water used in these two experiments is J-13 well water. Thus, these data are relevant to the repository and are directly applicable for comparison to the calculations presented in this report. Figure 7-1 shows that the geometric mean values of the plutonium solubility model are very close to the two sets of measured plutonium solubility values, with one set higher and the other set lower than the mean values. The other two data sets are plutonium concentrations measured in spent fuel leaching experiments by Wilson (1990a; 1990b). More information is contained in Microsoft Excel spreadsheet PNL-Wilson.xls in Spreadsheets.zip of Attachment I. Most of the data points from these two experiments fall between the mean values and the lower bound of the plutonium solubility model. The three exceptional data points are only slightly higher than the mean values, and no data point is above the upper bound of the model.



Data Source: Efur et al. 1998; Nitsche et al. 1993a; Wilson 1990a; Wilson 1990b (see Microsoft Excel spreadsheet PNL-Wilson.xls in Spreadsheets.zip of Attachment I)

Source: Pumodelvalid.jnb in Sigmaplots.zip (Attachment I)

Figure 7-1. Comparison of Experimental Data with the Predictions of Plutonium Solubility Model

The good match between the model results and experimental results, which were not used in the model development, strongly indicates that this proposed plutonium solubility model is representative and conservative and thus is valid. As a result, Criterion Seven has been satisfied.

In summary, both Criteria One and Seven have been met. Therefore, the required level of confidence has been obtained.

7.2 VALIDATION OF Np_2O_5 SOLUBILITY MODEL

Criteria One and Seven (see Table 7-1) were selected for validating the Np_2O_5 solubility model developed in Section 6.6.

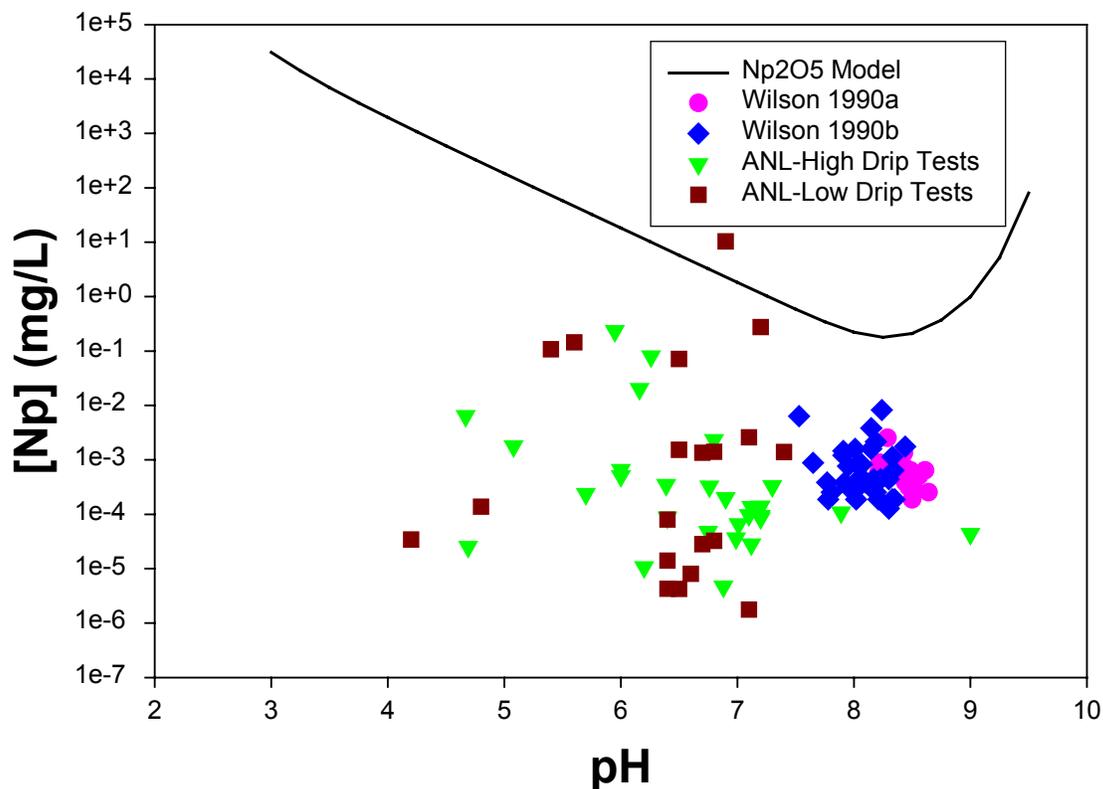
The selection of Np_2O_5 as the solubility controlling solid is based on Project's laboratory observations. Thus, Criterion One has been satisfied.

Figure 7-2 presents the Np_2O_5 solubility at 25°C and at f_{CO_2} of $10^{-3.5}$. As no Np_2O_5 solubility data that were not used to derive inputs for this model are available, no direct comparison between the modeling results and measured Np_2O_5 solubility is possible. However, Figure 7-2 also presents measured neptunium concentrations in several spent fuel corrosion experiments. These experiments were conducted at PNNL (Wilson 1990a; Wilson 1990b; See Microsoft Excel spreadsheet PNL-Wilson.xls in Spreadsheets.zip of Attachment I) and at ANL

(Finn et al. 1994; CRWMS M&O 2000d; CRWMS M&O 2000e; DTN: LL991001251021.090¹). This comparison shows that the Np_2O_5 solubility model developed in this report is conservative and thus is adequate for TSPA use. The fact that the measured neptunium concentrations in spent fuel corrosion experiments are 4 to 6 orders of magnitude lower than the modeled pure neptunium phase solubility indicates that neptunium may be controlled by different mechanism(s) than by pure phase solubility. Thus, Criterion Seven has been satisfied.

In summary, post-development model validation shows that the Np_2O_5 solubility model is conservative and adequate for TSPA use. Both Criteria One and Seven given in the technical work plan (BSC 2002a, p. 18) have been met. The level of confidence required for this model has been obtained.

¹ The concentration reported in this DTN is, according to the data report (CRWMS M&O 2000d, p. 13), “the ratio of the moles of the element released divided by the liters of injected EJ-13” water. This is the concentration as the injected water leaves the Zircaloy-4 holder, which can be only calculated. As the report pointed out, the released mass may include both dissolved mass and suspended as colloids in solution. Thus, the concentration values reported in this DTN may be higher than the dissolved concentration in solution. However, this fact does not affect the use of these data to validate the neptunium solubility model because (1) colloids are not the major mechanism for neptunium release under oxidation conditions due to the fact that NpO_2^+ has a low K_d value (Silva and Nitsche 1995, Section 4.4) and “conditions for Np(V) colloid formation in environmental waters would usually not be achieved” (Silva and Nitsche 1995, Section 4.5); and (2) because the data were used to demonstrate that the neptunium solubility model is conservative. The fact that the reported neptunium concentrations may be higher than the dissolved concentration in solution but are still lower than the modeled solubility actually confirmed that the solubility model is conservative.



Data Source: Wilson 1990a; Wilson 1990b (see Microsoft Excel spreadsheet PNL-Wilson.xls in Spreadsheets.zip of Attachment I); CRWMS M&O 2000d and CRMWS M&O 2000e for ANL high drip and low drip tests (see Microsoft Excel spreadsheet ANL6dripData.xls in Spreadsheets.zip of Attachment I)

Sources: SigmaPlot file npsolnp2O5.jnb in SigmaPlots.zip (Attachment I)

Figure 7-2. Comparison of Np_2O_5 Neptunium Solubility Model with PNNL's and ANL's Measurements

7.3 VALIDATION OF URANIUM SOLUBILITY MODEL

Criterion One (see Table 7-1) was selected for validating the uranium solubility model developed in Section 6.7.

The selection of schoepite as the solubility controlling solid for uranium model is based on laboratory and field observations. Inspection of the EQ3NR output files reveals that for all the converged calculations, the saturation status of soddyite is super-saturated. This confirms that a less stable phase (schoepite) was selected for the uranium solubility calculation.

Laboratory and field observations also document that schoepite is less stable than uranyl silicates. For example, in ANL's drip test, Wronkiewicz et al. (1992, p. 122) observed that "Soddyite replaces dehydrated schoepite in some locations." In 1996, Wronkiewicz et al. (1996) concluded that in ANL's drip tests "the becquerelite that formed on the bottom surface, as a replacement for dehydrated schoepite, may eventually itself be replaced by alkali and alkaline earth uranyl silicates." The replacement of schoepite by uranyl silicates has also been observed in Pena Blanca natural analogs (Percy et al. 1994, p. 725).

Therefore, for the reference water composition given in Table 6.4-1, the model is conservative because the more soluble uranyl phase was used for the calculation. Therefore, the model is adequate for use in TSPA and meets Criterion One, and the required confidence level has been obtained.

7.4 VALIDATION OF THORIUM SOLUBILITY MODEL

Criteria Seven (see Table 7-1) was selected for validating the thorium solubility model developed in Section 6.8.

The minimum thorium concentration modeled is 6.36E-04 mg/L (2.7E-09 mol/L) at an f_{CO_2} of 10^{-5} bars and a pH of 6.25. At this pH and low f_{CO_2} the impact of Th - F⁻, SO₄²⁻ and CO₃²⁻ complexes is minimal and the hydroxyl complex Th(OH)₄(aq) dominates. This solubility should therefore represent the experimental solubility of thorium dioxide in pure water at moderate to high pH values. Hummel et al. (2002, Section 5.21) have developed an internally consistent set of thermodynamic data for thorium. As part of their reported work they summarize the results of a number of studies of thorium solubility in pure water. From these data, they show that at pH values above 6 the solubility is $10^{-8.5 \pm 0.6}$ mol/L (Hummel et al. 2002, Figure 5.21.1). The minimum solubility modeled in this report (2.7E-9) equals $10^{-8.6}$, close to the mean and well within the uncertainty of the measured values.

The above comparison demonstrates that the thorium solubility model meets Criterion Seven, and the required confidence level has been obtained.

7.5 VALIDATION OF AMERICIUM SOLUBILITY MODEL

Criteria One (see Table 7-1) was selected for validating the americium solubility model developed in Section 6.9.

As discussed in Section 6.9, the choice of AmOHCO₃ is validated by the work of Nitsche et al. (1993a; 1993b, p. 1494). In this work, AmOHCO₃ was identified as forming from solutions similar to the reference water. This satisfies Criterion One, and the required confidence level has been obtained.

7.6 VALIDATION OF ACTINIUM SOLUBILITY MODEL

The Criterion Eight (see Table 7-1) was selected for validating actinium solubility model developed in Section 6.10.

Only one set of actinium solubility measurements is known. These were used by Baes and Mesmer (1986, Table 7.2) as the basis of the solubility product used above. Thus no direct validation is possible.

It should be noted that actinium is commonly considered to be directly analogous to americium (e.g., Berner 2002, p. 37). The approach taken here is conservative in that it leads to actinium concentrations 10^6 times those of americium. Thus, the criterion of conservatism has been met and the required confidence level has been obtained.

7.7 VALIDATION OF PROTACTINIUM SOLUBILITY MODEL

The Criterion Eight (see Table 7-1) was selected for validating protactinium solubility model developed in Section 6.11.

As discussed in Section 6.11, protactinium is an analogue of neptunium. Berry et al. (1989) describe experiments on protactinium behavior in solutions of several types at a range of pH values. The protactinium behavior was dominated by sorption, but the authors were able to develop a solubility limit of 10^{-10} mol/L (2.3E-05 mg/L) at high pH values in waters typical of those emanating from cements. This is two orders of magnitude lower than the lowest solubility calculated for thorium (see Figure 6.8-1) and four orders of magnitude lower than the lowest neptunium solubility (see Figure 6.6-1).

This indicates that the solubility model developed for protactinium is conservative. Thus, the criterion of conservatism has been met and the required confidence level has been obtained.

7.8 VALIDATION OF RADIUM SOLUBILITY MODEL

The Criterion Eight (see Table 7-1) was selected for validating radium solubility model developed in Section 6.11.

The radium solubility given is based on the solubility of pure RaSO_4 , as discussed in Section 6.12. Field studies have shown that radium concentrations in some natural waters are orders of magnitude below levels corresponding to RaSO_4 saturation. Radium concentrations more probably correspond to the solubilities of radium in solid solutions of more common sulfate solids such as SrSO_4 or BaSO_4 (Langmuir and Riese 1985). A radium concentration based on pure RaSO_4 solubility is therefore a conservative value and adequate for TSPA use.

This indicates that the solubility model developed for radium is conservative. Thus, the criterion of conservatism has been met and the required confidence level has been obtained.

7.9 VALIDATION OF LEAD SOLUBILITY MODEL

The lead solubility limit recommended in this report is based on literature data and professional judgement, and no model calculation was conducted. Therefore, no model validation is necessary.

7.10 VALIDATION OF TECHNETIUM, CARBON, IODINE, CESIUM, AND STRONTIUM SOLUBILITY MODELS

Since no solubility models were developed for technetium, carbon, iodine, cesium, and strontium, no model validation is necessary.

8. CONCLUSIONS

Solubility models have been developed for 14 radioactive elements, resulting in 14 base-case models (for plutonium, neptunium, uranium, thorium, americium, actinium, protactinium, radium, lead, technetium, carbon, iodine, cesium, and strontium) and two alternative conceptual

models for neptunium. DTN: MO0306SPASL14E.001 is assigned to the solubility models developed in this model report. This DTN supercedes DTN: MO0012PARSL10.003 and DTN: MO0304SPAS14RE.000. DTN: MO0306MWDMISL4.000 is assigned to the model information used to develop the solubility models in this model report.

8.1 MODEL OUTPUT

The base-case model output is summarized in Table 8-1 and the model output for two neptunium alternative conceptual models is summarized in Table 8-2. The output for plutonium, neptunium, uranium, thorium, americium, actinium, and protactinium solubilities is in the form of look-up tables. These tables are located in Section 6, and are not repeated in this section. For some very soluble elements, there is no adequate basis to specify a solubility-controlling solid, so they are assumed to be highly soluble, and their releases are considered to be controlled by the dissolution rate of waste forms and the waste inventory. Elements in this category are technetium, carbon, iodine, cesium, and strontium.

Table 8-1. Summary of Base-Case Solubility Models

Element	Value	Note
Pu	See Table 6.5-3 (log of solubility in mg/L)	
Np	See Table 6.6-2 (log of solubility in mg/L)	
U	See Table 6.7-2 (log of solubility in mg/L)	
Th	See Table 6.8-2 (log of solubility in mg/L)	
Am	See Table 6.9-2 (log of solubility in mg/L)	
Ac	See Table 6.10-2 (log of solubility in mg/L)	
Pa	See Table 6.11-3 (log of solubility in mg/L)	
Ra	8.8E-8 mol/L (2.0E-2 mg/L) for pH range of 3.0 to 7.75 5.3E-6 mol/L (1.2 mg/L) for pH range of 7.75 to 9.75 500 for pH > 9.75	Constants for two intervals
Pb	4.8E-9 to 4.8E-7 mol/L (1.0E-3 to 1.0E-1 mg/L)	log Uniform Distribution
Tc	500	Controlled by dissolution rate
C	500	Controlled by dissolution rate
I	500	Controlled by dissolution rate
Cs	500	Controlled by dissolution rate
Sr	500	Controlled by dissolution rate

Table 8-2. Summary of Alternative Neptunium Solubility Models

Model Name	Value
NpO ₂ Solubility	See Table 6.6-6 (log of solubility in mg/L)
Secondary Phase Neptunium Solubility	See Table 6.6-13 (log of solubility in mg/L)

8.2 OUTPUT UNCERTAINTY

Uncertainties from various sources have been addressed in this report. They consist of (1) uncertainty in selection of the solubility controlling phase (for plutonium solubility model only), (2) uncertainty in log K of the solubility controlling phase, (3) the uncertainty associated with temperature variations, and (4) the uncertainty associated with variations in fluoride concentrations. For the secondary phase neptunium solubility model, an additional uncertainty term was given arising from the derivation of the concentrating factor (F_c) from experimental data. The output uncertainty for the base-case models is summarized in Table 8-3. The output uncertainties for the two neptunium alternative conceptual models are summarized in Table 8-4.

8.3 RESTRICTIONS

As discussed in Section 6.4, the solubility models developed in this model report are valid for broad ranges of water composition, as listed in Table 8-5. They may be applied both inside and outside waste packages. However, as stated in Section 6.4.4, they are subject to three restrictions. First, they are restricted to ionic strength no higher than 1 molal because the b-dot equation was used in model calculations. Second, because some calculations did not converge or gave an ionic strength higher than 1 molal, the ranges of the look-up tables may be narrowed from those given in Tables 8-2 and 8-4. Within those look-up tables, the value "500" was used to indicate that no solubilities were given for those ranges of conditions. This value is intended as a flag to indicate that release rates rather than concentration limits should be selected for these conditions in the TSPA modeling. For any conditions that fall between a valid solubility and a flag of 500, the flag should be used. Third, for any conditions outside of the 3.0-11.0 pH range, the -1.5 to -5.0 f_{CO_2} range, or with an ionic strength greater than 1.0 molal, the inventory concentrations calculated according to the dissolution rate of waste forms, water volume, and radionuclide inventory should be used.

Table 8-3. Summary of Uncertainty for Base-Case Solubility Models

Element (log of solubility in mg/L)	Sources of Uncertainty	Uncertainty Distribution	Characteristic Values	Notes
Plutonium solubility	Selection of the solubility controlling phase	Triangular	a = -3.33, b = 0, c = 3.33	Table 6.5-5
	log K	Normal	$\mu = 0, \sigma = 1.3$	
	F ⁻ (for CSNF waste packages)	Triangular	a = b = 0, c = 0.885	
	F ⁻ (for codisposal waste package & invert)	Triangular	a = b = 0, c = 2.94	
Neptunium solubility	log K	Normal	$\mu = 0, \sigma = 0.8$	Table 6.6-4
	F ⁻ (for CSNF waste packages)	Triangular	a = b = 0, c = 1.59E-2	
	F ⁻ (for codisposal waste package & invert)	Triangular	a = b = 0, c = 0.474	
Uranium solubility	log K	Normal	$\mu = 0, \sigma = 0.5$	Table 6.7-4
	F ⁻ (for CSNF waste packages)	Triangular	a = b = 0, c = 1.03	
	F ⁻ (for codisposal waste package & invert)	Triangular	a = b = 0, c = 2.82	
Thorium solubility	log K	Normal	$\mu = 0, \sigma = 0.7$	Table 6.8-4
	F ⁻ (for CSNF waste packages)	Triangular	a = b = 0, c = 3.10	
	F ⁻ (for codisposal waste package & invert)	Triangular	a = b = 0, c = 5.72	
Americium solubility	log K	Normal	$\mu = 0, \sigma = 1.0$	Table 6.9-4
	F ⁻ (for CSNF waste packages)	Triangular	a = b = 0, c = 5.91E-2	
	F ⁻ (for codisposal waste package & invert)	Triangular	a = b = 0, c = 1.46	
Actinium solubility	log K	Normal	$\mu = 0, \sigma = 2.0$	Table 6.10-3
	F ⁻ (for CSNF waste packages)	Triangular	a = b = 0, c = 0.04	
	F ⁻ (for codisposal waste package & invert)	Triangular	a = b = 0, c = 1.46	
Protactinium solubility	Analogous	Uniform	Over an interval of [-1.02, 3.04]	Table 6.11-4
	F ⁻ (for CSNF waste packages)	Triangular	a = b = 0, c = 3.10	
	F ⁻ (for codisposal waste package & invert)	Triangular	a = b = 0, c = 5.79	
Radium solubility	N/A		Distribution	
Lead solubility	N/A		Distribution	
Technetium solubility	N/A		Constant	
Carbon solubility	N/A		Constant	
Iodine solubility	N/A		Constant	
Cesium solubility	N/A		Constant	
Strontium Solubility	N/A		Constant	

Table 8-4. Summary of Uncertainty for Alternative Neptunium Solubility Models

Model Name	Sources of Uncertainty	Uncertainty Distribution	Characteristic Values
NpO ₂ Solubility (log[Np] mg/L) (Table 6.6-8)	log K	Normal	$\mu = 0, \sigma = 0.7$
	F ⁻ (for CSNF waste packages)	Triangular	a = b = 0, c = 0.0431
	F ⁻ (for codisposal waste package & invert)	Triangular	a = b = 0, c = 0.887
Secondary Phase Neptunium Solubility (log[Np] mg/L) (Table 6.6-14)	log K	Normal	$\mu = 0, \sigma = 0.5$
	F ⁻ (for CSNF waste packages)	Triangular	a = b = 0, c = 1.03
	F ⁻ (for codisposal waste package & invert)	Triangular	a = b = 0, c = 2.82
	F _c	Normal	$\mu = 0, \sigma = 0.5$

Table 8-5. Valid Range of the Solubility Models Reported in This Report

Variable	Value or Range
pH	3.0 to 11.0
log f _{CO2}	-5.0 to -1.5 bars
Temperature	25 to 100°C
F ⁻ concentration	1 to 10 times the base-case value for CSNF waste packages; 1 to 200 of the base-case value for codisposal waste packages; and 1 to 200 of the base-case value for the invert.
Ionic Strength	less than 1 molal

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9.2 CODES, STANDARDS, REGULATIONS, AND PROCEDURES

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9.3 SOURCE DATA

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LL991001251021.090. Draft - CSNF Waste Form Degradation: Unsaturated Drip Tests - G2020 Analysis and Modeling Report. Submittal date: 10/04/1999.

MO0006J13WTRCM.000. Recommended Mean Values of Major Constituents in J-13 Well Water. Submittal date: 06/07/2000.

MO0302SPATHDYN.000. Thermodynamic Data Input Files - Data0.YMP.R2. Submittal date: 02/05/2003.

SN0009T0811199.008. Revised Range of Waste Package Effluent Compositions. Submittal date: 09/28/2000.

SN0011T0810599.023. Final Waste Package Radionuclide Inventory Approximations for Total System Performance Assessment-Site Recommendation (TSPA-SR). Submittal date: 11/01/2000.

9.4 OUTPUT DATA

MO0306SPASL14E.001. Dissolved Concentration Limits of 14 Radioactive Elements for LA. Submittal Date: 06/20/2003.

MO0306MWDMISL4.000. Model Information of Solubility Limits of 14 Radioactive Elements for LA. Submittal Date: 06/20/2003.

9.5 SOFTWARE CODES

Software Code: GetEQData. V1.0.1. PC w/Windows 2000 and Windows NT. 10809-1.0.1-0.

Software Code: EQ3/6. V7.2b. UCRL-MA-110662 (LSCR198).

Software Routine: BUILDEQ3.BAS. V1.0. PC, Windows NT 4.0. 10365-1.00-00.

ATTACHMENT I

CD-ROM

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ATTACHMENT II
LIST OF COMPUTER FILES

ATTACHMENT II
LIST OF COMPUTER FILES

This attachment contains the name and size of the zip file placed on the electronic media (Attachment I). Winzip 8.1 was used to compress the files.

Directory of CD

06/12/2003	03:12p	1,991,041	2ndphasevalidation.zip
06/12/2003	03:13p	10,702,426	Am.zip
06/12/2003	03:17p	25,807,143	Np.zip
06/12/2003	03:34p	34,629,302	Pu.zip
06/12/2003	03:35p	1,577,568	Ra.zip
06/12/2003	03:40p	32,216,462	Sensitivities.zip
06/20/2003	09:23a	73,226	SigmaPlots.zip
06/20/2003	09:19a	3,089,886	Spreadsheets.zip
06/12/2003	03:42p	10,361,370	Th.zip
06/12/2003	03:43p	11,352,946	U.zip
	10 File(s)	131,801,370	bytes

The zip files contain files of various types:

Excel files (extensions = xls)

EQ3 input files (extension = 3i)

ASCII text file: provides input parameters for EQ3

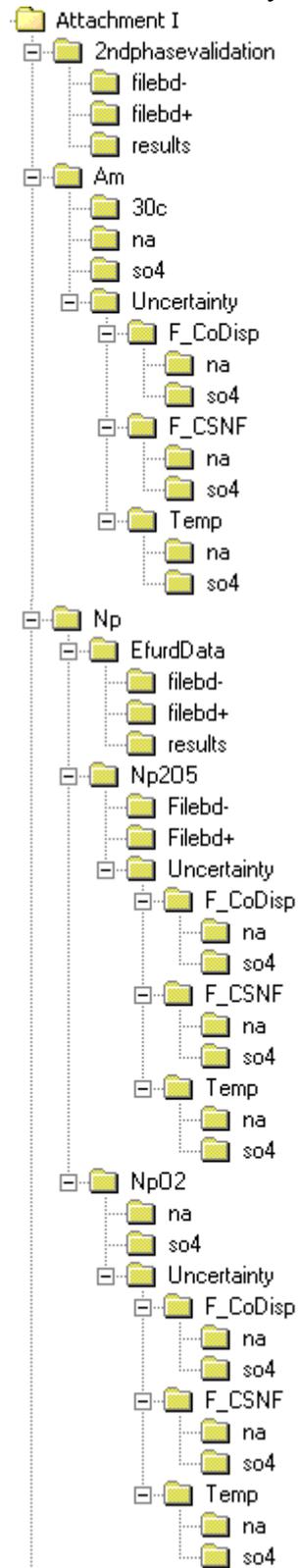
EQ3 output files (extension = 3o)

ASCII text file: provides detailed information about the system at each print point, which is specified by the user in the input file

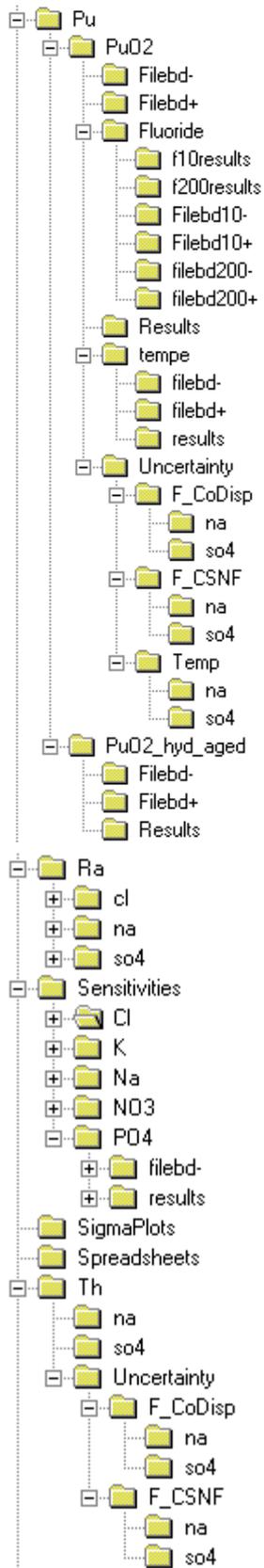
EQ3/6 text data files used for the calculations, 'data0.ymp.r2'

Winzip files (extension = zip).

The ZIP file directory structure is shown below:



Dissolved Concentration Limits of Radioactive Elements



Dissolved Concentration Limits of Radioactive Elements

